Solution-Phase Photodecomposition of Several Substituted Diphenyl Ether Herbicides

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The solution photoproducts of eight substituted diphenyl ethers irradiated at 300 nm were identified. Water, cyclohexane, and methanol were used as solvents. The major reaction pathways observed included reductive dehalogenation, decarboxymethylation, reduction of nitro substituents, and cleavage of the ether linkage to yield phenols. Nucleophilic substitution by the solvent was also observed.

The photochemical fate of substituted diphenyl ethers has received some attention in recent years. In a manner similar to that for the phenoxyacetic acids, nitrodiphenyl ethers are photolyzed to phenols in water. Fluorodifen yields *p*-nitrophenol and 2-nitro-4-(trifluoromethyl)phenol and small amounts of the reduced product upon irradiation (Eastin, 1972). Nakagawa and Crosby (1974a,b) studied the sunlight photolysis of nitrofen in aqueous methanol and found the predominant reaction to involve nucleophilic attack by the hydroxide moiety of water and by other added nucleophiles. A study of the photodegradation of chlorinated diphenyl ethers in nonaqueous solvents (Choudry et al., 1977) revealed extensive dechlorination reaction but no phenolic products.

We report on the fate of other substituents in various diphenyl ether herbicides irradiated at environmentally significant wavelengths in solvents of varying polarity and hydrogen-donating capability.

MATERIALS AND METHODS

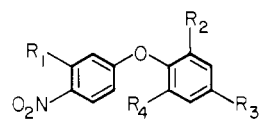
Diphenyl Ethers. All the substituted ethers (1–8) listed in Table I were obtained from Mobil Chemical Co. (courtesy of Dr. Bob Theissen) and used after recrystallization from ethanol and *n*-hexane. GLC cochromatography and infrared, nuclear magnetic resonance, and mass spectrometry were used for authentication.

Solvents. Methanol and cyclohexane were glass distilled (Mallinckrodt Chemical Works, St. Louis, Mo; analytical reagent). All water used in photolysis was distilled and deionized.

Analytical Equipment. Infrared spectra were determined with 5-mm potassium bromide disks on a Perkin-Elmer 337 grating spectrophotometer. Nuclear magnetic resonance spectra were recorded by using a Varian T-60 NMR spectrometer. Samples were dissolved in carbon tetrachloride or deuterated chloroform. Tetramethylsilane was used as the internal standard.

Analysis. Gas–liquid chromatography (GLC) was accomplished with a Beckman GC-65 instrument equipped with a flame ionization detector. The column packing was a mixture of 15% QF-1 and 10% DC-200 liquid phases on 80–100 mesh Gas-Chrom Q. Operating parameters were generally as follows: stainless steel column, 0.7 m × 4 mm i.d. (A), and Pyrex glass tube, 2 m × 2 mm i.d. (B). Column flow was 20 mL/min of helium in column A and 120 mL/min in column B. Injector and detector temperatures were 210 and 310 °C, respectively. All analyses were made by temperature programming. The initial temperature of 70° was held for 2 min and then programmed with a linear temperature increase of 7.5°/min from 70° to a final temperature of 230 °C for column A and from 100 to 240 °C at 10 °C/min for column B. Quantitation was accomplished by comparison of GLC peak areas with those of authentic standards or compounds of similar retention time.

Table I. Structure of Substituted Diphenyl Ethers (1-8) and Their Ultraviolet Absorption Characteristics



designation	substituents	ϵ[a]
1	$R_1 = R_4 = H; R_2 = NO_2; R_3 = CF_3$	5720[b]
2	$R_1 = R_4 = H; R_2 = R_3 = Cl$	20000
3	$R_1 = H; R_2 = R_3 = R_4 = Cl$	9000
4	$R_1 = CO_2CH_3; R_2 = R_3 = Cl; R_4 = H$	6500
5	$R_1 = CO_2CH_3; R_2 = R_3 = R_4 = Cl$	5000
6	$R_1 = CO_2C_2H_5; R_2 = R_3 = Cl; R_4 = H$	7500
7	$R_1 = CO_2CH_3; R_2 = Cl; R_3 = F; R_4 = H$	4400
8	$R_1 = CO_2CH_3; R_2 = R_3 = Cl; R_4 = F$	5550

[a] Molar absorptivity at 300 nm with 10^{-5} M hexane solution. [b] Ethanol solutions.

Thin-layer chromatography (TLC) was accomplished on precoated 20 × 20 cm analytical plates (2 mm) of silica gel HF-254 (Brinkman Instruments, Inc., Westbury, NY). The developing systems used were (A) benzene–chloroform (1:1), (B) chloroform–ethyl acetate–acetic acid (6:3:1), and (C) chloroform–methanol–acetic acid (90:5:5).

Mass spectra were obtained from a Du Pont 21-490 mass spectrometer interfaced with a Beckman GC-65 gas chromatograph. Spectra were determined by using the direct probe and GC inlet systems at an ionizing potential of 70 eV.

Photochemical Procedures. Samples were irradiated in a Rayonette Reactor (The Southern N.E. Ultraviolet Co., Middletown, CT) equipped with NPR-3000 lamps having a peak energy output of 300 nm. The irradiations were carried out at 30 °C in a 2-L borosilicate glass round-bottomed flask equipped with a magnetic stirrer to <20% conversion.

In general, amounts ranging from 0.5 to 2.0 g were dispersed in 2 L of distilled water or dissolved in either methanol or cyclohexane. The suspensions were irradiated for 2- and 10-day periods, and then the solvent was evaporated or in the case of aqueous mixtures, extracted with ether and then evaporated. The residue was dissolved in acetone and applied to TLC plates. Each band was extracted with either methanol or acetone and concentrated. A dark control was kept in each case and no reaction was observed in it over the irradiation time periods.

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Table II. Photoproducts of Substituted Diphenyl Ether (DPE) Herbicides in Water

DPE	product[a]	Rt,[b] min	R_f	m/e (M)
1	4-nitrophenol	22.5	0.37[c]	139
	4-(trifluoromethyl)-2-aminophenol	18.3	0.28	177
2	4-nitrophenol	22.5		139
	2,4-dichlorophenol	12.2		162
	2,4-dichloro-4′-amino-DPE	28.5		253
3	2,4,6-trichloro-3′-hydroxy-4′-nitro-DPE	49.9		333
	2,4-dichloro-4′-nitro-DPE (2)	34.4		283
4	2,4-dichloro-3′-(carboxymethyl)-4′-hydroxy-DPE		0.44[d]	312
	2,4-dichloro-3′-(carboxymethyl)-4′-amino-DPE		0.17[d]	311
5	2,4,6-trichlorophenol	17.3		196
	2,4,6-trichloro-3′-hydroxy-4′-nitroso-DPE	37.0		317
	methyl formate	8.6		60
6	2,4-dichloro-4′-nitro-DPE (2)	34.4		283
	ethyl formate	9.2		74
7	2-chloro-4-fluorophenol	10.0		146
	4-fluoro-3′-(carboxymethyl)-4′-nitro-DPE	33.5		291
8	2,4-dichloro-6-fluoro-4′-nitro-DPE	30.6		301
	4-chloro-6-fluoro-3′-(carboxymethyl)-4′-nitro-DPE	40.0		325
	methyl formate	8.6		60

[a] Only major products shown. [b] Column A retention times. [c] Solvent system D. [d] Solvent system A.

Analysis of the photoproducts was carried out either by direct injection of the reaction mixture in the GLC or by TLC separation followed by GLC analysis. The photoproducts and their chromatographic and mass spectrometric characteristics are given in Table II. The individual photoproducts were characterized by a combination of cochromatography with authentic materials and spectral examination. The production of volatile compounds (CO; CO_2) was not monitored.

RESULTS

Photolysis of Preforan (1). In water suspension *p*-nitrophenol and 4-(trifluoromethyl)-2-aminophenol were found to be the major products (>90% of total product formation). The GLC retention times, R_f values, and infrared spectra of *p*-nitrophenol matched those of the authentic sample. In its mass spectrum *p*-nitrophenol showed prominent signals at *m/e* 139 (M), 138 (M - H), 122 (M - OH), and 93 (M - NO_2). 4-(Trifluoromethyl)-2-aminophenol showed fragments at *m/e* 177 (M), 176 (M - H), 160 (M - OH), and 108 (M - CF_3).

Trace amounts (<1%) of 4-(trifluoromethyl)-2-nitrophenol (*m/e* 207) and of 4-hydroxy-3-nitrobenzoic acid, detected as its methyl ester (*m/e* 197), were observed.

Photolysis of **1** in cyclohexane yielded *p*-nitrophenol and 3-(trifluoromethyl)nitrobenzene (*m/e* 191). In methanol the predominant products arose from reduction of the nitro group to yield amino-**1** and from methoxylation of the ring. 4-Nitrophenol and 2-amino-4-(trifluoromethyl)anisole (*m/e* 191) were identified.

Photolysis of Nitrofen (2). In water this compound gave 2,4-dichloro-4′-aminodiphenyl ether as the major product (>80% of total product formation). The mass spectrum showed signals at *m/e* 253 (M) (2Cl), 218 (M - Cl), 183 (M - 2Cl), and 145 (M - 108). Small amounts (<10%) of *p*-nitrophenol and 2,4-dichlorophenol were also detected and identified by comparison of their GLC retention times and mass spectra with those of authentic samples. The infrared spectrum of 4′-aminonitrofen showed the characteristic -NH_2 band at 3300–3700 cm^{-1}.

Trace amounts of dechlorinated and hydroxylated products were also observed but not identified conclusively. In cyclohexane solution the major product was also aminonitrofen.

Photolysis of MC-338 (3). Irradiation in water yielded 2,4,6-trichloro-3-hydroxy-4′-nitrodiphenyl ether as the major product (>85%). In its mass spectrum the parent peak (M) appeared at *m/e* 333 with M + 2, M + 4, and M + 6 signals showing the presence of three chlorines. The presence of -OH is well supported from its IR band at 3100 cm^{-1} and intense M - 1 and M - 17 signals in the mass spectrum. The position of the OH group can be determined from the fragment observed at *m/e* 138 corresponding to M - $C_6H_2Cl_3O$. Since only the meta position in the chlorinated ring can be attacked by the solvent while retaining three chlorines, the compound must be the 3-hydroxy derivative of **3**.

A minor product of the reaction was nitrofen (**2**) with M at *m/e* 283 (2Cl) and M - 70 signals. Its retention time and mass spectrum matched that of authentic material. Trace amounts of *p*-nitrophenol and 2,4,6-trichlorophenol (*m/e* 196) were also detected.

In cyclohexane solution the major product identified was amino-**3** with M at 287 and fragments at *m/e* M - 16, M - 35, and M - 70.

Photolysis of MC-4379 (4). Irradiation in water gave as major products 2,4-dichloro-3′-(carboxymethyl)-4′-hydroxydiphenyl ether and 2,4-dichloro-3′-(carboxymethyl)-4′-aminodiphenyl ether. 4′Hydroxy-**4** was identified from its mass spectrum signals at *m/e* 312 (M, 2Cl), 311 (M - H), 295 (M - OH), and 281 (M - OCH_3). The infrared spectrum showed -OH at 3100 and CO at 1650 cm^{-1}. 4′-Amino-**4** had M at *m/e* 311 (2Cl), M - NH_2, and M - 70 (M - 2Cl) signals present. Trace amounts of 2,4-dichlorophenol (*m/e* 139) were observed.

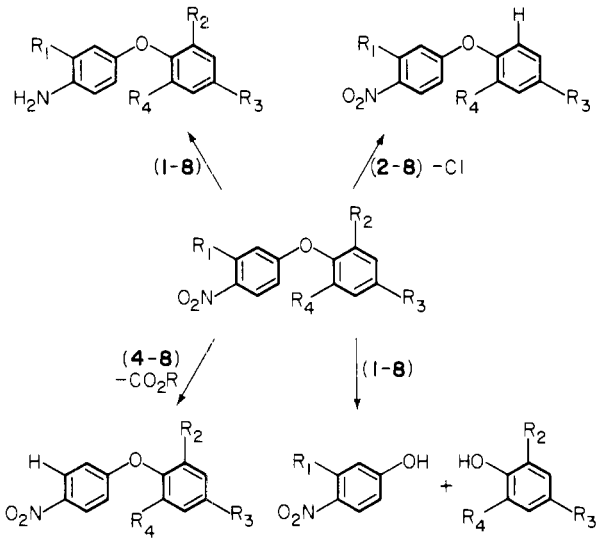
In cyclohexane 2,4-dichloro-4′-nitrodiphenyl ether (*m/e* 307) and methyl formate (*m/e* 60) were predominant products. In methanol, a dichloromethoxy phenol (*m/e* 176) was also observed in small yield (2%).

Photolysis of MC-3761 (5). In water **5** yielded predominantly 2,4,6-trichloro-3′-hydroxy-4′-nitrosodiphenyl ether and 2,4,6-trichlorophenol. The nitroso compound had M at *m/e* 317 (3Cl). Fragments at 287 (M - NO) and 235 (M - NO - OH - Cl) characterize it. 2,4,6-Trichlorophenol (*m/e* 196) showed identical GLC retention time and MS as an authentic sample. Methyl formate (*m/e* 60) also formed during the reaction.

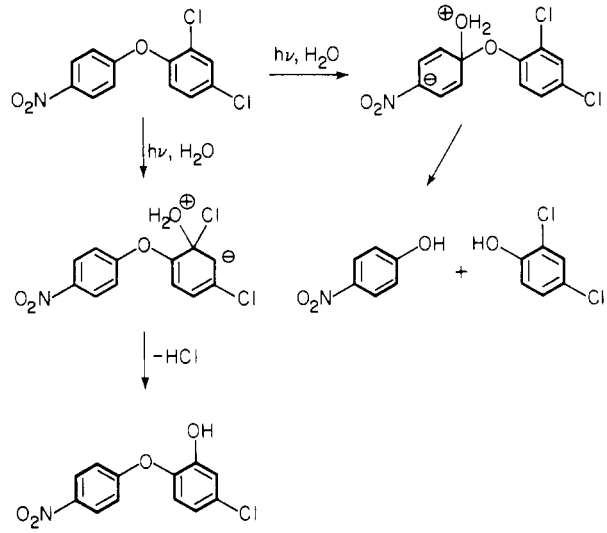
In cyclohexane the major product was 4′-amino-MC-3761 with M at *m/e* 345. In methanol 2,4,6-trichloro-3′-methoxy-4′-aminodiphenyl ether (*m/e* 317) formed preferentially.

Photolysis of MC-5127 (6). Irradiation of water suspensions of **6** resulted in the formtion of nitrofen (**2**) and ethyl formate as major products. The mass spectra of both compounds were identical with those of authentic samples.

Scheme I. Photoreactions of Substituted Diphenyl Ethers (1-8) in Water Suspensions



Scheme II. Photonucleophilic Substitution Reactions of Nitrofen (2) in Water



Trace amounts of 4'-amino-6 (m/e 325), 2,4'-dichlorophenol (m/e 162), and 4-amino-3-(carboxyethyl)phenol (m/e 181) were formed. Irradiation of the methanol solution of 6 yielded the same products as in water. In cyclohexane, reduction of 6 to amino-6 was the only reaction observed.

Photolysis of MC-6063 (7). The major reaction pathway in water led to formation of 2-chloro-4-fluorophenol (m/e 146, M - 35, M - 54) and 4-fluoro-4'-nitro-3'-(carboxymethyl)diphenyl ether (m/e 291, M - 19, M - 59). Small amounts of 3-nitro-3-(carboxymethyl)phenol (m/e 197) were also observed. In either cyclohexane or methanol the same products as in water were formed.

Photolysis of MC-7181 (8). In water the major products were identified as 4'-nitro-2,4-dichloro-6-fluorodiphenyl ether, 4-chloro-6-fluoro-3'-(carboxymethyl)-4'-nitrodiphenyl ether, and methyl formate. The decarboxymethylated product had signals at m/e 301 (2Cl) and M - 70. The dechlorinated product had M at m/e 325 (1Cl), M - 31 (M - OCH_3), and M - 59 (M - $COOCH_3$) signals. Trace amounts of 3-hydroxy-4-nitrophenol (m/e 155) and 2,4-dichloro-6-fluorophenol (m/e 180) were observed as well.

In cyclohexane, 4'-amino-8 (m/e 281) was formed predominantly. Completely dechlorinated 8 (m/e 291) was the major product in methanol.

DISCUSSION

The compounds studied absorb strongly in the 300-nm region (Table I). Their spectra consist of a smooth, featureless band with λ_{max} around 280 nm ($\epsilon_{max} \sim 10^4$) and a sharper, more intense band with λ_{max} near 220 nm, probably arising from the allowed π-π^* transition of the benzene rings. In any photochemical process the transitions occurring at the wavelength of irradiation are primarily responsible for the reactions the molecules will undergo. In the diphenyl ethers 1-8 it becomes difficult to assign unequivocally the said transition; due to the variety of substituent groups present several reactions are possible (Scheme I). Contributions by n $\rightarrow$ π^* transitions of the nitro and ester groups together with interactions of the halogen and ether oxygen nonbonding electrons with the π system give rise to the broad 280-nm band.

Nitro groups are known to undergo reductive processes in hydrogen-donating solvents such as cyclohexane and methanol (Chachaty and Forchioni, 1968; Cowley and Sulcliffe, 1968). One of the intermediates in the formation of the amines is the nitroso compound which we have observed as a major photoproduct of 5. The reduction to the amino-DPE must involve successive hydrogen abstractions to yield in turn $-NO_2H \rightarrow N(OH)_2 \rightarrow -NO \rightarrow -NHOH \rightarrow NH_2$. It would be reasonable to expect this process to take place more readily in cyclohexane than in water, and this is confirmed by our results.

Cleavage of aromatic chlorides upon irradiation has been well substantiated in the literature (Sundström and Ruzo, 1978; Ruzo et al., 1974). The resulting "free" phenyl radicals can then abstract hydrogen or trap the solvent. All DPE studied which contained chlorine exhibited products arising from such cleavage.

Hydroxy- and methoxylation on the aromatic rings were observed in the photolysis of several DPE. Compounds 3-5 gave major products arising from nucleophilic attack on the rings. In all cases at least trace amounts of photoproducts arose from this type of reaction. Ionic intermediates have been postulated in the photonucleophilic reactions of other haloaromatics (Havinga and Kronenberg, 1968; Barltrop, 1967). Nucleophilic attack on the ether carbons would lead to breakage of the C-O bond to yield phenols or anisoles, which are observed among the major photoproducts of 1-8. Nakagawa and Crosby (1974a,b) reported that phenols are the major products under sunlight irradiation. These processes are illustrated in Scheme II for compound 2.

Decarboxymethylation is known to occur in other systems (Thynne, 1968), yielding carboxyalkyl and alkoxy radicals, though, to our knowledge, no aromatic esters such as those reported here have been studied. The considerable amounts of formates recovered indicate the possibility of hydrogen abstraction by a carboxyalkyl radical.

Although small amounts (<1%) of some photoproducts were left unidentified, the major pathways of DPE photoreaction have been determined. It is of interest that these correlate well with the metabolic pathways observed in similar compounds (Eastin, 1971; Gutenman and Lisk, 1967). The photochemistry of diphenyl ethers may also be informative when related to the dependence of their pesticidal activity on light absorption (Matsunaka, 1969).

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A Gas–Liquid Chromatographic Method for Analysis of Phenolic Acids in Plants

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A GLC–MS method was developed to analyze phenolic acid extracts from plant material. Extracted acids were converted to their methyl esters by refluxing in 3 M hydrogen chloride in methanol, and the esters were reacted with bis(trimethylsilyl)trifluoracetamide plus 10% trimethylchlorosilane to silylate the phenolic groups. Derivatives of standard *p*-hydroxybenzoic, gallic, ferulic, sinapic, caffeic, *p*-coumaric, gentistic, and protocatechuic acids prepared by this procedure were analyzed by GLC on 3.75 m × 0.032 cm columns of 3% SE-30 and OV-17 on 100–120-mesh Chromosorb W. GLC–MS analysis of extracts from sphagnum moss, instant tea, and Stuart pecan kernels revealed the presence of *p*-hydroxybenzoic, coumaric, and protocatechuic acids, coumaric, gallic, and caffeic acids, and *p*-hydroxybenzoic, vanillic, coumaric, protocatechuic, syringic, gallic, gentistic, and (*p*-hydroxyphenyl)acetic acids, respectively.

Numerous methods have been reported for determining microquantities of phenolic acids in plants and have involved separations by paper chromatography, thin-layer chromatography (TLC), column chromatography (Geissman, 1962; Ribêreau-Gayon, 1972), or gas–liquid chromatography (GLC). Except when analysis is by GLC, qualitation of naturally occurring phenolics is usually based on TLC or paper chromatographic separations, followed by determination of absorption maxima in the UV region, identification of their colored complexes subjectively, and/or determination of R_f values. These procedures are not entirely satisfactory because of time requirements, resolving power, and lack of adaptability to quantitative procedures. Phenolic acids have been analyzed by GLC as their trimethylsilyl ether/esters (Chapman et al., 1970; Morita, 1972). However, investigators have reported difficulties in silylating dihydroxyphenolic acids (Karlson and Svendsen, 1965; Blakely, 1966). Phenolic acids have also been analyzed by GLC as their methyl ether/methyl esters (Erickson et al., 1973); however, several phenolic acids with similar methoxyl groups yield identical derivatives when completely methylated. Salomonsson et al. (1978) described a GLC technique for analyzing phenolic acids as their ethyl ether/ethyl esters.

By the GLC method we now report, the inadequacies of some of the preceeding methods have been eliminated by improved derivatization and analytical procedures, and analyses of phenolic acid isolates from natural products are now both rapid and quantitative.

EXPERIMENTAL SECTION

Reference Compounds. *p*-Hydroxybenzoic, vanillic, gallic, ferulic, sinapic, caffeic, *p*-coumaric, syringic, gentisic, protocatechuic, and (*p*-hydroxyphenyl)acetic acids were obtained from commercial sources. All reference acids and some of their corresponding methyl esters were analyzed by mass spectrometry for purity and spectral characteristics by means of the direct insertion probe. Standard mixtures of the trimethylsilyl ether/esters of these acids were prepared by the following procedure. One-tenth milligram of each acid was dissolved in 5 mL of 3 M hydrogen chloride in methanol; this mixture was divided into duplicate 2.5-mL aliquots, placed in screw-capped test tubes, and refluxed for 0.5, h for esterification. Hydrogen chloride and methanol were partially removed under vacuum (10 torr), and 0.2 mL of methylene chloride was added to the residue. Evaporation was repeated until the mixture was free of hydrogen chloride odor. The residue was then dissolved in 2 mL of redistilled acetonitrile, 0.1 mL of bis(trimethylsilyl)trifluoroacetamide (BSTFA) plus 10% trimethylchlorosilane (TMCS) (Regis Chemical Co.) was added, and the mixture was allowed to stand for 15 min. After silylation was accomplished, the solution was concentrated to 0.5 mL with a stream of purified N_2 for GLC analysis.

GLC–MS Analysis. GLC analyses were made with a 3.75 m × 0.32 cm glass column packed with 3% SE-30 on 100–120-mesh Chromosorb W. The oven temperature was programmed from 120 to 225 °C at 4 °C/min, and the helium flow was 25 mL/min. Additional analyses were made with a 3.75 m × 0.32 cm glass column packed with 3% OV-17 on 100–120-mesh Chromosorb W. The OV-17 column was programmed from 130 to 225 °C at 3 °C/min, and the helium flow was 28 mL/min. The injector and detector were maintained at 250 °C. Both columns were used a Perkin-Elmer Model 900 gas chromatograph that was equipped with a flame ionization detector and was connected to a Du Pont 21-490B mass spectrometer equipped with differential pumping on the analyzer section (Senter and Horvat, 1976). Phenolic acid derivatives for

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