

Table I. Melting Points and 2,4-D Content of Reagent Grade *o*- and *p*-Chlorophenoxyacetic Acids

Phenoxy-acetic acid	Melting points, °C			% 2,4-D
	Lit.	Bottle	Obsd	
<i>o</i> -Chloro	145.5 ± 0.5		136 ± 3	4.9 ± 0.5
<i>p</i> -Chloro	155.5 ± 0.5	158 ± 1	152 ± 2	1.0 ± 0.1

ever, quantitation of these impurities is still essential so that the true biological activity of the pesticide under examination can be found. As most biological scientists usually use pesticidal formulations of uncertain concentration and content, this problem is compounded even more, and it is not surprising that confusion in interpretation of experimental results has resulted. This paper has shown that chemical analysis and quantitation of a pesticide, and related impurities, are necessary before unambiguous interpretation of biological experiments.

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Shane S. Que Hee
 Ronald G. Sutherland*

Department of Chemistry and Chemical Engineering
 University of Saskatchewan
 Saskatoon, Saskatchewan S7N 0W0, Canada

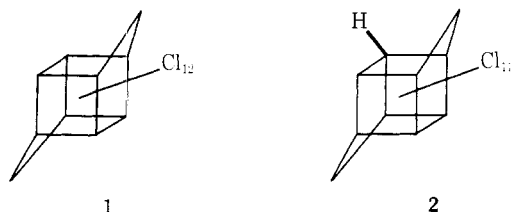
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Photoreduction of Mirex in Aliphatic Amines

Solutions of dodecachloropentacyclo-[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (Mirex) in aliphatic amines were irradiated with sunlight. Mass spectral, infrared, and nmr data were used to establish that the major photoproducts are 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 and 1,2,3,4,5,6,7,8,9,10-decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane. Spectroscopic evidence is reported which indicates a charge transfer complex is formed between the amine and Mirex.

The insecticide Mirex (1) (dodecachloropentacyclo-[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane) is utilized extensively in the southeastern United States to control the imported fire ants *Solenopsis invicta* and *Solenopsis richteri*. This chlorocarbon is thermally stable (Eaton *et al.*, 1960) and resistant to chemical degradation even by strong acids and bases as well as oxidizing and reducing agents (McBee *et al.*, 1956). Its photochemistry in hydrocarbon solvents with radiation down to 200 nm and its very slight decomposition by sunlight when adsorbed to silica have been described (Alley *et al.*, 1973; Gibson *et al.*, 1972). The major monodechlorination product in both cases is 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 (2) (Alley *et al.*, 1974). Mirex shows



virtually no absorption at wavelengths greater than 250 nm (Zijp and Gerding, 1958), and thus very little photochemical degradation by sunlight would be expected. The subject of this report is the facile degradation of Mirex by sunlight *via* its interaction with aliphatic amines.

EXPERIMENTAL SECTION

Technical Mirex (1), Allied Chemical Corp., was recrystallized from benzene. Cyclohexane (Phillips, 98%) was fractionally frozen and then distilled. Reagent grade triethylamine (Aldrich Chemical Co.) was distilled under nitrogen. The purity of the triethylamine was checked by

glpc using a 1.5-m Chromosorb 103 column at 150° and was found to be greater than 99.9%.

The reactions were monitored with a Varian 1400 gas chromatograph equipped with a hydrogen flame detector. The mass spectra were obtained with a Perkin-Elmer Model 270 gas chromatograph-mass spectrometer. The following gas chromatographic columns were used for the analyses: OV-1, 16-m support-coated, open-tubular (SCOT); 3-m 5% SE-30 on 80-90 Anakrom ABS; and a 1.5-m 0.35% diethylene glycol succinate (DEGS) on 100-120 mesh textured glass beads.

Spectra were obtained with a Perkin-Elmer Model 457 infrared spectrophotometer and a JEOL Model MH-60II nuclear magnetic resonance spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Photolysis of Mirex (1) in Triethylamine. A solution of Mirex (5 g) in 100 ml of triethylamine was irradiated in a Pyrex tube with a 275-W GE sunlamp. After 50 hr, glpc analysis indicated that 80% of the Mirex had reacted and three major products were formed with retention times (SE-30, 230°) relative to Mirex of 0.75, 0.70, and 0.60 with peak area ratios 30:3:20, respectively. Cyclohexane (100 ml) was added to this solution and it was then neutralized with 6 N hydrochloric acid. The aqueous portion was extracted twice with 100 ml of cyclohexane and the extracts were combined, dried, and concentrated. The resulting material was chromatographed on alumina. Elution with cyclohexane gave some fractions containing a small quantity of the product with a relative glpc retention time of 0.70. The infrared, nmr, and mass spectra of this compound were identical with those reported for 2 (Alley *et al.*, 1973).

Further elution of the alumina column with cyclohexane gave fractions that were mixtures of the other two photoproducts. These mixtures were further separated by

chromatography on silica gel. Elution with cyclohexane gave 0.90 g (25% yield) of white crystalline material (decomposed above 380°) which had a retention time relative to Mirex of 0.75. The infrared, nmr, and mass spectral data for this material were identical with those reported by Dilling *et al.* (1967) for 3. Continued elution of the silica gel column with cyclohexane gave 0.49 g (15% yield) of another white crystalline material which had a glpc retention time relative to Mirex of 0.60. The purified product (decomposed above 350°) gave the following spectra: ir (CS₂) 2940 (w), 1250 (sh), 1245 (s), 1195 (m), 1140 (w), 1120 (m), 1115 (m), 1100 (sh), 1095 (m), 1060 (sh), 1045 (s), 940 (w), 860 (w), 815 (w), 800 (w), 760 (w), 725 (w), 695 (w), 680 (w), 620 (s), 580 (s), 565 (w), 430 (w) cm⁻¹; nmr (CCl₄, TMS) δ 4.34 singlet (half-height, 2 Hz). The glpc conditions (SCOT, 170°) used to obtain the gc-mass spectra of this material separated it into two equal components. The mass spectra had peaks for C₁₀Cl₁₀H₂⁺ ions (parent) and C₅Cl₅H⁺ ions (cleavage of the pentacyclic skeleton) along with less informative ions. There were no clusters for C₅Cl₆⁺ or C₅Cl₄H₂⁺ ions.

Anal. Calcd for C₁₀Cl₁₀H₂: C, 25.19; Cl, 74.37; H, 0.42; average mol wt 477. Found: C, 25.28; Cl, 74.41; H, 0.50; mol wt (mass spectroscopy), 476 (largest peak in parent ion cluster).

A Mirex-triethylamine solution in a quartz tube was irradiated in a Rayonet reactor with a bank of 16 lamps (253.7 nm). The results were similar to those obtained in the preceding experiment except that the ratio of the monohydro photoproducts was 5:1.

Photolysis of 1,2,3,4,5,5,6,7,8,9,10-Undecachloropentacyclo[5.3.0.0.2⁶.0³.9.0^{4,8}]decane (3) in Triethylamine. A solution of 3 (0.1 g) in 20 ml of triethylamine was irradiated in a Pyrex tube with a 275-W GE sunlamp. The reaction progress was monitored by glpc. After 50% of compound 3 had reacted, the solution was neutralized with 6 N hydrochloric acid and extracted with cyclohexane. The major product had a glpc retention time and mass spectrum identical with 4 produced from direct photolysis of Mirex in triethylamine.

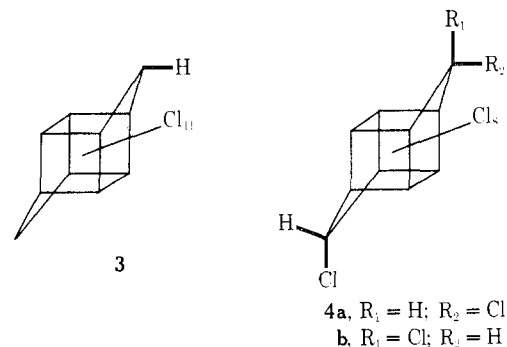
Ultraviolet Spectroscopy. Complex formation between the amine and 1 was studied by ultraviolet spectroscopy using solutions of triethylamine in cyclohexane. Absorption measurements were made in 0.1-, 1.0-, or 10-cm silica cells with a Beckman Model DK-2a recording spectrophotometer. In order to operate the spectrophotometer in both double beam and essentially single beam fashion, either appropriate concentration of the amine in cyclohexane or cyclohexane alone was used in the reference beam of the instrument. In the second case, the absorption of the amine was subtracted from the total absorption of the Mirex-amine solution to give the absorption of the complex.

RESULTS AND DISCUSSION

The photodecomposition of Mirex in aliphatic amines proved to be different from that observed in hydrocarbon solvents in two important aspects, the products obtained and the wavelength of light absorbed.

The major photoproduct in the presence of amines was 1,2,3,4,5,5,6,7,8,9,10-undecachloropentacyclo[5.3.0.0.2⁶.0³.9.0^{4,8}]decane (3). The identity of 3 was established by comparison of its infrared spectrum with that of authentic material prepared by the method of Dilling *et al.* (1967). A second monohydro derivative was formed in smaller quantities. This compound was identical with the major photoproduct (2) from the photolysis of Mirex in hydrocarbons.

In addition to the two monohydro photoproducts, a mixture of dihydro products was also formed in this reaction. The proton nmr spectrum of the mixture is consistent with structures 4a and 4b (*cis*- and *trans*-



1,2,3,4,5,6,7,8,9,10-decachloropentacyclo[5.3.0.0.2⁶.0³.9.0^{4,8}]decane) for these compounds. The chemical shift of the single resonance observed in the nmr spectrum of these dihydro derivatives of Mirex was δ 4.34 compared to δ 4.28 for 3 (Dilling *et al.*, 1967). The resonance of the hydrogen in 2 at δ 3.7 (Alley *et al.*, 1973) was significantly different from these values. Furthermore, compound 3 can be converted to a mixture of 4a and 4b by the photochemical reaction in triethylamine. These facts are consistent only with the proposed structures. This assignment was also supported (Alley *et al.*, 1974) by the mass spectrum of the dihydro derivatives which had C₅Cl₅H⁺ ions but no C₅Cl₆⁺ and C₅Cl₄H₂⁺ ions.

The wavelength of light required for the reaction was different in amines from that in hydrocarbons. Sunlight or a sunlamp caused rapid decomposition of Mirex in amines, but no reaction could be detected under similar conditions when the solvent was cyclohexane. Examination of the absorption spectra of solutions of Mirex and triethylamine provided an explanation for these observations. The molar absorptivities of Mirex and triethylamine are less than two at 270 nm, but solutions containing both of these compounds have a broad absorption band which extends to wavelengths longer than 320 nm. The appearance of this new band is typical of the behavior of charge transfer complexes (Stevenson and Coppinger, 1962; Lautenberger *et al.*, 1968). The absorbance at 270 nm (a shoulder in the charge transfer spectrum) varied linearly with the product of the amine and Mirex concentrations; and a Benesi-Hildebrand plot (Benesi and Hildebrand, 1949) indicated that a 1:1 complex was formed. The molar absorptivity of the complex was 1800, determined by measuring the absorbance of solutions with a 100-fold excess of amine. The equilibrium constant obtained from the Benesi-Hildebrand plot was 0.18.

The ratio of 2 to 3 produced in Mirex-triethylamine photolyses was a function of the wavelength of incident light. With a sunlamp, which presumably produced radiation having only wavelengths greater than 300 nm, the ratio of 3 to 2 was 10. When the 253.7-nm radiation of a low-pressure mercury source was used, this ratio was 5. A possible explanation for this change of product ratios is that longer wavelength radiation allows a greater contribution to the photochemistry of this system from excitation of the charge transfer band than when the same reaction is performed with the shorter wavelength 253.7-nm source.

Similar observations of photodecomposition of pesticides promoted by aromatic amines have been reported (Ivie and Casida, 1971; Miller and Narang, 1970; Miller *et al.*, 1973). In these cases, the intermediacy of a charge transfer complex was proposed but no spectroscopic observation of the charge transfer band was reported. Other studies have reported charge transfer complexes between alkyl halides and amines and the photochemistry resulting from absorption of light by these complexes (Stevenson and Coppinger, 1962; Lautenberger *et al.*, 1968; Ohashi *et al.*, 1973).

The significance of this work lies in the possibility that

photodegradable formulations of Mirex can be devised by the incorporation of amines into the baits used for control of the imported fire ants. Also, it is possible that environmental degradation mechanisms may exist that utilize these pathways. These areas and the extension of this reaction to other chlorinated materials are being actively investigated in these laboratories.

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Earl G. Alley*
 Bobby R. Layton
 James P. Minyard, Jr.

Mississippi State Chemical Laboratory
 Mississippi State, Mississippi 39762

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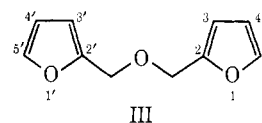
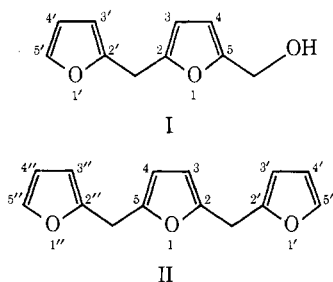
Mass Spectrometry of Three Furanic Compounds Containing Two or Three Furan Nuclei

Low-resolution mass spectra and high-resolution data are presented and discussed for the following compounds: [(5-hydroxymethyl-2-furyl)-(2'-furyl)]methane (I), [2-(2'-furfuryl)-5-(2''-fur-

furyl)]furan (II), and difurfuryl ether (III). Observed metastable ions are indicated as support for the proposed fragmentations.

Mass spectrometry is an important tool for the elucidation of the structure of natural products and of flavor constituents (Kolor, 1972). Furanic compounds from carbohydrate degradation are often found in foods and food-related model systems (Hodge, 1967; Ferretti *et al.*, 1970). Whereas a reasonable amount of published data on electron-impact induced fragmentation of certain classes of furanic compounds is available (Porter and Baldas, 1971), very little correlated mass spectral information exists for compounds containing more than one furan nucleus (Budzikiewicz *et al.*, 1967; Porter and Baldas, 1971). Compounds having two or three furan nuclei have been identified in roasted coffee beans (Stoll *et al.*, 1967; Stofelsma *et al.*, 1968), in popcorn (Walradt *et al.*, 1970), and in heated whey powder (Ferretti and Flanagan, 1971b). We previously reported (Ferretti *et al.*, 1974) mass spectral characteristics of four acyl derivatives of 2,2'-difurfylmethane in the hope that they may be of use to other investigators in identifying such compounds and structural-related ones.

This investigation is the continuation of our previous work, and deals with high-resolution measurements of the following compounds.



These compounds have been identified in a (milk-related) lactose-casein browning system (Ferretti and Flanagan, 1971a). The ether III and the trifuranic compound II have also been found in an *N*^α-formyl-L-lysine-D-lactose model system (Ferretti and Flanagan, 1973) and/or in heated whey powder (Ferretti and Flanagan, 1971b).

EXPERIMENTAL SECTION

For gas chromatography-mass spectrometry an LKB 9000 instrument and the same conditions previously described (Ferretti *et al.*, 1974) were used. The high-resolution mass spectra (resolution *ca.* 10,000) were determined with a CEC 21-110B instrument at 70 eV and an ion source temperature of 150°. Sample introduction, exact mass measurements, and calculations were performed as described previously (Ferretti *et al.*, 1974). The metastable ions were observed in the photographic charts from the LKB spectrometer.

The three compounds were synthesized and purified as reported earlier (Ferretti and Flanagan, 1971a).

RESULTS AND DISCUSSION

The mass spectra and elemental compositions of important ions of the following compounds are shown in Figure 1: [(5-hydroxymethyl-2-furyl)-(2'-furyl)]methane (I), [2-(2'-furfuryl)-5-(2''-furfuryl)]furan (II), and difurfuryl ether (III). Scheme I illustrates the possible fragmentation processes for compounds I and II, and Scheme II illustrates the degradation of III. In both schemes the observed metastable transitions are indicated by asterisks.