nitrite accumulation and their relative effectiveness in inhibiting the Hill reaction. This suggests that the nitrite test may be useful in determining the effect of a chemical on chloroplast electron transport. An advantage of this test is the time saved in excising tissue compared with isolating chloroplasts as required for the Hill reaction assay.

ACKNOWLEDGMENT

The authors express their gratitude to Henry A. McElravy, Jr., who synthesized most of the phenyl isocyanates.

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Insecticidal Activity of α,α,α-Trifluoroacetophenone Oxime Carbamates and Thiophosphates

Daniel D. Rosenfeld* and John R. Kilsheimer[1]

Approximately 20 *N*-methylcarbamates and the corresponding monothiophosphates of substituted 2,2,2-trifluoroacetophenone oximes have been synthesized and their insecticidal activity examined. This activity has been compared to their corresponding anticholinesterase values. The carbamate exhibiting the highest anticholinesterase activity contained an ortho methoxy substituent. The toxicity to house flies by topical application was less than expected, but the activity was raised to the expected level by synergism with piperonyl butoxide. A comparison between the substituted 2,2,2-trifluoroacetophenone oxime carbamates and the corresponding ring-substituted phenylcarbamates shows the former to be about 20–30 times more toxic to house flies.

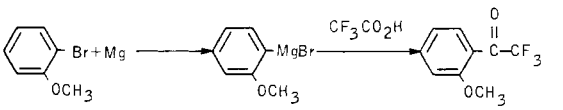
For many years phenol carbamates and phosphates have been known to impart insecticidal activity. Of more recent origin, the oxime carbamates and phosphates have aroused the interest of pesticide chemists. Such examples as Tranid, Temik, and Lannate have well established the insecticidal activity of this class of compounds. We now wish to report the results of our investigations into the biological activity of the oxime carbamates and thiophosphates of α,α,α-trifluoroacetophenones.

SYNTHESIS

None of the chemicals whose biological activity is discussed herein have appeared previously in the literature. The intermediate ketones for this study (except for the meta nitro-substituted ketone) were synthesized by reacting the appropriately substituted halogen compound with magnesium to form the Grignard, which was then treated with trifluoroacetic acid. This was found to be the best method of several that were available. The nitro ketone was prepared by the direct nitration with mixed acid of α,α,α-trifluoroacetophenone. Oximation of the ketones was carried out in anhydrous methanol with an excess of hydroxylamine. It was found that longer than usual reflux times were necessary for better yields. Several of the meta-substituted ketones did not give the expected oximes under these conditions. However, by vacuum distillation of the intermediate that was formed, we were able to isolate sufficient amounts of the oxime to complete our study of these chemicals. The identification and chemistry of these intermediates will be the subject of a future publication.

The oxime carbamates were prepared by reaction with methyl isocyanate, while the corresponding thiophosphates were synthesized by forming the sodium salt of the oxime, and then reacting this with diethylthiophosphoryl chloride. Table I lists the new oxime derivatives synthesized during this study, along with their analytical data. The following examples illustrate the synthetic procedures used.

Ketone. To a 5-l. flask fitted with a stirrer, reflux condenser, thermometer, and addition tube was charged 39 g (1.6 mol) of magnesium. This was flushed with a nitrogen stream and then 100 ml of ether and 1 ml of ethyl bromide were added. *o*-Bromoanisole (300 g; 1.6 mol) was dissolved in 1300 ml of anhydrous ether and added slowly to the magnesium. Addition time was 5 hr. The temperature during addition was maintained between 25 and 30°. The reaction mixture develops the characteristic dark brown color. The reaction was stirred for 2 hr after the addition was complete.



To the above was slowly added 61 g (0.54 mol) of trifluoroacetic acid in 200 ml of anhydrous ether. The addition took 2.5 hr with rapid stirring at a temperature of 35°. The mixture was then refluxed for 2 hr after the addition was completed.

The reaction was then cooled to 0° and 200 ml of H_2O was slowly added keeping the temperature between 0 and 10°. This was followed by 200 ml of concentrated HCl in 300 ml of H_2O. The organic layer was separated and washed with two 500-ml portions of 10% Na_2CO_3 followed by two 500-ml portions of H_2O. The ether layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was con-

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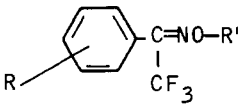
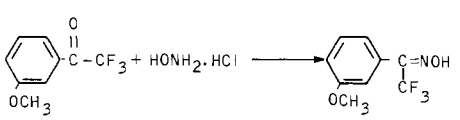
Table I. Physical Constants of New Substituted α,α,α-Trifluoroacetophenone Oxime Derivatives



		$R' = -C(=O)NHCH_3$				$R' = -P(=S)(OC_2H_5)_2$			
		Calcd		Found		Calcd		Found	
R	Mp, °C	C	N	C	N	C	P	C	P
H	96–98	48.9	11.4	48.8	11.8	42.3	9.05	42.5	9.02
o-F	76–81	45.4	10.6	44.9	10.2				
m-F	102–104	45.4	10.6	45.5	11.0	40.0	(N, 3.9)	40.2	(N, 3.8)
p-F	80–82.5	45.4	10.6	45.0	11.0	40.0	8.6	40.4	8.1
o-Cl	Oil	43.0	10.0	43.4	9.7	38.4	(N, 3.7)	39.2	(N, 3.2)
p-Cl	74–76	43.0	10.0	43.3	10.5	38.4	8.2	38.0	8.2
p-Br	Oil	37.2	8.6	37.6	9.0	34.3	7.5	34.6	7.1
o-CF_3	Oil	42.1	8.9	42.5	8.6	38.2	7.6	38.6	7.3
m-CF_3	121–124	42.1	8.9	41.8	9.4	38.2	7.6	38.4	7.2
o-OCH_3	85–87	47.8	10.2	47.4	9.8	42.1	8.3	41.9	8.4
m-OCH_3	81–83	47.8	10.2	48.1	10.5	42.1	(N, 3.8)	42.5	(N, 3.9)
p-OCH_3	85–87	47.8	10.2	47.4	10.4	42.1	8.3	42.4	8.2
o-OC_2H_5	79–82	49.6	9.6	49.5	9.1	43.6	(N, 3.6)	43.6	(N, 3.9)
o-O-*i*-C_3H_7	Oil	51.3	9.2	50.9	9.6	45.2	(N, 3.5)	45.3	(N, 3.2)
2,5-$(OCH_3)_2$	Oil	47.0	9.3	46.9	9.5				
o-CH_3	Oil	50.7	10.8	50.5	10.3	44.0	(N, 3.9)	44.3	(N, 3.6)
m-CH_3	66–69	50.7	10.8	50.3	11.1	44.0	8.7	44.4	8.3
p-CH_3	97–99	50.7	10.8	50.7	10.8	44.0	(N, 3.9)	43.9	(N, 3.8)
p-*i*-C_3H_7	61–64	54.2	9.7	54.0	10.1	47.0	8.1	47.4	7.8
p-SCH_3	51–56	45.2	9.6	44.8	10.0	40.3	8.0	40.7	7.7
p-$N(CH_3)_2$	129–130	49.8	14.5	50.1	14.6	43.7	8.1	43.4	7.9
m-NO_2	71–73	41.3	14.4	41.4	14.7				

centrated on a roto evaporator. The residue was vacuum distilled to give 65 g (60%) at 98–103° (10 mm). *Anal.* Calcd for $C_9H_7O_2F_3$: C, 53.0; H, 3.44; F, 28.0. Found: C, 53.26; H, 3.49; F, 27.4.

Oxime. A 2-l. flask was charged with 70.0 g (1 mol) of $H_2NOH \cdot HCl$ and 700 ml of anhydrous methanol. To this



was added 54 g (1 mol) of powered CH_3ONa. The NaCl was removed by filtration. The filtrate was then transferred to a 2-l. flask fitted with a water condenser and thermometer. The ketone, 73 g (0.63 mol), was added at once and the reaction was heated to reflux (68°) for 3 days.

The reaction mixture was distilled to remove 500 ml of methanol (*caution:* heating to dryness in the presence of excess hydroxylamine could result in an explosion hazard) and then 1 l. of H_2O was added. This was then extracted three times with 400 ml of ether. The ether was then dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated on a roto evaporator. The residue was vacuum distilled to give 42 g (50% of oxime at 91–93° (0.2 mm)). *Anal.* Calcd for $C_9H_8O_2F_3N$: C, 49.4; H, 3.66; N, 6.2; F, 26.4. Found: C, 48.9; H, 3.68; N, 6.1; F, 26.8.

Oxime Carbamate. A flask (500 ml) fitted with a reflux condenser and thermometer was charged with 200 ml of benzene and 11 g (0.05 mol) of oxime. A drop of dibutyltin

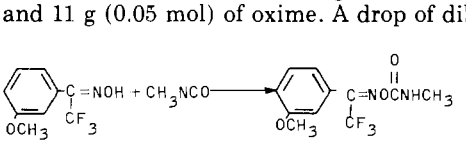
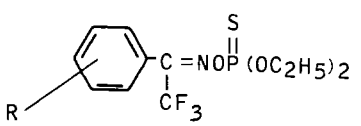
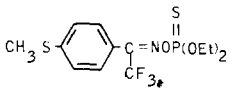
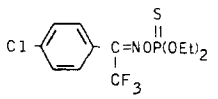


Table II. Biological Properties of Substituted α,α,α-Trifluoroacetophenone Oxime Thiophosphates



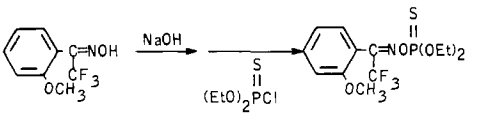
	Cholinesterase I_{50}, *M*	LD_{50}, ppm	
R	(of oxidized sample)	Aphid	House fly
H	1.8×10^{-5}	<250	25
p-F	1.9×10^{-7}	60	36
m-F	1.4×10^{-6}	>250	23
o-Cl	1.6×10^{-6}	>250	50
p-Cl	1.3×10^{-5}	70	5
p-Br	1.0×10^{-5}	250	19
o-CH_3	3.5×10^{-5}	150	70
m-CH_3	6.0×10^{-6}	>250	>250
p-CH_3	2.8×10^{-4}	>250	>250
o-CF_3	1.4×10^{-5}	250	6
m-CF_3	4.0×10^{-4}	>250	85
o-OCH_3	3.4×10^{-5}	110	65
p-OCH_3	2.7×10^{-5}	92	65
m-OCH_3	1.3×10^{-6}	>250	25
o-OC_2H_5		>250	110
o-O-*i*-C_3H_7	3.5×10^{-5}	>250	85
p-SCH_3	2.2×10^{-5}	20	85
p-*i*-C_3H_7	1.3×10^{-5}	110	110
p-$N(CH_3)_2$	7.4×10^{-6}	11	>250
m-NO_2		7	250

Table III. Antagonistic Effect of Piperonyl Butoxide on Trifluoroacetophenone Oxime Thiophosphates

Chemical structure	Bovine AChE I_{50}, M (of oxidized sample)	Topical LD_{50}, $\mu g/g$, female house fly	
		Alone	1:5 PB
	2.2×10^{-5}	10	23.5
	1.3×10^{-5}	11	16.5

diacetate was added as a catalyst. Methyl isocyanate (13.8 g; 0.5 mol) was added and heated to reflux (80°) for 2 hrs. The reaction was concentrated on a roto evaporator and the residue was recrystallized from 300 ml of a 3:1 hexane–ether solution. The yield was 11.1 g (84%); mp 81–82°.

Oxime Thiophosphate. A 500-ml flask fitted with a stirrer, reflux condenser, and thermometer was charged with 6.0 g (0.023 mol) of the oxime in 200 ml of THF. To this was added 2.2 g of a 50% NaOH solution (0.028 mol).



The temperature rose to 30°. After stirring for 0.5 hr at room temperature, the sodium salt of the oxime precipitated. The $(EtO)_2P(S)Cl$ (5.2 g; 0.028 mol) was added. The temperature rose to 35°. This was allowed to stir overnight at room temperature.

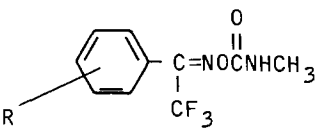
The reaction mixture was poured into 500 ml of 10% NaOH and extracted with 3 × 75 ml of benzene. The benzene solution was washed with 2 × 200 ml of 10% NaOH followed by 2 × 250 ml of H_2O. The benzene solution was dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated on a roto evaporator to give 9.4 g (90%) of product as a pale yellow oil.

TEST METHODS

Aphid. A potted nasturtium plant was infested with bean aphids and then sprayed with an acetone emulsifier mixture of the test chemical. Mortality counts were taken after 24 hr.

House Fly. Caged flies were sprayed with an acetone emulsifier mixture of the test chemical and per cent mortality was recorded after 24 hr.

Table IV. Biological Properties of Substituted α,α,α-Trifluoroacetophenone Oxime Carbamates



R	Cholinesterase I_{50}, M	Rel I_{50}, M	LD_{50}, ppm		
			Mex. bean beetle	Aphid	House fly
H	5.3×10^{-7}	1.0	110	<250	25
o-F	3.4×10^{-8}	15.6	3.3	13	32
m-F	3.8×10^{-7}	1.4	50	50	35
p-F	4.5×10^{-7}	1.2	23	105	19
o-Cl	6.5×10^{-9}	81.5	32	50	200
p-Cl	3.9×10^{-7}	1.4	72	30	32
p-Br	2.0×10^{-7}	2.7	>250	23	92
o-CF_3	1.6×10^{-7}	3.3	80	43	110
m-CF_3	1.8×10^{-7}	3.0	80	>250	150
o-OCH_3	4.3×10^{-9}	123.2	15	7.5	90
m-OCH_3	2.3×10^{-7}	2.3	23	65	110
p-OCH_3	1.2×10^{-7}	4.4	29	210	12
o-OC_2H_5	3.1×10^{-8}	17.1	19	180	110
o-O-*i*-C_3H_7	3.6×10^{-8}	14.7	80	110	14
2,5-$(OCH_3)_2$	2.7×10^{-8}	19.6	32	150	170
o-CH_3	2.1×10^{-8}	25.2	23	50	>250
m-CH_3	4.0×10^{-8}	13.3	92	28	80
p-CH_3	1.0×10^{-7}	5.3	110	50	190
p-*i*-C_3H_7	1.7×10^{-7}	3.1	23	68	85
p-SCH_3	2.9×10^{-7}	1.8	50	24	>250
p-$N(CH_3)_2$	5.7×10^{-8}	9.3	110	>250	>250
m-NO_2	7.1×10^{-8}	7.5	>250	7	210
C_6H_{11}, in place of RPh	9.0×10^{-8}	5.9	25	68	>250
 , in place of RPh			210	50	50
Standards					
Carbaryl	5.1×10^{-6}		5	11	>250
Malathion	1.0×10^{-7}		110		5.2
Disyston	4.8×10^{-7}		36	2.1	32

Table V. Comparison between the Biological Activity of Aromatic Carbamoyl Oximes and Substituted Phenyl *N*-Methylcarbamates[a]

R	Bovine AChE I_{50}, *M*	House fly (♀) topical LD_{50}, μg/g (S_{bti})	Bovine AChE I_{50}, *M*	House fly (♀) topical LD_{50}, μg/g (S_{NAIDM})
H	5.3×10^{-7}	18.5	2.0×10^{-4}	500
p-F	4.5×10^{-7}	11.5	2.3×10^{-4}	480
m-F	3.8×10^{-7}		8.5×10^{-5}	390
o-F	3.4×10^{-8}		1.6×10^{-5}	250
p-Cl	3.9×10^{-7}	20.5	2.4×10^{-4}	>500
p-Br	2.0×10^{-7}	21.0	1.0×10^{-4}	>500
m-CH_3	4.0×10^{-8}	65.0	1.4×10^{-5}	50
p-OCH_3	1.2×10^{-7}	42.5	8.0×10^{-5}	>500
o-OCH_3	4.3×10^{-9}	95.0	3.7×10^{-5}	92.5
m-OCH_3	2.3×10^{-7}		2.2×10^{-5}	90.0
p-CH_3S	2.9×10^{-7}	21.5	3.4×10^{-5}	26.5
p-*i*-Pr	1.7×10^{-7}	21.0	7.0×10^{-5}	>500
p-$(CH_3)_2N$	5.7×10^{-8}	>500.0	2.4×10^{-4}	>500

[a] Metcalf *et al.*, 1962.

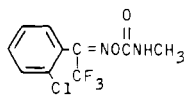
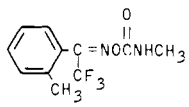
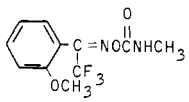
Mexican Bean Beetle. Bean leaves were dipped in an acetone emulsifier mixture of the test chemical and allowed to dry. The individual leaves were placed in petri dishes and the Mexican bean beetle larvae were introduced. Observations on per cent kill were taken after 3 days.

Cholinesterase Inhibition. The molar concentrations for 50% inhibition of bovine erythrocyte cholinesterase (I_{50}) were determined using the colorimetric procedure of Ellman (Voss, 1966). The inhibitor and enzyme were incubated for 30 min before addition of the substrate.

BIOLOGICAL ACTIVITY

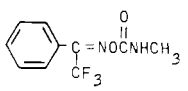
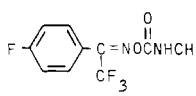
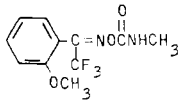
Oxime Thiophosphates. In the greenhouse screening tests the oxime thiophosphates were generally active against aphids (by contact action) and the house fly (*Musca domestica L.*). Tests against other species such as the Mexican bean beetle, southern armyworm, mites, and the corn rootworm were generally negative. Table II lists the various oxime thiophosphates prepared, along with the cholinesterase inhibition values of the oxidized compound (OXONO) and their biological activity. (The P=S compounds were dissolved in benzene and then heated with freshly prepared peracetic acid solution for 20 min at 75°. The peracetic acid was prepared by mixing 1 vol of 30% H_2O_2 and 5 vol of glacial acetic acid. The purity of the oxidized compound was not determined but it was felt that this type of oxidation was as least as severe as that encountered in a biological system.) As can be seen by the data in Table II, the most potent cholinesterase inhibitor (*p*-fluorotrifluoroacetophenone oxime thiophosphate) was not the most active insecticidal chemical. However, it was among the more active of the series. The toxicities of these oxime thiophosphates are antogonized by the addition of piperonyl butoxide as shown by the examples in Table III. It has been previously shown that methylenedioxyphenyl synergists such as piperonyl butoxide (Nakatsugawa and Dahm, 1962) can inhibit the oxidative desulfuration of phosphorothionates to their corresponding P=O analogs, which are more potent cholinesterase inhibitors.

Table VI. Hydrolytic Stability of α,α,α-Trifluoroacetophenone Oxime Carbamates at 70°[a]

Structure	Hydrolysis constant, K_{hyd}, hr^{-1}	Half-life, hr
	1.8×10^{-1}	3.9
	6.7×10^{-2}	10
	4.7×10^{-2}	15

[a] The laboratory hydrolysis determinations were carried out in a 1:4 mixture of ethanol–NaOH/citrate buffer (pH 8.3) at 70° with the insecticide initially present at a concentration of 6–10 μg/ml (0.05 *M*).

Table VII. Synergistic Effect of Piperonyl Butoxide on α,α,α-Trifluoroacetophenone Oxime Carbamates

Structure	Topical LD_{50}, μg/g, house fly (♀) Alone	1:5 PB	Deg of synergism (alone/PB)
	18.5	7.0	2.6
	11.5	7.0	1.6
	95	11.5	8.2

In a topically applied test α,α,α-trifluoroacetophenone oxime thiophosphate (LD_{50} = 20.5 μg/g) is about 18 times more toxic to house flies than acetophenone oxime thiophosphate (LD_{50} = 355 μg/g) itself.

Oxime Carbamates. The corresponding oxime carbamates were much more active as insecticides. These generally controlled the Mexican bean beetle, aphid, and house fly. Table IV lists the various oxime carbamates prepared, as well as their cholinesterase inhibition values and biological activity.

These oxime derivates are about 20–30 times more toxic to house flies than the corresponding substituted phenyl *N*-methylcarbamates (Table V).

The most active of the aryl oxime carbamate series were the ortho fluoro and the ortho methoxy compounds. Substituents in the ortho position appear to have the greatest effect on cholinesterase inhibition. In most cases these were also the more active chemicals in the insecticide screening tests. However, their potent cholinesterase inhibition values which ranged from 10^{-7} to 10^{-9} did not give the expected levels of insecticidal activity in the *in vivo* screening tests. Since the cholinesterase inhibition is obtained from an *in vitro* test, these values represent the simplest quantitative measure of biological activity for the oxime derivatives. The LD_{50} values for the insecticidal activity of the compounds are more complex measures. In this *in vivo* screening the chemicals must first penetrate to the site of action before they can exhibit their effectiveness. Therefore, it is not surprising that there is a lack of

Table VIII. Biological Activity of Trifluoromethylalkyl Ketoxime Carbamates

$RC(CF_3)=NOC(=O)NHCH_3$

R	Cholinesterase I_{50}, M	LD_{50}, ppm MBB	Aphid (C)	Aphid (S)	Corn rootworm
CH_3		>250	>250	>250	1.3
n-C_3H_7	3.9×10^{-7}	25	25	35	0.15
i-C_3H_7	1.0×10^{-7}	40	110	23	0.26
sec-C_4H_9	2.4×10^{-7}	14	70	27	0.29
n-C_8H_{17}	6.7×10^{-7}	>250	>250	>250	>2.5
CH_3OCH_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