

# Sensitized Photodecomposition and Photosensitizer Activity of Pesticide Chemicals Exposed to Sunlight on Silica Gel Chromatoplates

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Photodecomposition of several pesticide chemicals exposed to sunlight on silica gel chromatoplates is accelerated by photosensitizing agents, including some other pesticide chemicals. The following two surveys were made by a simple procedure involving exposure to sunlight for up to 1 hr: 28 candidate sensitizers of known triplet-energy values were tested individually for activity in sensitizing the photodegradation of each of 23 radio-labeled pesticide chemicals; 175 unlabeled pesticides were screened for photosensitizing activity against each of six  $C^{14}$ -labeled insecticide chemicals. The conversion of aldrin, dieldrin, and endrin to photoisomeric derivatives is accelerated by many compounds of high

triplet-energy state. Some aromatic amines sensitize the photodecomposition of DDT and several chlorinated cyclodienes, possibly by formation of charge transfer complexes. Anthraquinone shows the broadest spectrum of activity of the sensitizers tested in combination with organophosphorus compounds, methylcarbamates, pyrethroids, rotenone, dinitrophenol derivatives, piperonyl butoxide, and 2,4-D. There is a possibility of a photosensitizing pesticide chemical markedly altering the persistence of another pesticide chemical, but these interactions of a photosensitizing nature occur with only a few combinations of pesticides studied.

Organic photosensitizers are useful in accelerating many photochemical reactions. Benzophenone accelerates the conversion of certain chlorinated cyclodiene insecticide chemicals to their caged photoisomers when the compounds are exposed as benzene solutions to strong ultraviolet light (Rosen and Carey, 1968; Rosen and Siewierski, 1970; Rosen *et al.*, 1969). Rotenone and certain related chromanone derivatives are even more active than benzophenone in enhancing the rate of cyclodiene insecticide chemical photodegradation on plant surfaces (Ivie and Casida, 1970). It is likely that there are other interesting pesticide-photosensitizer interactions which might be useful in manipulating the persistence of pesticide chemical residues (Ivie and Casida, 1970). Accordingly, studies were undertaken to determine the extent and nature of such interactions occurring when surface deposits are exposed to sunlight. The development of a rapid screening procedure allowed the testing of many known photosensitizer or quencher chemicals for photosensitizing activity in degrading several pesticide chemicals. The survey also included a large number of pesticide chemicals themselves tested as photosensitizers, since many of these compounds are structurally related to known photosensitizers and environmental interactions of a photosensitizing nature might be expected to occur.

## MATERIALS AND METHODS

**Chemicals.** In each case the pesticide chemical to be analyzed was used as a  $C^{14}$ -labeled compound and the candidate photosensitizer was used as an unlabeled compound.

The  $C^{14}$ -labeled pesticide chemicals studied were prepared in this laboratory, in which case the labeled position has been reported (Krishna *et al.*, 1962; Kuwatsuka and Casida, 1965; Nishizawa and Casida, 1965; Yamamoto and Casida, 1968), or they were obtained as follows: aldrin- $C^{14}$ , dieldrin- $C^{14}$ , endrin- $C^{14}$ , and 3,4,5-trimethylphenyl methylcarbamate carbonyl- $C^{14}$  (SD-8530) (Shell Development Co., Modesto, Calif.); 2-dimethylamino-4,5-dimethyl-6-pyrimidyl dimethylcarbamate carbonyl- $C^{14}$  (pirimicarb) (Alan Calderbank,

Plant Protection Ltd., Jealott's Hill, England); Sumithion-*O*-methyl- $C^{14}$  (Yoshihiko Nishizawa, Sumitomo Chemical Co., Osaka, Japan); Imidan-carbonyl- $C^{14}$  and Dyfonatering- $C^{14}$  (Julius Menn, Stauffer Chemical Co., Mountain View, Calif.); malathion-1,2-succinyl- $C^{14}$  and DDT-ring- $C^{14}$  (World Health Organization, Geneva, Switzerland); diazinon-pyrimidyl-2- $C^{14}$  and isolan-carbonyl- $C^{14}$  (Geigy Chemical Co., Ardsley, N.Y.); 2,4-D- $\alpha$ - $C^{14}$  (New England Nuclear Corp., Boston, Mass.); Dessin-ring- $C^{14}$  (Union Carbide Chemicals Co., South Charleston, W. Va.); and 2-*sec*-butyl-4,6-dinitrophenol-ring- $C^{14}$  (DNBP) (obtained by hydrolysis of Dessin-ring- $C^{14}$  and supplied by Suresh Bandal, University of Calif., Berkeley). The specific activities were adjusted in each case to 0.5 to 1.5 mCi/mmol by dilution with unlabeled compounds.

Photosensitizers were from the Photosensitizer and Quencher Kit (Commodity No. Z901, J. T. Baker Chemical Co., Phillipsburg, N.J.), or from chemical supply houses. The majority of the pesticides used were technical or analytical grade samples, but some were used as wettable powders or emulsifiable concentrates, as defined later. Generic names of the compounds designated by common or trade names are given by the Farm Chemicals Handbook (1970), Kenaga and Allison (1969), or Martin (1968).

**Assay for Photosensitizer Activity.** Precoated thin-layer chromatograms (polyethylene backed, silica gel without fluorescent indicator, 0.1 mm gel thickness, type K301R2, Eastman Kodak Co., Rochester, N.Y.) were used for both exposing the chemicals to sunlight and subsequent analysis. Chemicals tested as photosensitizers were dissolved in chloroform or methanol at 10  $\mu$ g per  $\mu$ l with appropriate weight adjustments for formulated pesticides. On each thin-layer chromatoplate of 10  $\times$  20 cm, 11 equally-spaced pencil marks were made on the silica gel about 2 cm from the edge along one 20-cm side. With the aid of a microsyringe, 2  $\mu$ l of 10 different solutions of photosensitizers were applied to 10 of the spots, with the eleventh serving as a control receiving 2  $\mu$ l of chloroform or methanol only. After the solvent had evaporated, leaving a chemical deposit of about 0.5 cm diameter, the  $C^{14}$ -pesticide chemical (2  $\mu$ g in 2  $\mu$ l of methanol solution) was applied to each of the areas previously spotted with the candidate photosensitizer. Plates treated with the  $C^{14}$

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Table I. Relation of Triplet-Energy Values to Photosensitizing Activity in Degradation of Photosensitizer Rating<sup>a</sup> for

C <sup>14</sup> -Pesticide Chemical	Aceto-phenone (74)	Xanthone (74)	Carbazole (70)	Triphenyl-amine (70)	Dibenzo-thiophene (70)	Benzo-phenone (69)	Fluorene (68)	4,4'-Dichloro-benzo-phenone (68)	Thio-xanthone (65)	Anthra-quinone (62)
Aldrin	1	3	2	2	3	2	1	3	3	3
Dieldrin	0	3	2	3	3	2	0	2	2	1
Endrin	0	2	1	1	1	1	0	1	1	1
DDT	0	0	2	3	1	0	1	0	0	1
Diazinon	0	0	0	0	0	0	0	0	0	2
Dyfonate	0	1	0	1	0	1	0	1	1	3
Imidan	0	0	0	0	0	0	0	0	0	1
Malathion	0	0	0	0	0	0	0	0	0	3
Sumithion	0	1	0	0	0	0	0	0	1	1
Baygon	0	0	0	0	0	0	0	0	0	0
Carbaryl	0	0	0	0	0	0	0	0	0	1
Isolan	0	0	0	0	0	0	0	0	0	1
Mesurool	0	1	0	0	0	1	0	1	2	3
Pirimicarb	0	1	0	0	0	1	0	1	1	1
SD-8530	0	1	0	0	0	1	0	1	0	3
Zectran	0	1	0	0	0	1	0	2	2	2
Allethrin	0	1	0	1	0	1	0	1	1	2
Pyrethrin I	0	1	0	0	0	0	0	1	2	2
Rotenone	0	1	0	0	0	1	0	1	1	1
Dessin	0	0	0	0	0	0	0	0	0	2
DNBP	0	0	0	0	0	0	0	0	0	2
Piperonyl butoxide	0	2	0	0	0	2	0	2	2	2
2,4-D	0	1	0	1	0	1	0	1	0	2

<sup>a</sup> The photosensitizer ratings are as follows: 0—not active as a photosensitizer; 1—slight but definite activity; 2—intermediate activity; 3—high activity resulting in extensive to complete degradation of the C<sup>14</sup>-pesticide chemical. <sup>b</sup> The following compounds, with the indicated triplet-energy values, showed no significant photosensitizing activity against any of the 23 labeled pesticides: biphenyl (65), naphthalene (61), chrysene (57),

compounds, pirimicarb, Zectran, allethrin, pyrethrin I, and rotenone, were exposed to direct sunlight for 15 min; other C<sup>14</sup> pesticides were exposed for 1 hr. Two replicates were made for each potential photosensitizer involving freshly prepared photosensitizer solutions and different days for exposure to sunlight.

The thin silica gel coating of the plates, although increasing the surface area exposed to sunlight, apparently had no direct effect on the interactions of the compounds involved. This was established by exposing 80 different C<sup>14</sup>-pesticide-photosensitizer combinations to sunlight as small spots on thin layers of powdered glass. Extraction of the glass powder and subsequent analysis by thin-layer chromatography (tlc) and radioautography gave results comparable to those obtained with the silica gel chromatoplates. The use of silica gel as an adsorbent in photochemical studies of organic molecules has been reported (Leermakers *et al.*, 1966; Weis *et al.*, 1968), but these investigations utilized gel-solvent slurries exposed to artificial light.

**Chromatography and Photosensitizer Evaluation.** After the silica gel chromatoplates treated with the photosensitizers and C<sup>14</sup> pesticides had been exposed to sunlight, the plates were developed in appropriate solvent systems, and radioactive products were detected by radioautography. The solvent systems used for the labeled compounds were as follows: aldrin (hexane-benzene, 4:1); dieldrin and endrin (hexane-ethyl acetate, 4:1); DDT (hexane-benzene, 5:3); diazinon (hexane-methanol, 50:1); Dyfonate (hexane-acetone, 200:1); Imidan (hexane-acetone, 4:1); malathion (hexane-acetone, 3:1), Sumithion (hexane-acetone, 6:1);

Baygon and carbaryl (ether-hexane, 3:2); Mesurool and SD-8530 (ether-hexane, 2:1); pirimicarb and Zectran (ether-hexane, 3:1); isolan (ethyl acetate); allethrin and pyrethrin I (hexane-ether, 3:2); rotenone (benzene-methanol, 200:1); Dessin and DNBP (hexane-benzene-ether, 4:1:1); piperonyl butoxide (hexane-acetone, 20:1); 2,4-D (benzene saturated with formic acid).

Evaluation of the sensitizing activity of test photosensitizers was made by visual examination of the darkened areas on the radioautograms. Compounds were assigned photosensitizer ratings of 0 to 3, as indicated in Table I, and illustrated in Figure 2 based on the extent of degradation of the sensitized C<sup>14</sup>-compound compared to the degradation observed without added sensitizer. Control experiments with single replication were made in an identical manner, but the plates were held in darkness instead of the sunlight exposure prior to analysis; in all cases the sensitization was found to be dependent on exposure to sunlight.

## RESULTS

**Sensitization by Compounds with Known Triplet-Energy Values.** Twenty-one of the 28 photosensitizers or quenchers tested showed at least some photosensitizing activity (Table I). No direct correlation is evident between triplet-energy values and photosensitizing activity, although the chlorinated hydrocarbon insecticide chemicals, and particularly aldrin and dieldrin, are generally more susceptible to sensitization by the higher triplet-energy state compounds.

It is evident from Table I that photosensitization is sometimes highly selective for a particular pesticide chemical-

23 C<sup>14</sup>-Pesticide Chemicals Exposed to Sunlight as Deposits on Silica Gel Chromatoplates

Compounds<sup>b</sup> with Known E<sub>T</sub> Values<sup>c</sup>

Phen-anthrene (62)	Flavone (62)	4,4'-Bis-(dimethyl-amino)-benzophenone (61)	2'-Aceto-naphthone (56)	1'-Aceto-naphthone (56)	1'-Naphth-aldehyde (56)	Benzil (54)	trans-Stilbene (50)	Pyrene (49)	7H-Benz[de]anthracen-7-one (47)	Anthracene (42)
1	2	1	0	0	0	2	1	0	0	1
0	1	0	0	0	0	1	1	0	0	1
0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	1	1	0	0
0	0	0	0	0	0	1	0	0	0	1
0	1	0	0	0	0	1	0	0	1	2
0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	1	0	0	0	2
1	1	1	1	0	0	1	1	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
1	1	0	1	1	1	1	0	1	3	2
0	0	0	1	1	1	2	0	0	3	1
0	0	0	0	0	0	1	0	0	0	2
0	0	0	0	1	1	2	0	0	1	0
0	0	0	1	1	1	2	0	1	2	1
0	1	0	2	2	2	2	0	1	3	2
0	0	0	1	0	0	1	0	0	2	1
0	0	0	0	0	0	0	0	0	0	0
0	0	1	0	0	0	0	0	0	0	0
0	1	0	1	0	1	2	0	0	2	2
0	0	0	0	0	0	0	0	0	0	1

fluorenone (53), dicyclopentadienylniron (<43), 2,4-pentanedione, iron III derivative (<43), crystal violet (39). <sup>c</sup> E<sub>T</sub>—triplet energy values (kcal/mol) from Herkstroeter *et al.* (1964) or from the Photosensitizer and Quencher Kit (Commodity No. Z901, J. T. Baker Chemical Co., Phillipsburg, N.J.), as indicated in parentheses.

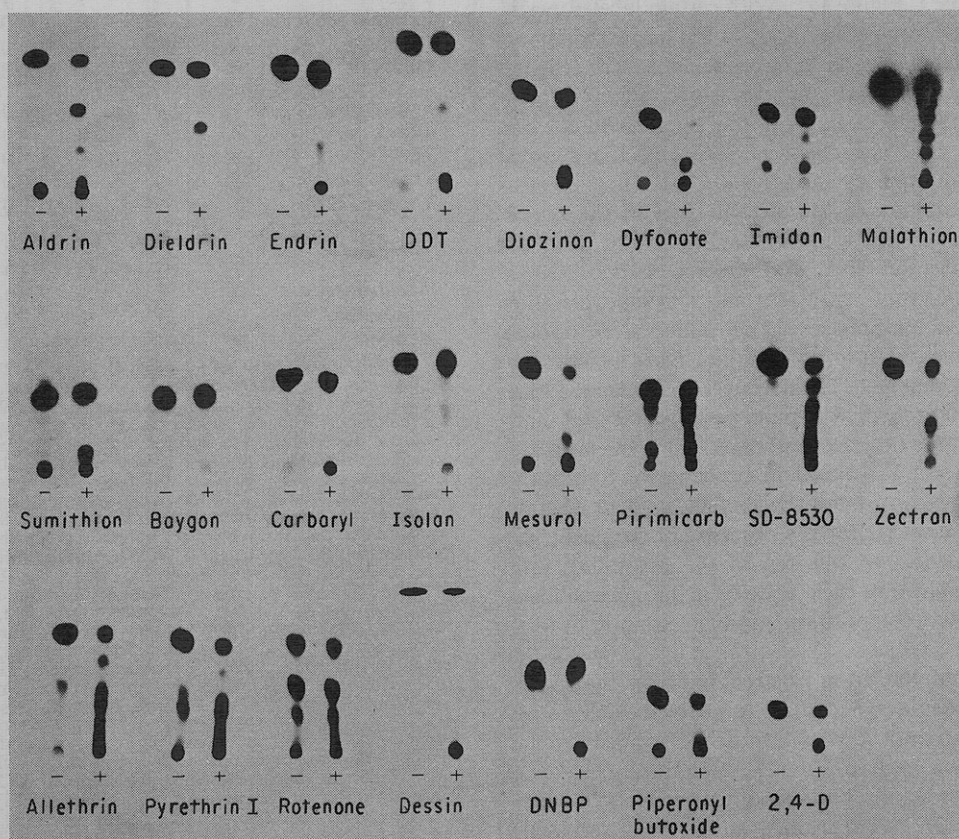
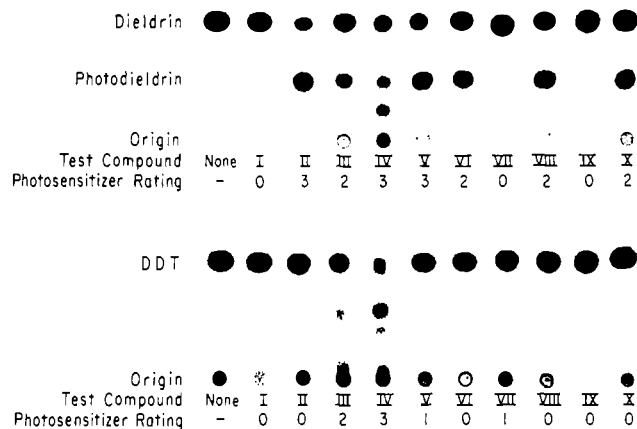


Figure 1. Composite tlc radioautogram showing the photosensitizing effects of anthraquinone on the extent of photodegradation of 23 C<sup>14</sup>-pesticide chemicals exposed to sunlight as deposits on silica gel chromatoplates. (−) 2 μg C<sup>14</sup>-pesticide chemical only; (+) 10 μg anthraquinone and 2 μg labeled pesticide chemical



**Figure 2.** Composite tlc radioautogram showing the photosensitizing effects of 10 high energy triplet-state photosensitizers on the extent of photodegradation of dieldrin-C<sup>14</sup> and DDT-C<sup>14</sup> exposed to sunlight for 1 hr as deposits on silica gel chromatoplates. The test compounds and their triplet-energy values are: I—acetophenone (74); II—xanthone (74); III—carbazole (70); IV—triphenylamine (70); V—dibenzothiophene (70); VI—benzophenone (69); VII—fluorene (68); VIII—4,4'-dichlorobenzophenone (68); IX—biphenyl (65); X—thioxanthone (65). Photosensitizer ratings are defined in Table I, footnote a

sensitizer combination when comparing sensitizers having similar triplet-energies. For example, both acetophenone and xanthone have triplet-energy states of 74 kcal/mol, yet while the latter efficiently sensitizes cyclodiene photoalteration, acetophenone has only very slight activity.

Only a few sensitizers show broad-spectrum activity. Anthraquinone is active with all of the pesticide chemicals except Baygon, which failed to respond to any of the sensitizers studied (Table I, Figure 1). With certain labeled pesticide chemicals, notably malathion and SD-8530, anthraquinone sensitization produces several breakdown products (Figure 1), while many other labeled compounds are sensitized only to products that remain at or near the origin with the tlc solvent systems used. The chemical nature of the various photoproducts produced by sensitization was not investigated, with the exception of the identification of the major products from aldrin, dieldrin, and endrin as the isomers produced by cyclization (Ivie and Casida, 1970). Other relatively broad spectrum sensitizers are xanthone, its thio analog, benzil, and anthracene. The patterns of photosensitization observed with anthracene are markedly similar to those of anthraquinone. Tlc investigations indicated that both compounds were chemically pure, but it was shown that, on tlc chromatograms, anthracene is converted in the presence of sunlight to a product identical in tlc behavior to anthraquinone. Thus, rapid oxidation on the silica gel to anthraquinone probably accounts for the observed photosensitizing activity of anthracene. In this regard the possibility that other sensitizers might owe their activity to photosensitizing impurities or photodecomposition products cannot be discounted.

The radioautogram shown in Figure 2 indicates that while most photosensitizers serve mainly to convert dieldrin to photodieldrin, this is not always the case. Triphenylamine and, to a lesser extent, carbazole are effective photosensitizers, yielding some photodieldrin but also other products of lower R<sub>f</sub> values. With DDT-C<sup>14</sup>, triphenylamine and carbazole are quite active in sensitizing photodecomposition, while other high energy triplet sensitizers are much less effective or are completely ineffective.

**Table II.** Photosensitizing Activity of 175 Unlabeled Pesticides in Degradation of Six C<sup>14</sup>-Insecticide Chemicals Exposed to Sunlight as Deposits on Silica Gel Chromatoplates

Unlabeled Pesticide <sup>b,c</sup>	C <sup>14</sup> -Insecticide Chemical and Photosensitizer Rating <sup>a</sup>					
	Dieldrin	DDT	Diazinon	Malathion	Sumithion	Carbaryl
Abate	2	0	0	0	0	0
Allethrin	0	0	0	0	1	0
Amiben (22E)	0	1	0	0	0	0
Anthraquinone	1	1	2	3	1	1
Baytex	1	0	0	0	1	0
Carbaryl	0	0	0	0	1	0
Carbyne (12E)	0	1	0	0	2	0
Co-Ral	0	0	0	0	1	0
Dimethoate (44E)	0	0	0	0	1	0
Diphenylamine	1	2	0	0	0	0
Dowicide A	0	1	0	0	0	0
Dyfonate	1	0	0	0	1	0
Dyrene (50W)	1	0	0	0	0	0
Genite	1	0	0	0	0	0
Imidan	1	0	0	0	0	0
Landrin	0	0	0	0	1	0
MCPA (22E)	0	0	0	0	1	0
Methyl trithion	0	0	0	0	1	0
Mobam	0	0	0	0	1	0
Morestan (89W)	0	0	0	0	1	1
Neopynamin	0	0	0	0	1	0
NRDC-104	0	0	0	0	1	0
Pentachlorophenol	0	0	1	1	0	0
Pentac	0	0	1	1	1	0
Phenothiazine	1	3	0	0	0	0
Phthalimide	1	0	0	0	0	0
Phygon	0	0	1	1	1	0
Pyramin (80W)	0	0	0	0	1	0
Rotenone	2	0	0	0	0	0
Sulfoxide	0	0	0	0	1	0
Sulphenone	1	0	0	0	0	0
Temik	0	0	0	0	1	0
Tetradifon	2	0	0	0	0	0
Thiabendazole	1	0	0	0	1	0
Tordon (22E)	1	0	0	0	0	0
Trithion	0	0	0	0	1	0
Tropital	0	0	0	0	1	0
Vegadex (50E)	0	0	0	0	1	0
Xanthrone	3	0	0	0	1	0
Zectran	0	0	0	0	1	0

<sup>a</sup> The photosensitizer ratings are defined in Table I, footnote a. <sup>b</sup> Unless otherwise specified, the chemicals were technical or analytical grade. Formulated chemicals are designated as W (wetttable powder) or E (emulsifiable concentrate), preceded by the approximate percentage of active material in the formulation. <sup>c</sup> The following compounds showed no significant photosensitizer activity with any of the labeled insecticides studied: Acaralate (25E), Actidione, Agritox, Alanap (90W), aldrin, Alipur (25E), amitrole, Aramite, Aspon, atrazine (80W), Avadex (46E), Azak (80W), azobenzene, Azodrin (80E), Bandane (50E), Banol, Banvel D (50E), Baygon, Betanal (17E), Betasan, BHC, Bidrin, bromacil (80W), Bux, Caparol (80W), captan, chlordane, chlorfenvinphos, Clobber, Cotoran (80W), Cyolane, 2,4-D, Dacthal (75W), Dasanit, DDT, DEF, Delnav, Dessin, diazinon, Dibrom, dicapthion, dichlorvos, dicryl, dieldrin, Difolatan, dimetilan, Dinoben (methyl ester, 25E), diphenamid (80W), diquat, DNBP, Dursban, MOCAP, nabam (22E), Nexion (25E), Ordram, ovex, paraquat, parathion, PCNB (75W), Perthane, Phaltan, phencapton, Phosdrin, piperonyl butoxide, Planavin (43E), Preforan (36E), Princep (80W), propanil (25E), propyl isome, Pyramat, Pyrolan, Ramrod (65W), Randox (50E), Ro-Neet, ronnel, Rowmate (45E), Ruelene, simetryne, Smito (85E), solan (50E), Strobane, Sumithion, Sutan, sweep (25E), Systox, Tandex (80W), Telodrin, Telvar (80W), Tenoran (50W), Thanite, Thiodan, Tillam, TOK (25E), Topcide (24E), toxaphene, Treflan (46E), 2,4,5-T, trietazine (50W), Tupersan (50W), UC-10854, vamidothion, Vernam, Zinophos (45E), Zolone (35E), and Zytron.

**Pesticides as Photosensitizers.** Many pesticide chemicals were tested for photosensitizing activity against six insecticide chemicals representing each of the three major insecticide classes: the chlorinated hydrocarbons, dieldrin and DDT; the organophosphorus compounds, diazinon, malathion, and Sumithion; and the methylcarbamate, carbaryl. The 175 pesticides screened were selected mainly on the basis of current commercial use. The results of this study are shown in Table II.

Forty of the unlabeled pesticides tested are active to some degree as photosensitizers, but only eight have photosensitizer ratings greater than 1 against any of the C<sup>14</sup>-insecticide chemicals studied. Two of these, anthraquinone and xanthone, are known triplet sensitizers and have been discussed previously. The activity of diphenylamine and phenothiazine against the chlorinated hydrocarbons, dieldrin and DDT, might be expected because they have an aromatic amine grouping in common with triphenylamine and carbazole. The most effective sensitizer against dieldrin is xanthone, but Abate, rotenone, and Tetradifon are also quite effective in converting dieldrin to its photoisomer. Of the six labeled insecticide chemicals studied, Sumithion and dieldrin are the most susceptible to photosensitization. However, of the 26 unlabeled pesticides having activity against Sumithion, only carbyne shows a photosensitizer rating greater than 1. Sensitization of dieldrin by each of the 16 active compounds, with the exception of the two aromatic amines, results primarily in its conversion to photodieldrin.

#### DISCUSSION

Photodegradation of the chlorinated hydrocarbon insecticide chemicals is more susceptible to triplet sensitizers than that of the organophosphorus compounds, methylcarbamates, pyrethroids, rotenone, dinitrophenol derivatives, methylenedioxyphenyl synergist, and the phenoxyacetic acid derivative studied. Compounds of similar triplet-energy values often do not give similar degrees of photosensitization, suggesting that differences in light absorbance characteristics of the sensitizers or differences in the type or extent of interaction with the pesticide chemicals may account in part for these observed activity differences. Sensitization *via* triplet-energy transfer is apparently not involved in most of these reactions. The photosensitizing action of aromatic amines (carbazole, diphenylamine, phenothiazine, and triphenylamine) on degradation of chlorinated hydrocarbon insecticide chemicals apparently involves a different mechanism than that of the other sensitizers tested. This conclusion is supported by the recent finding that alkyl halides, including DDT, are dechlorinated in the presence of aromatic amines and light by a photoinduced charge transfer from the amine to the halide (Miller and Narang, 1970).

The survey of different pesticide chemicals for photosensitizing activity brings in compounds of widely varying chemical structure that might interact by light-dependent mechanisms the same as or different from those previously discussed. Contact between different pesticide chemicals occurs commonly in the environment due directly to application of mixtures of compounds or indirectly to movement within the environment itself; thus, there is a possibility of a photosensitizing pesticide chemical markedly altering the persistence of another pesticide chemical. The present studies suggest that, with few exceptions, environmental contact between most pesticides would probably not result in interactions of a photosensitizing nature. However, some pesticides and several triplet-state photosensitizers are active in catalyzing the photodegradation of certain pesticide chemicals under the experimental conditions of this study. Certain of these interactions also occur on plant foliage exposed to sunlight (Ivie and Casida, 1970) and warrant further investigation.

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