

Table VIII. Biological Activity of Trifluoromethylalkyl Ketoxime Carbamates
 $RC(CF_3)=NOC(=O)NHCH_3$

R	LD ₅₀ , ppm				
	Cholinesterase I ₅₀ , M	MBB	Aphid (C)	Aphid (S)	Corn rootworm
CH ₃		>250	>250	>250	1.3
<i>n</i> -C ₃ H ₇	3.9 × 10 ⁻⁷	25	25	35	0.15
<i>i</i> -C ₃ H ₇	1.0 × 10 ⁻⁷	40	110	23	0.26
<i>sec</i> -C ₄ H ₉	2.4 × 10 ⁻⁷	14	70	27	0.29
<i>n</i> -C ₈ H ₁₇	6.7 × 10 ⁻⁷	>250	>250	>250	>2.5
CH ₃ OCH ₂	1.0 × 10 ⁻⁶	250	85	10	0.63
Standards					
Furadan				2	0.1
Thimet				2	0.2
Disyston	4.8 × 10 ⁻⁷	36	2.1		
Imidan		11	12	26	0.7

agreement between the insect toxicity of the various substituted oxime derivatives and their anticholinesterase activity. That this lack of agreement may be in part due to the hydrolytic instability of these chemicals can be seen by the extremely fast hydrolysis rates found (Table VI).

These rates do not take into account any enzymatic metabolism that might occur in the insect, and therefore reflect the optimum stability.

As expected, the activity of the oxime carbamates is synergized by piperonyl butoxide as shown by the examples listed in Table VII. When the aromatic ring was replaced by an aliphatic moiety, the oxime thiophosphates did not show any insecticidal activity, while the corresponding carbamates were active (Table VIII) against the Mexican bean beetle, aphids (by contact and systemic action), and the corn rootworm (*Diabrotica sp.*).

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Photonucleophilic Reactions of Nitrofen

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The sunlight photolysis of nitrofen (2,4-dichlorophenyl *p*-nitrophenyl ether) in aqueous methanol represents a photonucleophilic displacement of nitrophenate by the hydroxide ion of water. In the presence of potassium cyanide, irradiation of nitrofen resulted in 2,4-dichlorobenzonitrile and related compounds, while the photoreaction with piperidine provided *p*-nitrophenol as well as tarry

products from the further reactions of intermediate 2,4-dichlorophenol with the amine. 2,4-Dichlorophenol also reacted with cyanide to form 2,4-dicyanophenol (4-hydroxyisophthalonitrile). These and other photonucleophilic reactions may help to explain the environmental dissipation of many pesticides.

Diphenyl esters have come into widespread use as herbicides, especially in flooded rice fields. The sunlight photodecomposition of nitrofen (2,4-dichlorophenyl *p*-nitrophenyl ether or TOK, I) in aqueous media is characterized by rapid cleavage of the ether bond to form 2,4-dichlorophenol and *p*-nitrophenol as the principal products (Nakagawa and Crosby, 1974). The present paper deals with the mechanism of this seemingly unusual transformation and its environmental implications.

MATERIALS AND METHODS

Nitrofen was purified by evaporation of a commercial sample of TOK E-25 and threefold recrystallization of the residue from absolute ethanol, mp 70.5–71.0° (Weed Science Society, 1970; 71–72°).

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2,4-Dichlorobenzonitrile, mp 61°, was prepared from 2,4-dichlorobenzoyl chloride (Lutz *et al.*, 1947; 61–62°) via 2,4-dichlorobenzamide, mp 192–193° (Lutz *et al.*, 1947; 193–194°), and *p*-nitrobenzoyl chloride was converted to *p*-nitrobenzamide, mp 200° (Harris, 1965; 200°). *N*-(*p*-Nitrophenyl)piperidine was prepared from *p*-chloronitrobenzene and piperidine (LeFevre and Turner, 1927), mp 104° (Lellmann and Geller, 1889; 105°). The preparation of 2,4-dichlorophenyl 4'-aminophenyl ether and *N*-*p*-(2,4-dichlorophenoxy)phenylformamide was described by Nakagawa and Crosby (1974).

Piperidine was purified by fractional distillation, bp 106°, and other reagents were commercial products purified by crystallization or gas-liquid chromatography (glc).

Irradiation. A 100-ml aliquot of a stock solution containing 4 g/l. (14 mM) of nitrofen in methanol was diluted with 900 ml of deionized water or solutions of either potassium cyanide (1.0 M), potassium bromide (1.0 M), or piperidine (0.5 M) in deionized water. The suspension was irradiated for 60 hr at 23–35° in a borosilicate glass photoreactor (Crosby and Tang, 1969) equipped with an F40BL

fluorescent lamp (General Electric Co., Schenectady, N. Y.), while either filtered compressed air or pure nitrogen was introduced through the gas inlet at about 20 ml/min. Acetone or acetonitrile could replace methanol as the nitrofen solvent.

For rate measurements, nitrofen was dissolved in buffer solutions prepared from appropriate volumes of 0.2 M boric acid, 0.05 M sodium citrate monohydrate, and 0.1 M trisodium phosphate and containing 10% methanol to give a 10^{-5} M solution. Samples were irradiated at >300 nm in a photoreactor (Crosby and Wong, 1973), 1-ml aliquots were extracted into hexane, and the extracted nitrofen was determined by glc.

Identical control suspensions were held in the dark, and, to confirm the orientation rule, a mixture of nitrofen (283 mg, 1 mmol) and piperidine (8.5 g, 100 mmol) was boiled under reflux for 4 hr without irradiation.

Separation and Identification. Each sample (pH 11–12) was extracted 4 times with ether, and the combined extracts were washed with a small volume of water, dried over anhydrous sodium sulfate, and concentrated to small volume under reduced pressure to provide the "neutral extract." The remaining aqueous phase was acidified to pH 1 with 4 N sulfuric acid and extracted in the same way to provide the "acidic extract." Before glc, the acidic extract was methylated with excess ethereal diazomethane.

Glc analyses and separations were carried out with F and M Model 720 temperature-programmed instrument equipped with a thermal conductivity detector and a 2 ft \times $\frac{1}{8}$ in. o.d. stainless steel column containing 6% SE-30 on 60–80 mesh Chromosorb G treated with HMDS (for the neutral extract) or 5% Carbowax 20M on 70–80 mesh Chromosorb W treated with DMCS (for the acidic extract). Fractions were collected from the effluent gas in Pasteur pipets and purified by rechromatography.

Isolates were identified by comparison of elution temperature (or retention time), spectra, and melting point with those of authentic specimens. Infrared (ir) spectra were measured in potassium bromide disks with a Perkin-Elmer Model 337 infrared spectrophotometer. Mass spectra were measured with a Finnigan Model 3000 gas chromatograph peak identifier (gc-ms) equipped with a 3 ft \times $\frac{1}{8}$ in. o.d. glass column containing 6% SE-30 on 60–80 mesh Chromosorb G treated with HMDS.

4-Hydroxyisophthalonitrile [2,4-Dicyanophenol, V (X = OH)]. 2,4-Dichlorophenol (200 mg) and sodium cyanide (50 g) were dissolved in 1 l. of deionized water and irradiated for 60 hr. The photolysis mixture was carefully acidified (*caution: HCN*) and extracted with ether, the dried ether extract evaporated, and the residue recrystallized from water to provide a single product, mp 214° . The ether resulting from methylation with diazomethane was purified by glc: ir 2270 (CN), 2247 cm^{-1} (CN); mass spectrum m/e 158 (P), corresponding to $\text{C}_9\text{H}_6\text{N}_2\text{O}$.

The original crude phenol was boiled with 4 N potassium hydroxide solution, acidified, and extracted with ether. Evaporation of the dried ether extract provided an acid, mp 316° ; mp of 4-hydroxyisophthalic acid is 310° (Calvet and Mejuto, 1930).

Material Balance. A suspension of nitrofen (1.44 mmol) in 1 M sodium cyanide solution was irradiated in the usual way for 60 hr, extracted, and subjected to glc after methylation of the acidic extract with diazomethane. The area under each chromatogram peak was measured with a planimeter and quantitated by reference to a standard curve in each instance. Control recoveries were nearly quantitative.

RESULTS AND DISCUSSION

Diaryl ethers usually are considered to be rather stable. However, irradiation of diphenyl ethers with mercury arc

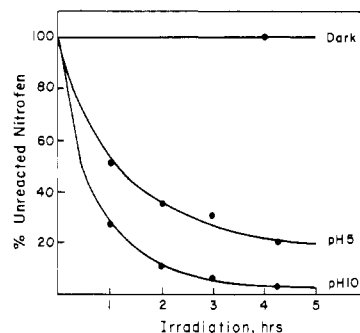


Figure 1. Rates of nitrofen photolysis at pH 5 and 10. No dark reaction was observed at either pH.

light (254 nm) provided *o*- or *p*-phenylphenols through a free-radical rearrangement (Kharasch *et al.*, 1952; Kelly *et al.*, 1966; Ogata *et al.*, 1970), and analogous products were formed in the riboflavine-sensitized photolysis of chlorophenols (Plimmer and Klingebiel, 1971) *via* intermediate phenyl ethers. The intermediate aryl radicals presumably might react with water to form phenols directly (Joscheck and Miller, 1966) or with oxygen to give hydroperoxy radicals (Kharasch and Sharma, 1966) which then could provide the phenols by disproportionation (Traylor and Bartlett, 1960; Denney and Rosen, 1964). Alternatively, *p*-nitrophenyl ethers have been shown to undergo ionic, photonucleophilic displacement reactions with nucleophiles such as pyridine (Steller and Letsinger, 1970), and the analogous reaction with hydroxide ion also would produce the observed phenols.

The conversion of nitrofen to the same amounts and proportions of phenols in both the presence and absence of air precludes the mechanism involving arylhydroperoxy radicals. In fact, the absence of the biphenyls expected to result from the anaerobic generation of aryl radicals suggested that radical processes are not important in this instance. Furthermore, the strict limitation of the irradiation to quantum energies less than 98.6 kcal/mol (290 nm) makes the generation or abstraction of hydroxyl radicals from water (H-OH bond energy, 118 kcal/mol) seem unlikely.

Conversely, the lack of dependence of phenol formation upon oxygen, the strong dependence on hydroxide ion concentration (Figure 1), and the analogous reaction of nitrophenyl ethers with pyridine (Steller and Letsinger, 1970) all suggest the operation of an ionic (photonucleophilic) mechanism (Crosby *et al.*, 1972). In order to examine this possibility, nitrofen was irradiated in the presence of aqueous solutions of potassium bromide, potassium cyanide, or piperidine as representative nucleophiles.

Only with piperidine was any reaction observed in the dark. In light, nitrofen and ionic bromide formed low levels of a dichlorobromobenzene detected by gc-ms, together with 2,4-dichlorophenol from further reaction with water. Irradiation with cyanide ion resulted in extensive transformations; the neutral products were primarily 2,4-dichlorobenzamide (III, X = CONH₂) and smaller proportions of the expected 2,4-dichlorobenzonitrile (III, X = CN), 2,4-dichlorophenyl *p*-aminophenyl ether (VI, R = H), *N-p*-(2,4-dichlorophenoxy)phenylformamide (VI, R = COCH₃), and unchanged nitrofen (Table I). The methylated acidic extract contained principally *p*-nitroanisole (from IV) together with methyl 2,4-dichlorobenzoate (III, X = COOCH₃) and 4-methoxyisophthalonitrile [2,4-dicyanoanisole, from V (X = OH)]. Similar results were obtained with aqueous acetone or aqueous acetonitrile as solvent; the formamide artifact (VI, R = COCH₃) resulting from a coupled oxidation-reduction (Nakagawa and Crosby, 1974) did not appear.

Table I. Products from the Photoreaction of Nitrofen with Sodium Cyanide^a

Product	Amount, mmol	Yield, %
2,4-Dichlorobenzonitrile	0.07	5
2,4-Dichlorobenzamide	0.47	33
2,4-Dichlorobenzoic acid	0.07	5
2,4-Dichlorophenol ^b	~0.14	10
Total conversion	~0.75	53
<i>p</i> -Nitrophenol	0.75	53
Nitrofen recovered	0.32	22
Other products ^c	~0.37	25

^a Nitrofen, 1.44 mmol; irradiation time, 60 hr. ^b As 2,4-dicyanophenol. ^c Principally the amino and formamido derivatives.

The 2,4-dichlorophenol expected in the acidic fraction was not observed, and separate irradiation of this compound for 60 hr in potassium cyanide solution resulted in 75% loss and the isolation of a single product, identified as 2,4-dicyanophenol (4-hydroxyisophthalonitrile). Polyphenols resulting from displacement of Cl by OH would be destroyed rapidly (Crosby and Tutass, 1966; Nakagawa and Crosby, 1974) and were not detected. Over 40% of the nitrofen reacted with cyanide to form 2,4-dichlorobenzonitrile and *p*-nitrophenol (Table I), another 10% formed 2,4-dichlorophenol by reaction with hydroxide ion at the high pH of the cyanide solution, and about 25% was reduced to the aminodiphenyl ether. Clearly, the photolysis of nitrofen primarily represents photonucleophilic displacement reactions in which *p*-nitrophenate is the leaving group (Steller and Letsinger, 1970) (Figure 2).

The reaction of *o*- and *p*-nitrodiphenyl ethers with piperidine results in displacement of phenol and formation of *N*-(nitrophenyl)piperidines (Groves and Turner, 1929; Henley and Turner, 1930; Fox and Turner, 1930; Hart and Bournes, 1966), and nitrofen likewise reacted very slowly in the dark to provide trace amounts of *N*-(*p*-nitrophenyl)piperidine (II, X = C₅H₁₀N) and 2,4-dichlorophenol (Figure 2). Irradiation of the mixture in aqueous methanol provided a complex tar similar to those resulting from 2,4-dichlorophenol and piperidine, but no *N*-(2,4-dichlorophenyl)piperidine was isolated. The major product was *p*-nitrophenol (isolated as *p*-nitroanisole); considering the facile formation of dicyanophenol from dichlorophenol and cyanide, the absence of dichlorophenylpiperidine can be explained by its rapid further photoreaction with excess reagent to form notoriously unstable di- and triaminobenzene derivatives.

Consistent with the photonucleophilic reactions of anisole and nitroanisoles with hydroxide ion (Havinga *et al.*, 1956; Havinga and deJongh, 1962; Kronenberg *et al.*, 1966; Bartrop *et al.*, 1967; Letsinger and Steller, 1969), the orientation of displacement reactions on the light-activated aromatic ring of nitrofen is opposite to that observed (and predicted) for the ground state, perhaps due to intermediates such as those proposed in Figure 2. No hydroxylated biphenyls were observed, and ionic reactions clearly predominated.

While it seems unlikely that nitrofen might encounter appreciable concentrations of bromide or cyanide in the environment, natural waters contain a variety of amines and other reactive nucleophiles (Hunter, 1971), both natural and man-made; Ross (1962) has calculated that, at pH 7.5, a significant proportion of the amino and sulfhydryl groups associated with water are in nucleophilic-reactive form. Herbicides such as nitrofen possess a number of displaceable groups (chloro, nitro, and nitrophenyl) which could result in photodecomposition to a rather complex

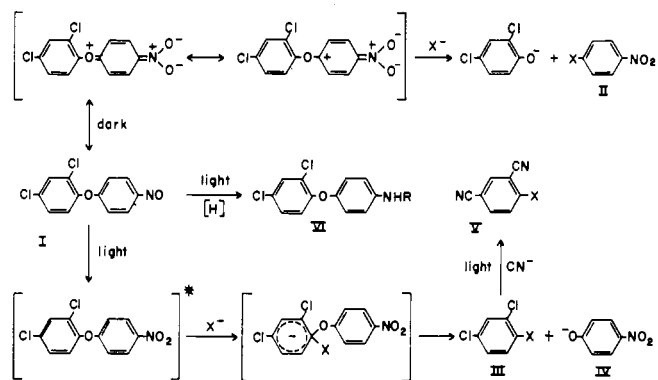


Figure 2. Proposed mechanisms for the reactions of nitrofen with nucleophiles.

array of phenylated products detectable only with difficulty.

However, it seems plausible that these reactions could be put to practical use. The importance of photonucleophilic reactivity in the environmental inactivation of diphenyl ether herbicides suggests that judicious choice of the aromatic substituents might be made to confer almost any desired degree of stability; conversely, more reactive nucleophiles such as agricultural ammonia might be applicable in herbicide-treated fields to enhance the photochemical destruction of undesirable residues. Photolysis products will tend to reflect the chemical nature of the herbicide's immediate surroundings; a dispersed hydrocarbon formulation (such as TOK E-25) should be conducive to photoreduction and products such as VI (R = H), while the concentrating of hydrocarbon-soluble nucleophiles or the evaporation of solvent would promote photonucleophilic reactions.

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Photodecomposition of Mirex on Silica Gel Chromatoplates Exposed to Natural and Artificial Light

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Exposure of mirex to sunlight or ultraviolet light as deposits on silica gel thin-layer chromatoplates resulted in its slow degradation to several products. Photoproducts characterized included Kepone hydrate, a monohydromirex derivative previously identified (1,2,3,4,5,5,6,7,9,10,10-undecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane), and 1,2,3,4,6,7,9,10,10-nonachloropentacyclo-

[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one, isolated as the hydrate. Because certain of the mirex photoproducts are considerably more polar than either mirex or its monohydro derivative, any environmental degradation of mirex *via* these pathways would possibly result in enhanced biodegradability and a reduced tendency toward storage and accumulation in adipose tissues.

The insecticide mirex (dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (I)) is highly effective in controlling the imported fire ant (*Solenopsis spp.*), which infests large areas of the southeastern United States and extends westward into Texas. The compound is generally applied by aircraft as a bait formulation at rates of only a few grams of toxicant per acre to provide effective fire ant suppression.

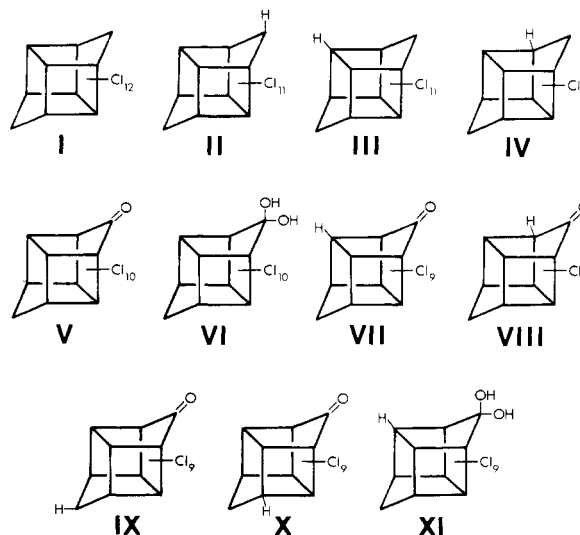
Mirex may be an environmental hazard because it is highly toxic to certain aquatic organisms, particularly crustaceans (Ludke *et al.*, 1971), and is high in chronic toxicity to some fishes (Van Valin *et al.*, 1968). Mirex is low in acute toxicity to mammals (Gaines and Kimbrough, 1970; Martin, 1972), but it is an inducer of hepatic mixed function oxidases (Baker *et al.*, 1972; Mehendale *et al.*, 1973). Dietary mirex at levels as low as 5 ppm causes reduced litter size in mice (Ware and Good, 1967) and at 25 ppm causes cataracts in rats (Gaines and Kimbrough, 1970).

Studies to date have indicated that mirex is highly resistant to metabolic attack by higher organisms, including laboratory rats (Gibson *et al.*, 1972; Mehendale *et al.*, 1972), Japanese quail (Ivie *et al.*, 1974a), cattle (Dorough and Ivie, 1974), and plants (Mehendale *et al.*, 1972). More recent studies have indicated that mirex is metabolized very slowly by sewage sludge organisms under anaerobic conditions, and the single metabolite generated has been identified as the monohydro product II (1,2,3,4,5,5,6,7,8,9,10-undecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane) (Andrade and Wheeler, 1973).

The metabolic stability of mirex and its highly lipophil-

ic nature suggest that this chlorocarbon may show considerable potential for biological magnification through accumulation of residues in certain tissues of a variety of food chain organisms. Indeed, studies involving long-term administration of mirex to certain mammals, birds, and fish indicate that mirex is retained and accumulates at high levels in fatty tissue (Ivie *et al.*, 1974b).

Certain aspects of the photochemistry of mirex have been reported. Monohydro- and dihydromirex photoproducts were isolated after ultraviolet (uv) lamp irradiations of mirex in hydrocarbon solvents (Alley *et al.*, 1973), and the same monohydro derivative was observed after exposures of mirex deposits on silica gel surfaces (Gibson *et al.*, 1972). Definitive structure assignment of the monohydro product as 1,2,3,4,5,5,6,7,9,10,10-undecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (III) has recently been made (Alley and Layton, 1973). The third possible monohydro product of mirex, IV, has not been observed.



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