Excretion of the intact parent material was found to be negligible. Repeated washings of the holding container after 3 hr exposure yielded less than 2% recovery. Similar results were observed by Wilkinson (1967) in his study of a series of 1,3-benzodioxole derivatives. Burt and Lord (1968) reported a 9% recovery of the penetrated amount of diazoxon after 2 hr from cockroaches topically treated with LD_{90} dose.

Analysis of the amounts of a toxicant that has reached exposed insects by spray or vapor requires a recovery of at least 90%. The elapsed time when 90% recovery is feasible (arbitrarily called tr_{90}) can be graphically estimated or calculated from the regression equations in Figure 5 using log 90. Tr_{90} for chlorpyrifos was 5 min and for endosulfan was 27 min. These insecticides change their native structure very rapidly in houseflies. The quantitation of their residues must take into consideration the elapsed time between application and sampling. Houseflies kept in Dry Ice or organic solvents such as acetone or hexane showed minimal enzymatic loss of insecticide. The data on the disappearance rates were used as guidelines for sampling times in the study of the dose toxicity of chlorpyrifos and endosulfan insecticides (Himel and Uk, 1971).

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Photochemistry of Bioactive Compounds. Photolysis of *m*-(*N*,*N*-Dimethylformamidine)phenyl *N*-Methylcarbamate Hydrochloride in Water

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The photolysis (λ >286 nm) of *m*-(*N*,*N*-dimethylformamidine)phenyl *N*-methylcarbamate hydrochloride (**I**) was carried out in water at pH 3.1 and 7.1 at a concentration of 250 ppm. The photoproducts, after they were isolated and purified by two-dimensional tlc, were identified as *m*-formamidophenol (**VI**) (~60%), *m*-aminophenyl *N*-methylcarbamate (**IV**) (~25%), *m*-formamidophenyl *N*-methylcarbamate (**III**) (~10%), and *m*-hydroxyphenyl *N*-methylcarbamate (**VIII**) (~5%) by comparison of their infrared and mass spectra with their respective authentic samples.

The new pesticide *m*-(*N*,*N*-dimethylformamidine)phenyl *N*-methylcarbamate hydrochloride (**I**) has a broad spectrum of activity against mites, and apparently will gain widespread large-scale application (Jenny, 1971). Carbamate insecticides and their photoproducts were reported to be potent cholinesterase inhibitors (Abdel-Wahab and Casida, 1967; Crosby *et al.*, 1965). Recent studies on the metabolism of **I** by orange seedlings revealed the conversion of **I** to *m*-(*N*-methylformamidine)phenyl *N*-methylcarbamate (**II**), *m*-formamidophenyl *N*-methylcarbamate (**III**), *m*-aminophenyl *N*-methylcarbamate (**IV**), *m*-(*N*,*N*-dimethylformamidine) phenol (**V**), *m*-formamidophenol (**VI**), *m*-aminophenol (**VII**), and possibly the glucosides of **I**, **III**, **VI**, and **VII** (Knowles, 1970). The metabolism of **I** by rats and rat liver homogenates (Knowles and Sen Gupta, 1970; Knowles, 1970) have also been reported. The major products were the same as those produced by orange seedlings.

Irradiation of **I** with uv (254 nm) and fluorescent light, and the "dark" reaction of **I** on silica gel chromatoplates all gave products identified as **I**, **II**, **III**, **IV**, **V**, **VI**, **VII** and unidentified products at the origin, after the chromatoplates were developed in methylene chloride–benzene–diethylamine (Knowles, 1971). In all cases, the major decomposition product was **VI**.

Hydrolysis of **I** at the carbamate and the amidine groups apparently proceeded easily in soil. At pH 9, 50% reaction was reached in 100 min (Jenny, 1971). Photocatalyzed hydrolysis of carbamates (Pape *et al.*, 1970) and amidines (Su and Zabik, 1972) were reported to occur readily.

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In order that our studies may be more relevant to *in situ* environmental conditions, compound **I** was photolyzed at $\lambda > 286$ nm in distilled water and in "natural" water obtained from the Red Cedar River on the campus of Michigan State University.

MATERIALS AND METHODS

***m*-(*N*,*N*-Dimethylformamidine)phenyl *N*-Methylcarbamate Hydrochloride (I).** Analytical grade compound **I** was obtained from NOR-AM Agricultural Products, Inc., Woodstock, Ill. The compound always appeared as a long streak on tlc plates irrespective of solvent polarity. Two-dimensional tlc indicated the compound to be homogeneous. Ir (potassium bromide pellet), nmr (deuterated water), uv spectroscopy (methanol), and mass spectrometry (direct probe, 70 eV ionizing voltage) all gave spectra consistent with compound **I**. It was used without further purification.

Irradiation. Typically, 1 g of pesticide **I** was dissolved in 4 l. of water (1.5×10^{-3} *M* or 250 ppm) in a 5-l. round-bottomed flask, and the reaction solution was stirred throughout the reaction. Immersed in the flask was a water-cooled 450-W high-pressure mercury lamp. The emission intensity at 3.8 cm from the lamp (the average sample distance from lamp), as measured by a YSI-Kettering Model 65 radiometer, was 2×10^5 ergs/cm^2-sec. The lamp was enclosed in a Pyrex tube which filtered out wavelengths below 286 nm. The radiated energy above λ 286 nm was approximately 83% of the total emitted energy of the lamp. As a reference, the sun's intensity in Cincinnati, Ohio, at noon on a clear day averages 8×10^4 ergs/cm^2-sec (Nadar and White, 1969).

Compound **I**, a hydrochloride salt, was completely soluble in distilled water and lowered the pH of the reaction solution to 3.1. The "natural" water from the Red Cedar River at the intersection of Farm Lane on the campus of Michigan State University has a pH of 7.9; but with 250 ppm of **I** dissolved in it, the pH became 7.1. The photolyses were carried out at these pH's.

After 4 days of irradiation, the water was removed by vacuum evaporation at room temperature.

Control "dark reactions" at pH 3.1 lasting 4 days and a half-hour photolysis of **I** were subjected to the same procedures, and they showed no discernible reaction.

Thin-Layer Chromatography. Brinkmann silica gel F-254, 0.25-mm thick, 20 × 20-cm chromatoplates (Brinkmann Instruments, Inc., Westbury, N.Y.) were utilized for detection of the number of components present in photoproducts, and for ascertaining sample purity. Uniplate silica gel G, 0.25 mm thick, 20 × 20 cm chromatoplates (Analtech, Inc., Wilmington, Del.) were employed as preparative plates for separation and isolation of photoproducts. The tlc behavior of all the compounds studied was identical for these two kinds of plates.

Because compound **I** is a hydrochloride salt, and since its hydrolysis is base-catalyzed (Jenny, 1971), the tlc plates were developed in nonbasic solvents. For best results, compound **I** and its photoproducts were developed two-dimensionally. The first solvent system consists of ethanol–chloroform–acetone–benzene (42:38:12:8, v/v) (system A), and the second being ethanol–chloroform–cyclohexane–acetone–benzene (33:30:10:10:7, v/v) (system B). Four components were clearly discernible after the product mixture was thus chromatographed.

Separation and Purification. The photoproducts were separated and isolated by preparative tlc using solvent systems A and B. Each of the four components were subsequently rechromatographed two-dimensionally. The solvent systems were benzene–ethylacetate (60:40, v/v) for the first dimension, and cyclohexane–chloroform–ethanol (60:30:10, v/v) for the second dimension.

Mass Spectrometry. A duPont Model 21-490 mass spectrometer (duPont Co., Instrument Division, Monrovia, Calif.) was used for product analysis and identification. Samples were analyzed by direct introduction with probe and source temperatures of 180–200°C, and ionizing voltage of 70 eV.

Product Identification. Mass spectrometry and infrared spectroscopy were the principle tools employed for product analyses. These techniques confirmed the integrity of the tlc isolation procedures.

Synthesis of *m*-Hydroxyphenyl *N*-Methylcarbamate (VIII). The synthesis of compound **VIII** by reaction of resorcinol and methylisocyanate has been reported (Balba and Casida, 1968). Our procedure was as follows. To 0.1 mol of resorcinol in 10 ml of anhydrous diethyl ether was added dropwise 0.1 mol of methylisocyanate. The reaction mixture was thoroughly agitated until homogeneous, and allowed to stand for 48 hr. The products were a mixture of mono- and dicarbamates. Compound **VIII**, the noncarbamate, was isolated by passing the products through a silicic acid (100 mesh) column with ether as eluant.

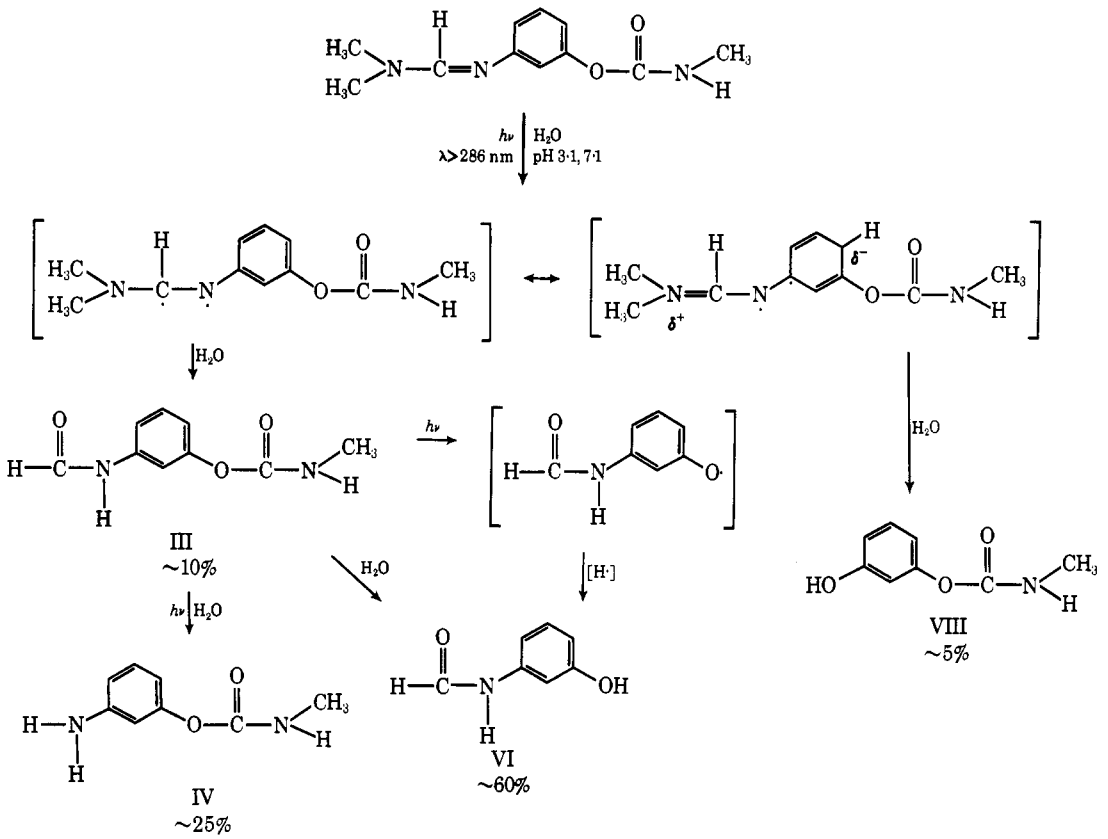
RESULTS AND DISCUSSION

Irradiation at $\lambda > 286$ nm of an aqueous solution of **I** (250 ppm) was found to yield **III**, mp 95°C, (~10%); **IV**, mp 180°C, (~25%); **VI**, mp 105°C, (~60%); and *m*-hydroxyphenyl *N*-methylcarbamate (**VIII**), mp 88°C (~5%). All melting points are uncorrected. The isolation and purification procedures employed permitted only estimated yields. No obvious difference was observed in yields or reaction products between reactions run in distilled water and "natural" water.

The photoproducts were analyzed by mass spectrometry and infrared spectroscopy. The mass spectra of compounds **III**, **IV**, **VI**, and **VIII** showed molecular ion peaks at *m/e* 194, 166, 137, and 167, respectively. Their mass spectral fragmentation patterns were consistent with their structures, and were identical with their respective authentic samples. Compounds **III**, **IV**, and **VIII** exhibited fragmentation patterns characteristic of carbamates (Budzikiewicz *et al.*, 1967) and, as expected, each showed a strong *m/e* 57 peak corresponding to the methylisocyanate fragment (Damico and Benson, 1965). Likewise, the ir spectra of the photoproducts were identical with their respective authentic samples.

Based on product formation, the carbamate group was more stable than the amidine group in the molecule, and apparently quite stable toward hydrolysis under reaction conditions (~60% in 4 days). The major photoreaction in aqueous solution of the amidine group was its conversion to the formamide group (Su and Zabik, 1972). In this study, however, two additional reactions were observed for the amidine group: conversion to the amine and replacement with the hydroxyl group. To our knowledge, compound **VIII**, which apparently arose from the replacement of the amidine group with the hydroxyl group, has never before been observed in related studies of pesticide **I**.

Formally, the photoproducts may arise as in the following sequence. Other products arising from further reaction of



IV and VIII to their respective hydrolyl analogs have not been detected.

SUMMARY AND CONCLUSIONS

The photolysis of I in water gave four products, *viz.*, III, IV, VI, and VIII, in yields estimated at 10, 25, 60, and 5%, respectively. The reactions of I were carried out in distilled water and in "natural" water at wavelengths higher than 286 nm, which makes the study more relevant to its actual photochemical transformations in the environment. The major reactions are those expected from known reactions: the conversion of the amidine to the formamide (Su and Zabik, 1972), and the hydrolysis of the carbamate to the hydroxyl groups (Pape *et al.*, 1970). Probable reaction schemes that will account for the products have been suggested.

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