

# Photodegradation of Dichlorprop and 2-Naphthoxyacetic Acid in Water. Combined GC–MS and GC–FTIR Study

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We have examined the photochemical transformations of dichlorprop (**1**) and 2-naphthoxyacetic acid (**2**) in aqueous solution, by means of combined GC–MS and GC–FTIR analysis. Photolysis of **1** under oxygen atmosphere led to 2-chlorophenol (**5**), 2,4-dichlorophenol (**6**), 4-chlorophenol (**7**), 2,4-dichlorophenyl acetate (**8**), the lactone of 2-(4-chloro-2-hydroxyphenoxy)propionic acid (**9**), and 2-(2-chlorophenoxy)propionic acid (**10**). Irradiation under argon atmosphere led again to **5**, **6**, **7**, and **10** together with 2,4-dichlorophenyl ethyl ether (**11**). Photolysis of **2** under aerobic conditions gave  $\beta$ -naphthol (**12**), together with minor amounts of 2-hydroxy-1-naphthaldehyde (**13**) and naphtho[2,1-*b*]furan-2(1*H*)-one (**14**). Under argon atmosphere only **12** and **14** were detected. Therefore, the most general processes were photolytic cleavage of the aryl–halogen bond (route i) and the aryloxy–carbon bond (route ii). Similar photodegradation pathways had been previously observed for 2,4-D and 4-CPA and were confirmed in this work. The formation of **8**, **11**, and **13** must occur *via* cleavage of the carbon–carbon bond  $\alpha$  to the carboxy group (route iii). Formation of this type of photoproducts in phenoxyalkanoic acid pesticides is unprecedented. Its structure was further assessed by alternative synthesis.

**Keywords:** Dichlorprop; 2-naphthoxyacetic acid; 2,4-D; 4-CPA; GC–MS; GC–FTIR; photodegradation; photodecarboxylation; photodehalogenation; photorearrangement

## INTRODUCTION

The phenoxyalkanoic acids and their esters have been extensively used as herbicides especially for control of annual and perennial weeds. In agriculture, they are employed for protection of large crops. The most common technique involves either foliar application or topical application on soil by spraying of aqueous formulations of pesticides (Hassall, 1969).

Sunlight-induced degradation is one of the factors controlling the fate and persistence of pesticides and other chemicals in the environment (Lohmann and Petrak, 1989; Parlar, 1990; Klopffer, 1992). Also, photolysis is involved in the photoactivation and photocontrolled release of a number of bioactive molecules including some insecticides, fungicides, and herbicides. Hence, identification of the photoproducts allows us to establish the involved photolytic pathways, thus providing valuable information on possible ways of protecting the environment.

In this context, we have examined the photochemical transformations of two phenoxyalkanoic acid derivatives dichlorprop (**1**) and 2-naphthoxyacetic acid (**2**) in aqueous solution, by means of combined GC–MS and GC–FTIR analysis of the resulting reaction mixtures. In order to simulate solar light, the output from a medium pressure mercury lamp was filtered through pyrex ( $\lambda > 290$  nm). For comparison, the analogous 2,4-dichlorophenoxyacetic acid (2,4-D, **3**) and 4-chlorophenoxyacetic acid (4-CPA, **4**) have been included in the study, as their photochemical behavior has been well established by several research groups (Crosby and Tutass, 1966; Crosby and Wong, 1973; Smith, 1989).

While we have confirmed these results for 2,4-D and 4-CPA, we have obtained chemical evidence for the involvement of new reaction pathways in the case of dichlorprop and 2-naphthoxyacetic acid.

## EXPERIMENTAL PROCEDURES

**Chemicals.** 2-(2,4-Dichlorophenoxy)propionic acid (**1**), 2-naphthoxyacetic acid (**2**), 2,4-dichlorophenoxyacetic acid (**3**), and 4-chlorophenoxyacetic acid (**4**) were purchased from Aldrich (Madrid, Spain). All the solvents used were of analytical reagent grade and were redistilled before use. Water was obtained with a Milli-Q water purification system (Millipore).

**Apparatus and Chromatography.** In order to identify the photoproducts, the reaction mixtures were analyzed by GC, GC–MS, and GC–FTIR. GC were obtained with a Hewlett-Packard 5890 with an FID fitted with a capillary column (HP-5, 25 m  $\times$  0.32 mm  $\times$  0.52 mm).

GC–MS spectra were obtained with a Hewlett-Packard spectrometer (HP 5988 A, 70 eV, electron impact ionization) provided with a capillary column (SPB-5, 30 m  $\times$  0.25 mm  $\times$  0.25 mm). GC–MS conditions: initial temperature 60 °C for 3 min, rate 30 °C/min up to 300 °C for 10 min. Injector port temperature was 250 °C. Helium was the carrier gas (1.5 mL/min). The ratios  $m/z$  and their relative abundances in percentages (in brackets) are given only for the most significant peaks (down to 7% of the main signal).

IR spectra were obtained with a GC–FTIR instrument (Hewlett-Packard 5890 GC, coupled with a 5965 A FT-IR detector and provided with a capillary column like GC–MS). The GC–FTIR conditions: temperature program 100–300 °C, rate 30 °C/min. Wavenumber absorptions ( $\text{cm}^{-1}$ ) are given only for the hydroxyl or carbonyl bands.

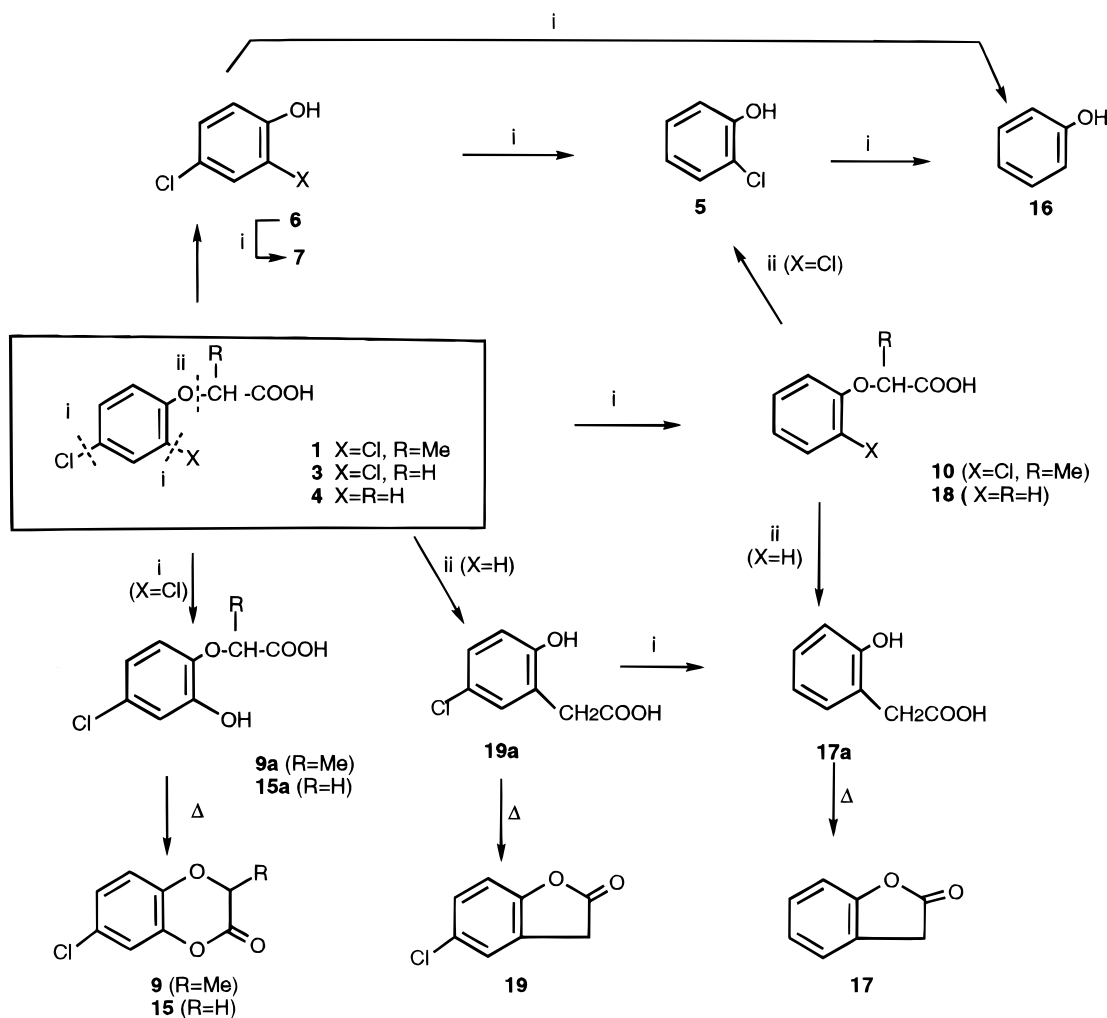
**Procedures. Irradiation Experiments.** Irradiation of four pesticides (ca.  $4.2 \times 10^{-3}$  M) was carried out in aqueous solution at room temperature, under air atmosphere and magnetic stirring. Irradiation took place in an immersion well photoreactor for 7 h, through a Pyrex sleeve, using a 125 W medium-pressure mercury lamp as light source.

Parallel experiments were carried out under an argon atmosphere. For that purpose, the samples were placed in Pyrex test tubes and sealed with septa. Then, argon was bubbled through the solutions for 10 min prior to irradiation, using a long syringe for inlet and a short one for outlet. The irradiated solutions were acidified with 4 N  $\text{H}_2\text{SO}_4$  and extracted twice with dichloromethane. The organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated at reduced pressure (14 Torr) at room temperature. On the

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**Table 1. GC-MS and GC-FTIR Data of the Photoproducts**

photoproduct	MW	method	retention time (min)	spectral data
5	128	GC-MS ( <i>m/z</i> , %)	4.40	130(32), 128(100), 100(12)
6	162	GC-MS ( <i>m/z</i> , %)	6.13	166(11), 164(68), 162(100), 126(20), 100(11)
7	128	GC-MS ( <i>m/z</i> , %)	6.24	130(34), 128(100), 100(24)
8	204	GC-MS ( <i>m/z</i> , %)	7.24	206(6), 204(15), 162(100), 133(15), 43(37)
		GC-FTIR ( $\text{cm}^{-1}$ )	6.89	1795 (CO)
9	198	GC-MS ( <i>m/z</i> , %)	7.80	200(9), 198(27), 127(18), 155(100), 144(7)
		GC-FTIR ( $\text{cm}^{-1}$ )	7.57	1810 (CO)
10	200	GC-MS ( <i>m/z</i> , %)	8.31	202(37), 200(100), 155(50), 128(25)
11	190	GC-MS ( <i>m/z</i> , %)	7.17	194(10), 192(66), 190(100), 162(38), 133(8)
12	144	GC-MS ( <i>m/z</i> , %)	8.15	144(100), 116(27), 115(94)
13	172	GC-MS ( <i>m/z</i> , %)	8.57	172(30), 144(54), 126(12), 116(25), 115(100)
		GC-FTIR ( $\text{cm}^{-1}$ )	9.21	1655 (CO)
14	184	GC-MS ( <i>m/z</i> , %)	9.25	184(100), 156(68), 128(73), 102(11)
		GC-FTIR ( $\text{cm}^{-1}$ )	10.05	1836(CO)
15	184	GC-MS ( <i>m/z</i> , %)	7.00	186(12), 184(40), 156(20), 155(100)
		GC-FTIR ( $\text{cm}^{-1}$ )	7.88	1816 (CO)
17	134	GC-MS ( <i>m/z</i> , %)	7.13	134(100), 122(8), 106(44), 105(29), 78(10)
		GC-FTIR ( $\text{cm}^{-1}$ )	6.50	1838 (CO)
18	152	GC-MS ( <i>m/z</i> , %)	7.48	152(75), 128(5), 107(100), 77(10)
19	168	GC-MS ( <i>m/z</i> , %)	7.59	170(27), 168(81), 142(26), 140(85), 112(100)
		GC-FTIR ( $\text{cm}^{-1}$ )	7.38	1842(CO)

**Scheme 1. Photodegradation Pathways of 2-(2,4-Dichlorophenoxy)propionic Acid (1), 2,4-Dichlorophenoxyacetic Acid (3), and 4-Chlorophenoxyacetic Acid (4) Involving Cleavage of the Carbon-Chlorine (Process i) and Oxygen-Carbon (Process ii) Bonds**

basis of the weight of the dry residues, the mass balance was always higher than 95%.

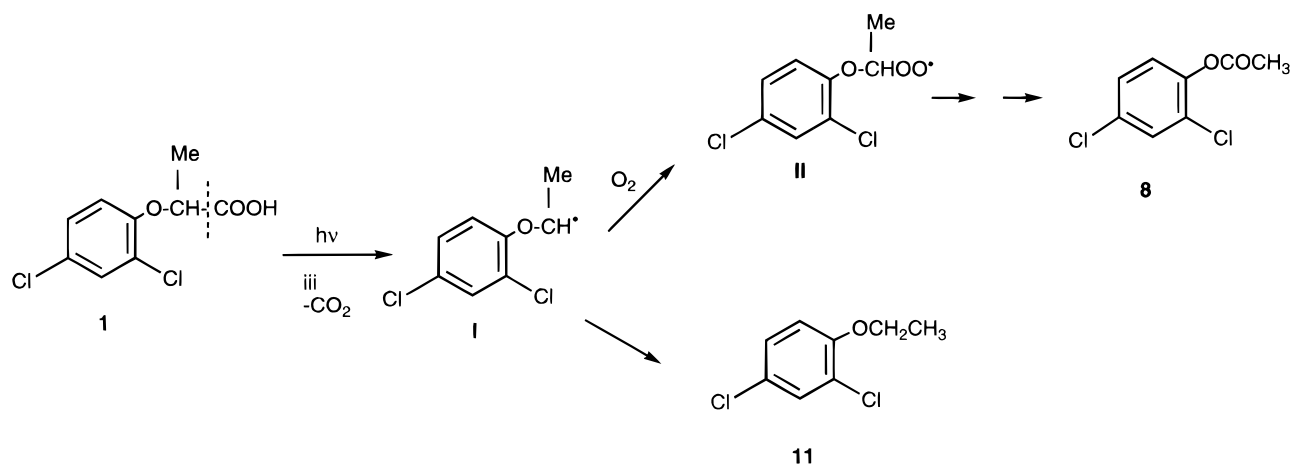
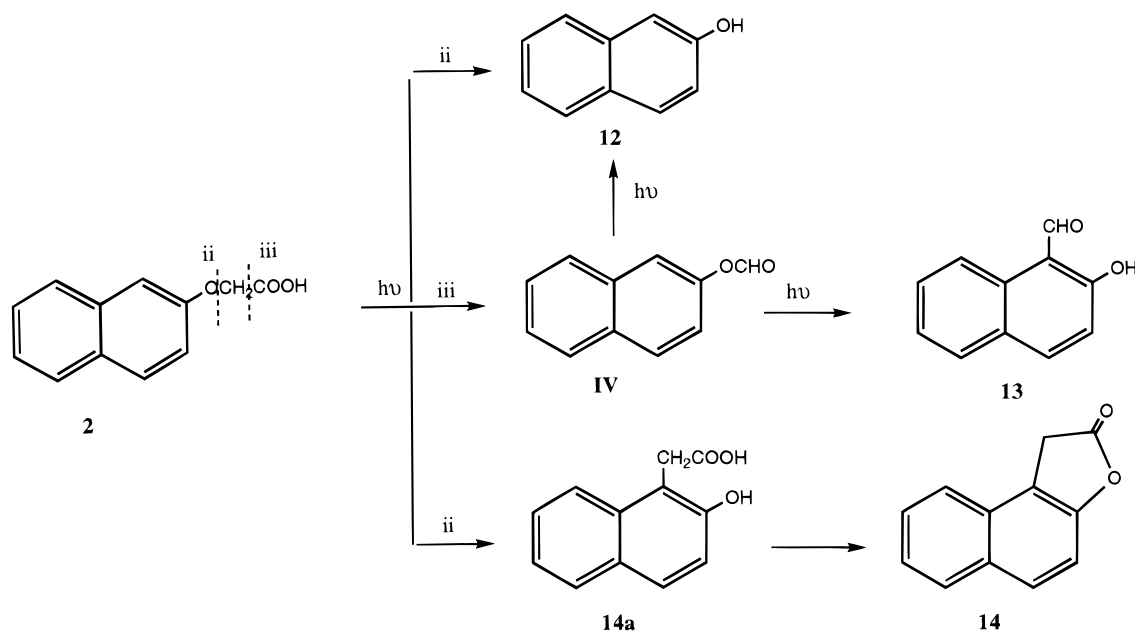
**Identification of the Photoproducts.** In all experiments, analysis of the photomixtures was done by GC-MS and GC-FTIR. The structures of the known photoproducts were established by comparison of their spectral properties with those of authentic samples purchased from commercial sources. Their yields were established by GC taking into account the

different response factors. They are given in % of the starting amount of parent compound.

## RESULTS AND DISCUSSION

The photoproduct retention times, MS fragmentation patterns, and IR spectral data are shown in Table 1.

Photolysis of **1** (Schemes 1 and 2) under oxygen atmosphere led to six different photoproducts identified

**Scheme 2. Photodecarboxylation Routes of 2-(2,4-Dichlorophenoxy)propionic Acid (1)**

**Scheme 3. Photodegradation of 2-Naphthoxyacetic Acid (2)**


as the previously known 2-chlorophenol (**5**, 6%), 2,4-dichlorophenol (**6**, 19%), 4-chlorophenol (**7**, 6%), 2,4-dichlorophenyl acetate (**8**, 6%) (Sithole et al., 1986), the lactone of 2-(4-chloro-2-hydroxyphenoxy)propionic acid (**9**, 6%) (Cavill and Ford, 1954), and 2-(2-chlorophenoxy)propionic acid (**10**, 13%). Irradiation under argon atmosphere (Schemes 1 and 2) led again to **5** (10%), **6** (26%), **7** (14%), and **10** (7%) together with the photodecarboxylation product 2,4-dichlorophenyl ethyl ether (**11**, 5%) (Fast et al., 1989). Hence, the total percent photolysis was 56% under air and 62% under argon.

Photolysis of **2** (Scheme 3) under aerobic conditions gave  $\beta$ -naphthol (**12**, 73%) as the major photoproduct, together with minor amounts of 2-hydroxy-1-naphthaldehyde (**13**, 3%) and naphtho[2,1-*b*]furan-2(1*H*)-one (**14**, 4%) (Kito et al., 1991). Upon irradiation under argon atmosphere only **12** (24%) and **14** (8%) were detected. Hence, the total percent photolysis was 80% under air and 32% under argon.

When irradiation of **3** (Scheme 1) was carried out under oxygen, only four photoproducts were detected and identified: the phenol derivatives **5** (5%), **6** (58%), and **7** (26%) and the lactone of 4-chloro-2-hydroxyphenoxyacetic acid (**15**, 5%) (Brown and McCall, 1955; Zepp et al., 1975; Cavill and Ford, 1954). Under argon atmosphere, the products were **5** (4%), **6** (30%), **7** (8%),

and **15** (9%). Hence, the total percent photolysis was 94% under air and 51% under argon.

Finally, photolysis of **4** (Scheme 1) under oxygen atmosphere led to five different products: phenol (**16**, 38%), **7** (28%), 2-(3*H*)-benzofuranone (**17**, 7%) (Binkley and Oakes, 1974), phenoxyacetic acid (**18**, 3%), and 5-chloro-2-(3*H*)-benzofuranone (**19**, 12%) (Vallejos and Christidis, 1993). From the photolysis under argon atmosphere, the major photoproducts detected were phenols **16** (51%) and **7** (43%) together with minor amounts of **19** (4%). Hence, the total percent photolysis was 88% under air and 98% under argon.

When aqueous solutions of 2-(2,4-dichlorophenoxy)propionic acid (**1**) were irradiated, the most general processes were photolytic cleavage of the aryl-halogen bond (route i) and the aryloxy-carbon bond (route ii) (see Schemes 1 and 2). Similar photodegradation pathways had been previously observed for 2,4-D and 4-CPA and were confirmed in this work (Crosby and Tutass, 1966; Crosby and Wong, 1973; Smith, 1989).

The formation of 2,4-dichlorophenyl acetate (**8**) and 2,4-dichlorophenyl ethyl ether (**11**) must occur *via* cleavage of the carbon-carbon bond  $\alpha$  to the carboxy group to give radicals (**I**) (route iii). Trapping of **I** by oxygen would lead ultimately to the isolated product **8** through the intermediacy of hydroperoxy radicals (**II**).

In the absence of oxygen, radical **I** would lead to the ethyl ether **11**.

Lactones **9** and **15** are the thermal cyclization products of hydroxyacids **9a** and **15a** (Brown and McCall, 1955; Cavill and Ford, 1954). Likewise, the benzofuranones **17** and **19** arise from hydroxy acid precursors **17a** and **19a**. It is worth mentioning that, in addition to the widely used GC-MS techniques, GC-FTIR provides a very useful tool for the analysis of the reaction mixtures resulting from photolysis of phenoxyalkanoic acid pesticides. Thus, phenols exhibit a sharp hydroxy band at  $3581\text{ cm}^{-1}$ , and phenoxyalkanoic acids give rise to typical hydroxy and carbonyl bands at  $\nu > 3500$  and ca.  $1800\text{ cm}^{-1}$  respectively (data not given in Table 1). More interestingly, the unexpected acetate **8** displayed a C=O absorption at  $1795\text{ cm}^{-1}$ , and the lactones were also recognized through their carbonyl bands. The  $\nu$  values were higher for C=O groups within five-membered rings (ca.  $1840\text{ cm}^{-1}$  in **17** and **19**) than for the six-membered analogues (ca.  $1810\text{ cm}^{-1}$  in **9** and **15**).

The photodegradation of 2-naphthoxyacetic acid was also examined. When irradiation was carried out under aerobic conditions, a mixture of three products (**12**–**14**) resulted. Under argon only **12** and **14** were obtained (Scheme 3). In general, the photodegradation pathways were similar to those outlined in the case of the analogue pesticides **1**–**3**. Thus, cleavage of the aryl-oxy-carbon bond (route ii) predominates, to give naphthol or the rearranged hydroxy acid **14a**, which is detected as the corresponding lactone **14** ( $\nu = 1836\text{ cm}^{-1}$ ). Carbon-carbon cleavage (route iii) must also occur to some extent. Although formate **IV** is not detected, the isomeric 2-hydroxy-1-naphthaldehyde (**13**) was clearly identified by its MS and FTIR spectra (see Table 1).

Formation of this type of photoproducts in phenoxyalkanoic acid pesticides is unprecedented. Its structure was further assessed by alternative synthesis, consisting in the irradiation of  $\beta$ -naphthol in aerated chloroform (Jimenez et al., 1995). All the spectra of the synthesized standard were coincident with those of the product resulting from irradiation of **2**. From the mechanistic point of view, the photochemical transformation of formate **IV** into hydroxyaldehyde **13** can be explained as a photo-Fries rearrangement, which is well documented in the literature (Miranda and Garcia, 1992; Miranda, 1995).

In summary, the phenoxyalkanoic acid derivatives dichlorprop and 2-naphthoxyacetic acid are photolabile and undergo cleavage of carbon-halogen, carbon-oxygen, and/or carbon-carbon bonds. Most of their photodegradation pathways are similar to those of 2,4-D and 4-CPA, which have been well documented in the scientific literature. However, other processes such as non-oxidative decarboxylation (to give **11**) or the formation of formyl phenols (e.g., **13**) are unprecedented in the field of pesticide photochemistry.

#### ABBREVIATIONS USED

2,4-D (**3**), 2,4-dichlorophenoxyacetic acid; 4-CPA (**4**), 4-chlorophenoxyacetic acid; GC, gas chromatography;

FID, flame ionization detector; MS, mass spectrometry; FTIR, infrared spectrophotometry.

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