Photodecomposition of Nitrofen

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Photodecomposition of the herbicide nitrofen (2,4-dichlorophenyl p-nitrophenyl ether) in aqueous suspensions under sunlight or simulated sunlight was characterized by rapid cleavage of the ether linkage to form 2,4-dichlorophenol and p-nitrophenol. Other prominent products included hydroquinone and 4-nitrocatechol, 2,4-dichlorophenyl p-aminophenyl ether, 4,4'-bis(2,4-dichlorophenoxy)azobenzene, and an artifact, N-[4-(2',4'-dichlorophenoxy)]phenylformamide. Other pathways involved the replacement of the ring chlorines by hydroxyl or hydrogen, ring hydroxylation, denitration by hydroxide prior to cleavage of the ether linkage, and possible intramolecular rearrangement of the nitrofen to a biphenyl.

Nitrofen (or TOK), 2,4-dichlorophenyl p-nitrophenyl ether (I),[2] is receiving increased use for both pre- and post-emergence weed control in such major crops as rice, sugar beets, and cole crops. However, among the economically important herbicides, the environmental fate of the diphenyl ethers has received surprisingly little attention. Nitrofen has been reported to darken under exposure to ultraviolet (uv) light (Weed Society of America, 1970), but the identity of the decomposition products has not been reported.

The application of these herbicides in rice paddy water has potential agricultural importance for both the United States and other nations, but present practice requires exposure of the chemical to intense sunlight. The present investigation was concerned with the stability of nitrofen to sunlight under controlled conditions and the identity of any photolysis products.

EXPERIMENTAL SECTION

Materials. Nitrofen (I) was isolated from the commercial TOK E-25 emulsifiable concentrate (25% nitrofen in petroleum hydrocarbons) by evaporation of the solvent under reduced pressure and repeated recrystallization of the residue from n-hexane and from absolute ethanol until a constant mp of 70.5–71.0° (Weed Society of America, 1970; 71–72°) and homogeneity to gas chromatography (glc) and thin-layer chromatography (tlc) were attained.

4-Chlorocatechol (III), commercially available (Aldrich Chemical Co.) as a dark powder, was crystallized from benzene to remove insoluble resin and then sublimed (Crosby and Tutass, 1966) to provide colorless crystals. 2,4-Dichlorophenol (II), p-nitrophenol (V), and other chemicals were used in commercial form.

2,4-Dichlorophenyl p-aminophenyl ether (VII), prepared by reduction of nitrofen in aqueous ethanol with concentrated hydrochloric acid and zinc dust, provided colorless needles after purification by column chromatography on silicic acid: infrared (ir) 3425 (NH), 3311 (NH) cm^{-1}; mass spectrum m/e 253 (parent). Anal. Calcd for $C_{12}H_9Cl_2NO$: C, 56.67; H, 3.55; N, 5.51. Found: C, 56.71; H, 3.52; N, 5.61.

4,4'-Bis(2,4-dichlorophenoxy)azobenzene (VIII) was prepared (Bigelow and Robinson, 1964) by reduction of a suspension of 5.6 g of nitrofen with 2.6 g of zinc dust in a mixture of 100 ml of methanol, 3.6 g of sodium hydroxide, and 10 ml of deionized water. After 5 hr of boiling under reflux, the mixture was diluted with 100 ml of hot metha-

nol to dissolve organic materials and filtered, and the precipitate (sodium zincate) was washed on the filter with hot methanol. The solvent was evaporated under reduced pressure at 50–60°, the remaining material was subjected to column chromatography on silicic acid and eluted with benzene, and the first yellow effluent was collected. This fraction was purified by tlc on silica gel G (Merck, 0.5 mm) with benzene to separate the product from unchanged nitrofen; extraction and recrystallization from chloroform gave 0.9 g of yellow needles: mp 163°; mass spectrum m/e 502 (parent) (isotope abundance P + 2, 142.3%; P + 4, 65.0%). Anal. Calcd for $C_{24}H_{24}Cl_4N_2O_2$: C, 57.12; H, 2.78; N, 5.55. Found: C, 56.96; H, 2.61; N, 5.56.

N-[4-(2',4'-Dichlorophenoxy)]phenylformamide (IX) was prepared by boiling 2.0 g of VII with 500 mg of formic acid for 3 hr, followed by dilution with ether; the ether solution was washed with water, dried over anhydrous sodium sulfate, and evaporated to an oily residue which crystallized from n-hexane–chloroform (1:1) as colorless leaflets: mp 96–98°; yield, 1.6 g; ir 3311 (NH), 1675 (CO) cm^{-1}; mass spectrum m/e 281 (parent). Anal. Calcd for $C_{13}H_9Cl_2NO_2$: C, 55.32; H, 3.19; N, 4.96. Found: C, 55.29; H, 3.19; N, 5.12.

p-Chlorophenyl p-nitrophenyl ether (XIV) and o-chlorophenyl p-nitrophenyl ether (XV) were prepared by the reaction of 1-chloro-4-nitrobenzene with p-chlorophenol and o-chlorophenol, respectively (Mason and Brooker, 1968): XIV, mp 76–78° (Mason and Brooker, 1968; 74–78°); XV, mp 78–80° (Mason and Brooker, 1968; 80°).

Irradiation. Since nitrofen is practically insoluble in water, bulk samples for irradiation were prepared by dissolving 100 mg of the herbicide in 100 ml of double distilled methanol and dispersing the solution into 900 ml of deionized water to provide a concentration of 100 ppm.

Simulated sunlight irradiation was carried out in a borosilicate glass photoreactor (Crosby and Tang, 1969) equipped with a condenser and an F40BL fluorescent lamp (General Electric Co., Schenectady, N. Y.), generally for 5 days at 23–40°. Filtered compressed air or nitrogen was introduced through the gas inlet of the reactor at about 20 ml/min. Sunlight irradiation was carried out for 10 days in erlenmeyer flasks containing 4 l. of bulk sample suspension and covered with a beaker at the mouth to prevent contamination. Alternatively, 400 mg of nitrofen previously ground in a mortar was suspended in 4 l. of deionized water and the mixture exposed under sunlight for the same period.

To determine the sequence of photolysis reactions, 200 mg each of 2,4-dichlorophenol, p-nitrophenol, and 2,4-dichlorophenyl p-aminophenyl ether was suspended in 1 l. of deionized water and irradiated in the same way. In all instances, controls were held in the dark at room temperature for the same periods.

Extraction and Separation. As outlined in Figure 1, the irradiated sample was made alkaline (pH 12) with 4 N

nitrofen suspension

Figure 1. Extraction scheme for nitrofen photolysis products.

RESULTS AND DISCUSSION

Suspensions of nitrofen exposed to sunlight or to uv light in the laboratory rapidly became brown in color, and a dark amorphous precipitate appeared. On acidification of the aqueous phase B, more of the solid precipitated. It was insoluble in acid and in organic solvents, soluble in alkalies, and its appearance and properties were very similar to those of the polymeric humic acids encountered as products of 2,4-D photolysis (Crosby and Tutass, 1966).

Quite similar polymeric material was obtained from irradiated samples of 2,4-dichlorophenol and p-nitrophenol. However, while their ir spectra were similar, they were not in good agreement with that of the humic acid obtained from irradiation of 2,4-D (Crosby and Tutass, 1966), perhaps due to the differences in pH of the reaction medium and the irradiation periods.

The products isolated from the photolysis of nitrofen in 10% aqueous methanol suspensions are indicated in Table I; the same major compounds also were observed when nitrofen was irradiated in deionized water alone. In no instance was reaction observed in the control kept in the dark at room temperature.

Mass Spectra. Because only microgam amounts of most of the minor (methylated) acidic products could be isolated. mass spectra provided the most important structural data. Each compound gave a strong molecular ion with an isotopic cluster from which the number of chlorine atoms was easily determined. The nitro group was confirmed by the $P - NO$ peak (Kinstle and Oliver, 1969), but the corresponding $P - NO_2$ ion seldom was observed. The $P - CH_3$ ion was indicative of the methoxyl group.

In each instance. the chlorinated ring provided fragments which defined the ring substituents. As expected (Ballantine and Pillinger, 1968), the $ClArO^+$ ion was always present but was accompanied by a usually more intense fragment at one higher mass unit. The effect was observed only with diphenyl ethers and may result from transfer of an ortho hydrogen from the opposite ring. Except with nitrofen, no nitro-containing fragments were observed in mass spectra. However, where the nitro group was replaced by a methoxyl (XIII–XV, XVIII), the CH_3O-ArO^+ ion also became prominent. Benzotropylium ions (Beynon et al., 1959; Eland and Danby, 1965) were not observed.

Neutral Fraction C. Glc indicated the presence of one major and two minor volatile constituents in addition to unchanged nitrofen. The major one was identified as N-[4-(2′,4′-dichlorophenoxy)]phenylformamide (IX); a gas chromatogram of the minor products (220°) showed an unresolved shoulder,. and the constituents were identified as p-chlorophenyl p-nitrophenyl ether (XIV) accompanied by the o-chlorophenyl p-nitrophenyl isomer (XV).

Tlc of the neutral fraction in solvent B resulted in detection of seven fluorescent zones. A major constituent appearing at R_f 0.09 proved again to be the artifact IX. Another major constituent, detected in visible light at R_f 0.80, was not volatile on glc, but repeated tlc on washed plates provided the yellow crystalline 4,4′-bis(2,4-dichlorophenoxy)azobenzene (VIII). No attempt was made to identify any other neutral constituents because of the very small amounts.

Basic Fraction E. Glc showed 2,4-dichlorophenyl p-aminophenyl ether (VII) to be the only volatile constituent of this fraction. Tlc in solvent B revealed the presence of at least five constituents, with VII again the major one. Attempts to isolate the other substances by elution from chromatoplates and subsequent crystallization were unsuccessful. Irradiation of nitrofen suspensions in pure water revealed that the formation of VII did not depend on the presence of methanol. although the rate of reduction was slower in the absence of the organic solvent.

Acidic Fraction F. Tlc of this fraction in solvent A

sodium hydroxide solution and extracted four times with ether to provide a combined ether extract A and an aqueous phase B. Extract A was washed with 1 N sulfuric acid to provide the "neutral fraction" C and an aqueous phase D. Fraction D was made basic to pH 12 with 4 N sodium hydroxide and extracted with ether to provide the "basic fraction" E. The original aqueous phase B was acidified (pH 1) with 4 N sulfuric acid and extracted with ether to provide the "acidic fraction" F. Each ether extract was washed with water and dried over sodium sulfate, and the solvent evaporated in a stream of nitrogen. Prior to glc, the acidic fraction was methylated with excess ethereal diazomethane prepared in the usual way from N-methyl-N-nitroso-p-toluenesulfonamide (Diazald®).

Chromatography. The F&M Model 720 gas chromatograph was equipped with a thermal conductivity detector and either a 2 ft × ⅛ in. o.d. stainless steel column containing 6% SE-30 on 60–80 mesh Chromosorb G (HMDS treated) or 5% QF-1 and 1% DEGA on the same solid support; nitrogen flow, 20 ml/min. Preparative runs were programmed for 10°/min starting at 100°; collections were made by inserting the small end of a Pasteur pipet into the exit port of the chromatograph as the desired fraction emerged, and each fraction was reinjected and re-collected for purification.

Tlc was conducted on 0.5-mm thick Merck silica gel G, containing 1% zinc silicate phosphor, in solvent A (n-hexane-ethyl ether-glacial acetic acid, 10:10:1) or solvent B (chloroform–methanol, 19:1 (v/v)).

Identification. Ir spectra were measured in KBr disks with a Perkin-Elmer Model 337 spectrophotometer and, where possible, compared with those of authentic specimens collected from glc or tlc under identical conditions. Mass spectra were measured with a Varian Model M66 medium resolution mass spectrometer equipped with a heated inlet, or with a Finnigan Model 3000 Peak Identifier (gc-ms) equipped with a 3 ft × ⅛ in. o.d. glass column containing 6% SE-30 on 60–80 mesh Chromosorb G treated with HMDS, and again compared with standard spectra.

Rate Measurement. One-liter samples of nitrofen bulk solution in an erlenmeyer flask were exposed under sunlight in the usual way, extracted, and subjected to gas chromatography as described. The acidic extract was methylated with ethereal diazomethane before gas chromatography. The area under each chromatogram peak was measured with a planimeter and values were determined by reference to a standard curve in each instance. Control recoveries were nearly quantitative.

Table I. Properties of Nitrofen Photolysis Products

Sample	ET,a °C, or other	Mass spectrum, m/e	Formula	Proposed structure
		Fraction C (Neutral)		
C1	220	249 (P), 251, 253; 219 (P − NO)	$C_{12}H_8ClNO_3$	XIVb (+XV)
C2	235	283 (P), 285, 287; 253 (P − NO); 162 (Cl2PhOH)	$C_{12}H_7Cl_2NO_3$	Ib
C3	255	281 (P), 283, 285; 253 (P − CO); 108 (H2NPhO·)	$C_{13}H_9Cl_2NO_2$	IXb
C4	mp 163	502 (P); 467 (P − Cl)	$C_{24}H_{14}Cl_4N_2O_2$	VIIIb
		Fraction E (Basic)		
E1	253	253 (P), 255, 257; 108 (H2NPhO+)	$C_{12}H_9Cl_2NO$	VIIb
		Fraction F (Acidic)c		
F1	118			IVb
F2	128			IIb
F2A	132			IIIb
F3	145			Vb
F4	153	206 (P), 208, 210; 191 (P − CH3)	$C_8H_8Cl_2O_2$	XIX
F5	158			VIb
F6	201	268 (P), 270, 272; 253 (P − CH3); 162 (Cl2PhOH); 123 (MeOPhO+)	$C_{13}H_{10}Cl_2O_2$	XI
F7	205	264 (P), 266; 249 (P − CH3); 158 (ClMeOPhOH); 123 (MeOPhO+); 121 (MeOPhCH2−)	$C_{14}H_{13}ClO_3$	XII
F8	211	264 (P), 266; 249 (P − CH3); 158 (ClMeOPhOH); 123 (MeOPhO+)	$C_{14}H_{13}ClO_3$	XIII
F9	220	297 (P); 299, 301; 282 (P − CH3); 123 (PhNO2)	$C_{13}H_9Cl_2NO_3$	XVIII
F10	226	279 (P), 281; 264 (P − CH3); 249 (P − NO); 157 (ClMeOPhO+)	$C_{13}H_{10}ClNO_4$	X
F11	230	298 (P), 300, 302; 283 (P − CH3); 192 (ClMeOPhOH); 123 (MeOPhO−)	$C_{14}H_{12}Cl_2O_3$	XX
F12	239	313 (P), 315, 317; 298 (P − CH3); 283 (P − NO); 191 (Cl2MeOPhO+)	$C_{13}H_9Cl_2NO_4$	XVI
F12A	239	309 (P), 311; 294 (P − CH3); 279 (P − NO); 188 [Cl(MeO)2PhOH]	$C_{14}H_{12}ClNO_5$	XVII
F13	244	313 (P), 315, 317	$C_{13}H_9Cl_2NO_4$	
F14	250	324 (P), 326	$C_{16}H_{17}ClO_5$	XXII
F15	261	343 (P), 345, 347; 313 (P − NO); 192 (Cl2MeOPhOH)	$C_{14}H_{11}Cl_2NO_5$	XXI

a Elution temperature in programmed glc. b Ir spectrum and chromatographic properties authenticated with standards. c Methylated before glc.
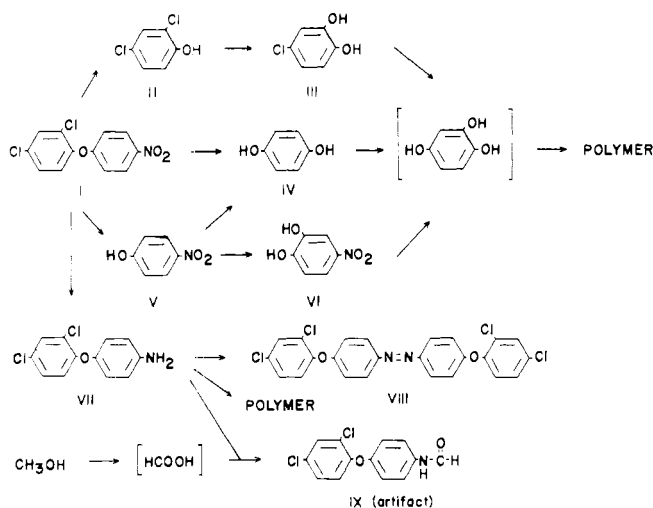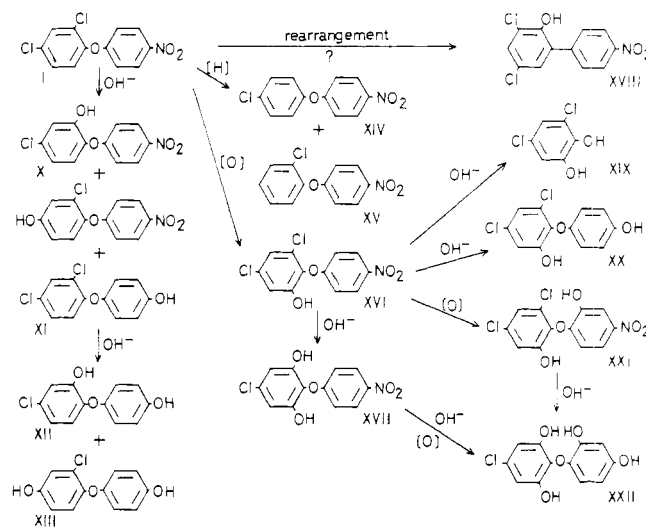

Figure 2. Major photolysis pathways of nitrofen.

Figure 3. Minor photolysis pathways of nitrofen.

showed the presence of two major and at least seven minor constituents. The major ones, R_f 0.62 and 0.50, were identified as 2,4-dichlorophenol (II) and p-nitrophenol (V), respectively. Gas chromatography of the methylated acidic fraction resolved 15 constituents which formed two definite groups in volatility (Table I). The more volatile group contained the methyl derivatives of 2,4-dichlorophenol (II) and p-nitrophenol (V), and rechromatography provided the methyl esters of 4-chlorocatechol (III), hydroquinone (IV), and 4-nitrocatechol (VI).

The nine diphenyl ethers (X-XIII, XVI, XVII, XX-XXII) which eluted above 200° (Table I) constituted the second group. The mass spectrum of F6 identified it as methylated 2,4-dichlorophenyl p-hydroxyphenyl ether (XI), and the isomers XII and XIII (F7, F8) were differentiated as the corresponding 2-hydroxy-4-chloro and 4-hydroxy-2-chloro analogs, respectively, by the characteristic mass spectral rearrangement ion MeOPhCH2− of XII (Ballantine and Pillinger, 1968). Unfortunately, the position of hydroxylation in the remaining compounds remained undefined due to their complexity, although the number of hydroxyl groups on each was clear enough.

The observed photolysis products of nitrofen were rationalized by the pathways proposed in Figures 2 and 3. 2,4-Dichlorophenol (II) and p-nitrophenol (V) were by far

Table II. Photolysis of Nitrofen in Sunlight

Time, weeks[a]	Nitrofen, mmol	DCP,[b] mmol	PNP,[c] mmol
0	1.00	0.00	0.00
1	0.35	0.43	0.52
2	0.26	0.40	0.59
3	0.20	0.31	0.56
4	0.12	0.23	0.50

[a] Total time, not length of irradiation. [b] 2,4-Dichlorophenol. [c] p-Nitrophenol.

the principal products, and other mononuclear products were derived from them. As in the photolysis of 2,4-dichlorophenoxyacetic acid (Crosby and Tutass, 1966), each of the Cl atoms was replaced by OH, first to form III and then, eventually, polymer. Nitrofen, itself, underwent the same reaction to provide one or both isomers of X, and its chlorines also were replaced by H (Crosby and Leitis, 1969; Crosby and Wong, 1973) to give XIV and XV. Other possible instances of the conversion of Cl to OH included XI to XII and XIII, XVI to XVII, and XXI to XXII.

There is evidence that these reactions represent photonucleophilic displacements (Crosby and Wong, 1970). For example. chloride (Omura and Matsuura, 1969), methoxide (Letsinger and Steller, 1969), and nitrite (Havinga and Kronenberg, 1968) already have been shown to be displaced by hydroxide in the presence of uv light to provide the corresponding phenols. In the present investigation, the nitro group of nitrofen was displaced by hydroxide to give XI; XVI underwent the same reaction to give XX, XVII and XXI gave XXII, and nitrophenol (V) likewise formed hydroquinone (IV). The photolysis of nitrofen to II and V was independent of air and took place in either water or aqueous methanol, but its rate was strongly dependent upon hydroxide ion concentration; this reaction, too, probably represents a photonucleophilic displacement (Steller and Letsinger, 1970; Crosby et al., 1972) in which p-nitrophenate was the displaced ion.

Photooxidation of aromatic rings, previously observed in monuron photolysis (Crosby and Tang, 1969), may be more general than had been supposed. The chlorinated (more electronegative) ring of nitrofen was hydroxylated to give XVI, and XIX then was formed by nitrophenate displacement or by direct oxidation of II; XVI was further oxidized to XXI. Surprisingly. p-nitrophenol itself could be oxidized to VI, which also appeared as a photolysis product of nitrofen.

The suggested formation of o-hydroxydiphenyl ethers such as X, XII, and many others during nitrofen photolysis led to consideration of the possible presence of chlorinated dibenzo-p-dioxins such as are obtained upon irradiation of pentachlorophenol (Crosby and Wong, 1970; Plimmer et al., 1973). As in the irradiation of di- and trichlorophenols (Crosby and Wong, 1970; Plimmer and Klingebiel, 1971), none of the nitrofen fractions revealed dioxins to mass spectrometry; in view of the photochemical instability of the expected products (Crosby et al., 1971), this result is not surprising.

The free-radical rearrangement of diphenyl ethers to biphenyls by uv irradiation (Kelly et al., 1969; Hageman et al., 1970; Ogata et al., 1970) also was suggested for the conversion of nitrofen to XVIII. Although the molecular ion and mass spectral fragments of fraction F9 were consistent with the biphenyl structure. there was no other verification. However, the ease with which very similar hydroxylated diphenyl ethers rearrange (Plimmer and Klingebiel, 1971) suggests that the corresponding biphenyls occur among the large number of observed but unidentified minor photolysis products of nitrofen.

Under the influence of light, nitrofen was reduced to the corresponding azobenzene (VIII) and aniline (VII).

While these products were formed by irradiation in water alone, the presence of methanol also resulted in the formyl derivative IX as a major product. It is probable that IX is formed by a coupled oxidation-reduction of nitrofen and methanol (Ciamician and Silber, 1905) and represents an artifact in terms of possible occurrence in the environment.

Sunlight Irradiation. The results observed in sunlight were qualitatively similar to those in laboratory experiments. Rapid cleavage of the ether took place to provide the corresponding phenols as the major products and the expected 2,4-dichlorophenyl p-aminophenyl ether, N-[4-(2',4'-dichlorophenoxy)]phenylformamide, 4,4'-bis(2,4-dichlorophenoxy)azobenzene, 4-nitrocatechol, and the phenolic diphenyl ethers also were observed on chromatograms. Hydroquinone (IV) and 4-chlorocatechol (III) were not detectable as photodecomposition products, but humic acids and the unidentified polymeric material derived from 2,4-dichlorophenyl p-aminophenyl ether appeared during sunlight irradiation.

Table II indicates the photolysis rate of nitrofen in sunlight. Nitrofen disappeared rapidly in the first week, but the degradation then became so slow that approximately 10% of the initial amount was still detected after 4 weeks exposure. This result may be due to shielding by the insoluble polymeric materials which could have coprecipitated undissolved particles of nitrofen. The level of the principal constituents—II and V measured as methyl derivatives—increased rapidly in the first week and then decreased relatively slowly. at which point conversion to other products (notably humic acids) became apparent. Pure p-nitrophenol was much more stable than 2,4-dichlorophenol under these conditions; it degraded to form 4-nitrocatechol, hydroquinone, and a nonvolatile, dark polymer, while the photolysis products of dichlorophenol were tarry and undefined. Control recoveries were nearly quantitative.

Altogether, the diphenyl ether structure is represented in a surprising number of herbicides, including nitrofen, chloroxuron, MO, Credazine, and fluorodifen, and each could be expected to conform to the same photolysis pathway. In fact, Eastin (1972a) recently has shown that fluorodifen also is unstable to light. Although the mammalian metabolism of nitrofen has not been disclosed, Huggins et al. (1948) reported that 4-nitrophenyl ether was converted to p-nitrophenol by rat liver and kidney, and Eastin (1972b) and Rogers (1971) reported reduction and ether cleavage in various plants; photolysis once again may be observed to provide the same products as metabolism.

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Photochemistry of N-(α-Trichloromethyl-p-methoxybenzyl)-p-methoxyaniline

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N-(α-Trichloromethyl-p-methoxybenzyl)-p-methoxyaniline was photolyzed in aqueous solution and on glass, silica gel, cellulose, and leaves. The major photolysis product was N,2-dianisyl-2-hydroxyacetamide. Anisaldehyde, anisic acid, anisidine, and N,2-dianisyl-2-oxoacetamide were also found in certain cases. In wet ether α,α-dichloroacetophenone and anisidine were formed as major products. A comparison with degradation products formed in a model ecosystem is made.

We have been interested in the feasibility of building a photodegradable pesticide. This study has utilized photosensitized decomposition of organic chlorides by aromatic amines (Miller and Narang, 1970) as a molecular test system. In this reaction the amine absorbs light in the solar region (>290 nm) and excited amine molecules attack the chloride. The reaction was previously shown to be applicable to chlorinated insecticides. DDT, for example, is readily degraded by diethylaniline using 310-nm light in aerated solutions (Miller et al., 1973). Our approach then was to incorporate the sensitizer into a chlorinated molecule with insecticidal activity. In this way each molecule would have a propensity for self-destruction in sunlight, regardless of its chemical environment. Fortunately, Hirwe et al. (1972) recently synthesized a series of compounds with attributes desirable for our goal. One of these was N-(α-trichloromethyl-p-methoxybenzyl)-p-methoxyaniline (1). Compounds in this series have insecticidal activity comparable to DDT, degrade more readily than DDT, and apparently do not build up through the food chain. From our point of view these compounds seemed quite likely to photodegrade since they incorporated an aromatic amine into a chlorinated pesticide. The present study elucidates the photoproducts from 1 in media similar to those in nature and compares these photoproducts with those found from degradation in a model ecosystem.

$$CH_3O-\langle\bigcirc\rangle-NHCH-\langle\bigcirc\rangle-OCH_3$$

with CCl_3 on the CH

1
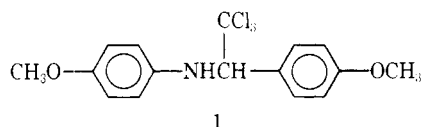
RESULTS

Photolysis in Solution. Compound 1 was photolyzed in a Rayonet reactor using 295–320-nm light. Initial product

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studies were facilitated by using a solvent mixture of 60% tetrahydrofuran (THF) and 40% water. A 3.5 × 10⁻² M solution was allowed to react for 24 hr in air and worked up by vacuum evaporation and extraction. Chromatographic separation of the neutral products was accomplished on a silica gel column. The results are illustrated in Scheme I and detailed in Table I.

Scheme I
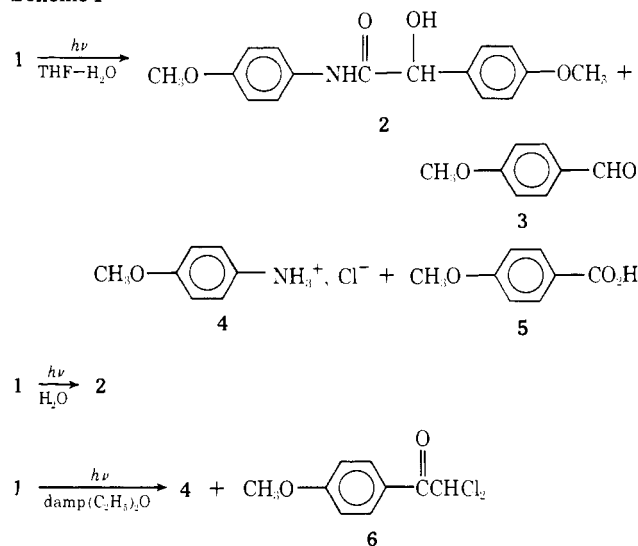
Photolysis of 1 in damp diethyl ether or damp THF gave α,α-dichloroacetophenone (6) and 4 as the major products. Small amounts (~1%) of water are necessary for the formation of 4 and 6. In rigorously dry ether a complex, presently unresolved mixture of products was produced.

For further studies of this reaction it was desirable to have a rapid, quantitative analytical technique for the