

# FMN-Sensitized Photolyses of Chloroanilines

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The sunlight exposure of several chloroanilines in aqueous solution in the presence of FMN leads to a number of products, among them azobenzenes and anilazobenzenes. Thus, 3,4-dichloroaniline gives 3,3',4,4'-tetrachloroazobenzene and 4-(3,4-dichloroanilino)-3,3',4'-trichloroazobenzene; 4-chloroani-

line gives 4,4'-dichloroazobenzene and 4-chloro-4'-(4-chloroanilino)azobenzene; 4-chloro-2-methylaniline gives 4,4'-dichloro-2,2'-dimethylazobenzene and 4-chloro-4'-(4-chloro-2-methylanilino)-2,2'-dimethylazobenzene.

The major pathways involved in the environmental chemistry of pesticides are biological metabolism and photolysis. To determine the ultimate fate of a pesticide, it is important to study not only the environmental chemistry of the pesticide itself, but also that of its photolysis products and biological metabolites. This paper deals with the photolysis of the biological metabolites of several pesticides that contain chloroaniline moieties. A number of these pesticides have been reported to be converted to chloroanilines in various biological systems.

The anilide herbicides, 3,4-dichloropropionanilide (propanil), N-(3,4-dichlorophenyl)-2-methylpentamide (karsil), and N-(3,4-dichlorophenyl)methacrylamide (dicryl) are converted by soil microorganisms to 3,4-dichloroaniline (Bartha, 1968). Another member of this family, N-(3-chloro-4-methylphenyl)-2-methylpentamide (solan) is converted to 3-chloro-4-methylaniline (Bartha, 1969). Still and Kuzirian (1967) studied the formation of 3,4-dichloroaniline in propanil-treated rice.

The phenylurea herbicides, 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron) and 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea (linuron) are also converted to 3,4-dichloroaniline in soil, but at a much slower rate than propanil (Belasco and Pease, 1969; Dalton *et al.*, 1966).

Nashed and Ilnicki (1970) have found 3,4-dichloroaniline in aerial portions of corn and soybeans grown in nutrient solution containing linuron. Another member of the phenylurea group, 3-(4-chlorophenyl)-1,1-dimethyl-urea (monuron), is converted to 4-chloroaniline in cotton plants (Smith and Sheets, 1967) and by sunlight (Tang and Crosby, 1969).

Low yields of 3-chloroaniline have also been obtained by the action of soil microorganisms on isopropyl-N-(3-chlorophenyl) carbamate (Kaufman and Kearney, 1965). The formamidinetype acaricide, N'-(4-chloro-*o*-tolyl)-N,N-dimethylformamidin (chlorphenamidin) is converted to 4-chloro-2-methylaniline on apple leaves (Sen Gupta and Knowles, 1969). Hydrolysis of chlorphenamidin to 4-chloro-2-methylaniline in neutral solution also occurs.

Recently, Plimmer and Kearney (1969) photolyzed 3,4-dichloroaniline to 3,3',4,4'-tetrachloroazobenzene (I) in benzene solution with the aid of the photosensitizer, benzophenone. Because some azobenzenes are known carcinogens (Weisburger and Weisburger, 1966), it was decided to extend Plimmer's investigations under more natural conditions—sunlight, aqueous solution, and riboflavin-5'-phosphate, sodium (FMN) sensitizer.

## EXPERIMENTAL

**Materials.** 3,3',4,4'-Tetrachloroazobenzene and 4,4'-dichloroazobenzene were obtained from Richard Bartha, Rutgers University, New Brunswick, N.J. 4,4'-Dichloro-2,2'-dimethylazobenzene was supplied by Ciba Agrochemical Co. Copper bronze, grade MD 201, was purchased from Alcan Metal Powders, Elizabeth, N.J. 3,4-Dichloroaniline, 4-chloroaniline, 4-chloro-2-methylaniline, and 2-chlorobenzoic acid were purchased from Aldrich Chemical Co., Milwaukee, Wis. The first two of these materials were recrystallized from petroleum ether (30 to 60° C) and hexane, respectively. The third material was purified according to Knowles and Sen Gupta (1969), and the fourth was used as received.

**Irradiation Conditions.** Aqueous solutions of 1–2 mmol/l. of 3,4-dichloroaniline, 4-chloroaniline, or 4-chloro-2-methylaniline containing either no sensitizer or 0.01 to 2 mmol/l. FMN were exposed to sunlight for 5 hr in stoppered borosilicate glass flasks. Solutions of these materials were also exposed to a Duro-Test Corp. 20-watt Vitalite fluorescent lamp for 5 hr in a reaction chamber similar to one used by Tang and Crosby (1969). The Vitalite lamp is claimed by the manufacturer to approximate sunlight in spectral characteristics and intensity.

**Isolation of Reaction Products.** The photolyzed chloroaniline solutions were extracted twice with a total of half their volume ethyl acetate. The combined ethyl acetate layers were then extracted with 2N hydrochloric acid to remove the chlorinated aniline, washed with water, dried over sodium sulfate, and concentrated. The concentrates were then separated on 750- $\mu$  silica gel G plates using benzene as eluent. This treatment resulted in separation of at least eight variously colored bands in the case of solutions photolyzed in the presence of FMN. Because we were primarily interested in the

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Table I.  $R_f$  Values of Materials

	Benzene	Hexane-Benzene (70:30)
I	0.84	0.71
II	0.81	0.44
III	0.81	0.63
IV	0.63	0.15
V	0.84	0.74
VI	0.78	0.30

azobenzene derivatives, only the bright yellow band was removed from the plate in each case. The yellow material was then eluted on 750- $\mu$  silica gel G plates with a solution of hexane and benzene (70:30). This treatment resulted in the separation of two bright-yellow bands. The faster moving yellow bands in each case turned out to be the azobenzene derivative, while the slower moving bands were the corresponding anilinoazobenzenes. The  $R_f$  values for these materials in both solvent systems are tabulated in Table I.

**Synthesis of 4-Chloro-4'-(4-chloroanilino)azobenzene (IV).** This material was prepared by the reaction of 4-chlorobenzene diazonium chloride with 4-chlorodiphenylamine in a manner completely analogous to Torrey and MacPherson's (1909) procedure for the synthesis of 4-anilinoazobenzene. After recrystallization from a solution of hexane and benzene (10:1) a 75% yield of IV, m.p. 125-7° C, was obtained. 4-Chlorodiphenylamine was prepared in 11% yield from 4-chloroaniline and potassium 2-chlorobenzoate according to Ullmann (1907) except that activated (Kleiderer and Adams, 1933) copper bronze was substituted for copper powder. The material was recrystallized from petroleum ether (30 to 60° C) and melted at 72-3° C.

#### RESULTS AND DISCUSSION

Exposure of an aqueous solution of 3,4-dichloroaniline to sunlight for 5 hr resulted in very little change. In the presence of FMN, however, several brightly-colored materials were readily formed. Two of these materials were identified as 3,3',4,4'-tetrachloroazobenzene (I) (by infrared spectroscopy) and 4-(3,4-dichloroanilino)-3,3',4'-trichloroazobenzene (II). The latter material exhibited a mass spectrum with a parent ion at  $m/e$  443 with isotope abundance (Beynon, 1960) indicating five chlorine atoms. Other prominent peaks at  $m/e$  298 (loss of  $C_6H_3Cl_2$ ), 270 (loss of  $C_6H_3Cl_2$  and nitrogen) 173 (loss of trichlorodiphenylamine) and 145 (subsequent loss of nitrogen) were in accord with the proposed structure. The base peak appeared at  $m/e$  270. The intensities, expressed as a percentage of the intensity of the base peak, were 55, 9, 9, and 34% for  $m/e$  443, 298, 173, and 145, respectively. Further support for the proposed structure of II was obtained from its infrared spectrum which had -NH absorption at 3450  $cm^{-1}$  and unsymmetrical arylazo absorption (Colthup, 1964) at 1411  $cm^{-1}$ . In the visible region, II had an absorption maximum at 4080 Å in methanol. The spectral data cannot definitely rule out the alternate possibility, 3-(3,4-dichloroanilino)-3',4,4'-trichloroazobenzene. However, formation of the latter is less likely than formation of II on the basis of resonance theory. An interesting property of II is that it did not pass through a 1/4-in., 2-ft glass column containing 5% DC-200 on Gas Chrom Q, even at 210° C. It is the latter property of II (in addition to its property of co-chromatography with I when eluted with benzene) which has contributed to its success in escaping detection in several previous investigations. Recently, however, Linke (1969)

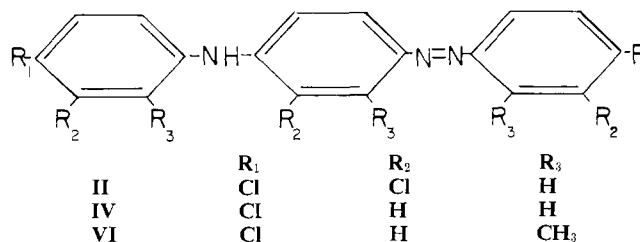


Figure 1

isolated II from soil incubated for 4 weeks with 500 ppm of propanil. In addition, Linke obtained material which had the same infrared spectrum as II and melted at 147-9° C by the action of peroxidase on 3,4-dichloroaniline.

Photolysis of 4-chloroaniline and 4-chloro-2-methylaniline gave products analogous to those of 3,4-dichloroaniline. The first material gave 4,4'-dichloroazobenzene (III) and 4-chloro-4'-(4-chloroanilino)-azobenzene (IV); the second material, 4,4'-dichloro-2,2'-dimethylazobenzene (V) and 4-chloro-4'-(4-chloro-2-methylanilino)-2,2'-dimethylazobenzene (VI). The symmetrical azobenzenes, III and V, were positively identified by comparison of their infrared spectra to those of the authentic materials. The anilinoazobenzenes, IV and VI, had mass, infrared, and visible spectra in accord with II. The structure of IV was further confirmed by its synthesis from 4-chlorobenzene diazonium chloride and 4-chlorodiphenylamine.

It is anticipated that there may be some question as to the validity of studying the photolysis of pesticides and their metabolites in the presence of photosensitizers. The authors feel that in order to determine what photoconversions are possible in the environment, it is even more invalid to ignore photosensitization. Chemicals in the environment obviously do not exist in isolation. Translocation through plants or dispersion in aqueous media that contain microorganisms enhance the possibilities of contact with photosensitizers such as the flavins and chlorophylls. A recent report (Ivie and Casida, 1970) that the rate of cyclohexene photoisomerizations is enhanced by the naturally-occurring photosensitizer, rotenone, lends support to the importance of considering sensitized photolyses in the environment.

The results obtained in the present study are obviously preliminary. The important questions to be answered are whether the laboratory-produced photoproducts are actually present in the environment, whether they are persistent, and whether they are indeed hazardous. The entire problem of possible azobenzene and anilinoazobenzene residues in the environment is further complicated by the recent findings of Bordeleau *et al.* (1969) and Kearney *et al.* (1969), *i.e.*, formation of three (instead of two) azobenzenes in soil when two different chloroanilines are incubated together. Extending these results to the formation of anilinoazobenzenes, one can

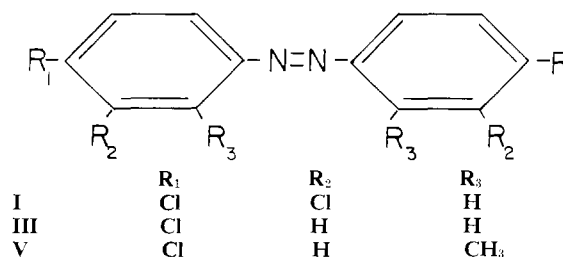


Figure 2

theoretically find eight (2<sup>3</sup>) different anilinoazobenzenes in addition to the three azobenzenes. If three chloroanilines are present, then one may find a mixture containing six different azobenzenes and 27 (3<sup>3</sup>) different anilinoazobenzenes.

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