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Photochemistry of Bioactive Compounds. Photolysis of Arylamidine Derivatives in Water

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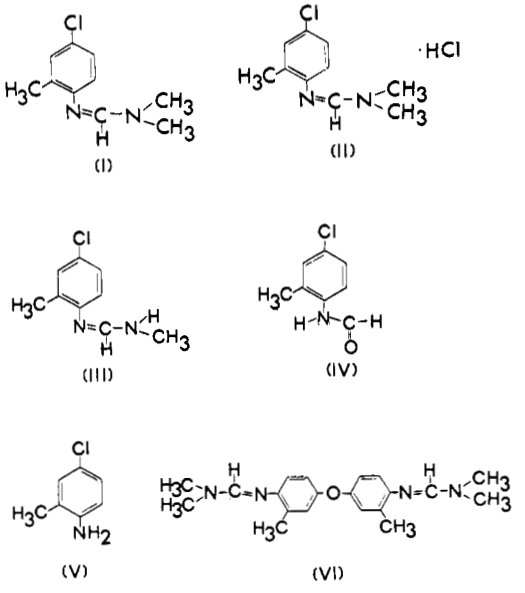
N'-(4-Chloro-*o*-tolyl)-*N*,*N*-dimethylformamidine (I) and its hydrochloride salt (II) were irradiated (λ >286 nm) in water at pH 7.1 and 3.1, respectively. Spectral and tlc analyses indicated reaction for I, but no reaction for II. The photoproducts for I were *N*-(4-chloro-*o*-tolyl)formamide (IV) (~95%) and bis-4-(*N*,*N*-dimethyl-*N'*-*o*-tolylformamidine) ether (VI) (~5%). Infrared and mass spectral data for VI are presented. Formal mechanisms for reactions giving rise to these products have been proposed.

The new pesticide *N'*-(4-chloro-*o*-tolyl)-*N*,*N*-dimethylformamidine (I) and its hydrochloride salt (II) both have effective action against mites (Dittrich, 1966, 1967) and insects (Jenny, 1971). Experiments on the metabolism of I by apple seedlings (Sen Gupta and Knowles, 1969) revealed conversion of I to *N*-methyl-*N'*-(4-chloro-*o*-tolyl)formamidine (III), *N*-(4-chloro-*o*-tolyl)formamide (IV), 4-chloro-*o*-touluidine (V), and possibly the glucoside *N*-(4-chloro-*o*-tolyl)-D-glucosylamine. Photolyses (254 nm, 364 nm, and sunlight) of I on silica gel chromatoplates and in ethanol solution (Knowles and Sen Gupta, 1969) were reported to yield I, III, IV, V (IV being the major product), plus several unidentified compounds. The authors also observed the hydrolysis of I on silica gel chromatoplate in the dark to yield IV. These investigators employed the solvent system diethylamine–benzene (5:95 v/v) for developing thin-layer chromatoplates. In our study the control "dark reaction" of I and II showed no detectable reaction in water. The tlc solvent system in this case was the less basic ethanol–benzene–chloroform (20:20:60 v/v).

We now report the photolyses (λ >286 nm) of I and II in distilled water at pH 7.1 and 3.1, respectively, and in "natural water" (pH 7.9) obtained from the Red Cedar River at the intersection of Farm Lane on the campus of Michigan State University, East Lansing, Mich. A previously unreported photoproduct of I has been isolated and characterized by detailed analysis of the ms and ir spectra.



MATERIALS AND METHODS

***N'*-(4-Chloro-*o*-tolyl)-*N*,*N*-dimethylformamidine (I).** Compounds I (98.7% purity, Batch 0267/5444) and II (99.6% purity, Batch 2033-3) were obtained from NOR-AM Agricultural Products, Inc., Woodstock, Ill. Purification of I was achieved by sublimation at room temperature (~25°C) and 0.1 Torr. The sublimed material was shown to be pure by tlc and glpc. The hydrochloride salt II was pure as determined by tlc, and was used without further purification.

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Ir (potassium bromide pellet), nmr (deuterochloroform), uv (methanol), and ms (direct probe and glpc–ms combination, 70 eV ionizing voltage) all gave the expected spectra.

Thin-Layer Chromatography. Brinkmann silica gel F-254, 0.25 mm thick, 5 × 20 cm chromatoplates (Brinkmann Instruments, Inc., Westbury, N.Y.). were employed for ascertaining sample purity. Uniplate silica gel G, 0.25 mm thick, 20 × 20 cm chromatoplates (Analtech, Inc., Wilmington, Del.) were utilized as preparative plates for separation and isolation of photoproducts. These two kinds of plates gave identical R_f's for all of the compounds studied. The solvent system was ethanol–benzene–chloroform (20:20:60 v/v). Other investigators (Geissbühler and Gross, 1965; Knowles and Sen Gupta, 1969) have used benzene–diethylamine (95:5 v/v). Both solvent systems gave good separation of the photolyzate mixture. However, to minimize the possibility of reaction on the tlc plates, especially in view of the fact that the hydrochloride salt II was being studied, the less basic solvent system was selected.

Gas Chromatography. A Varian Aerograph Series 1400 gas chromatograph (Varian Associates, Palo Alto, Calif.) equipped with a H_2-flame detector was used. The column was stainless steel $^1/_8$-in. i.d. × 6-ft, packed with 6% OV-1 liquid phase on 80/100 mesh Gas Chrom Q (Applied Science Lab., Inc., State College, Pa.). All analyses were carried out isothermally at 200°C column temperature, with a column flow rate of 40 ml/min prepurified helium.

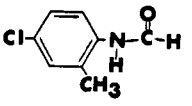
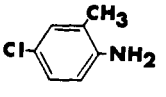
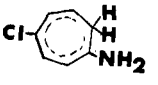
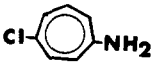
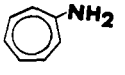
Mass Spectrometry. A Du Pont Model 21-490 mass spectrometer (Du Pont Co., Instrument Division, Monrovia, Calif.) was used. Samples were analyzed at 180–200°C probe and source temperatures, and 70 eV ionizing voltage. The mass spectrometer is connected by a jet separation interface to a Varian Aerograph Series 1400 gas chromatograph described above, for glpc–ms analyses.

Irradiation. Typically, 1 g of pure finely divided pesticide was mixed in 4 l. of water (~1.5×10^{-3} *M* or 250 ppm) in a 5-l. round-bottomed flask. Immersed in the flask was a water-cooled 450-W high pressure mercury lamp. The emission intensity at 3.8 cm of the lamp (the average distance the samples were from the lamp), as measured by a YSI-Kettering Model 65 radiometer, was 2×10^5 ergs/cm²-sec. The lamp was enclosed in a Pyrex tube which filtered out wavelengths below 286 nm. The radiated energy above λ 286 nm was ~83% and that for 286 > λ > 366 nm was ~31% 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/cm²-sec (Nader and White, 1969).

Compound I is only slightly soluble in water and was photolyzed as a heterogeneous suspension at pH 7.1 in the case of distilled water and 7.9 for "natural water." The hydrochloride salt II, however, was completely soluble in distilled water, and lowered the pH of the reaction solution to 3.1. No attempt was made to adjust the pH to neutrality, since it was our intent to photolyze the acid salt directly.

The reaction mixtures were irradiated for from 4 to 12

Table I. Mass Spectral Fragments of Compound IV

m/e	Molecular formula	Suggested fragments, ⊕	Abundance, % of base peak
171		^{37}Cl of 169	24
169	C_8H_8ClNO		75
143		^{37}Cl of 141	22
141	C_7H_8ClN	 or 	66
140	C_7H_7ClN		55
106	C_7H_8N		100

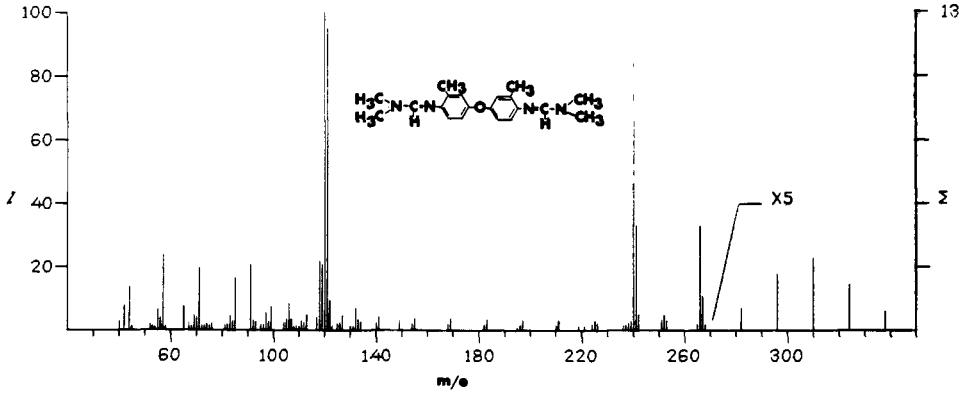
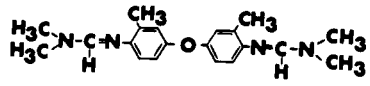
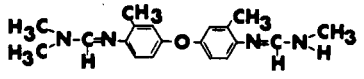
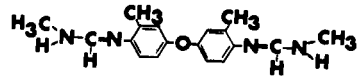
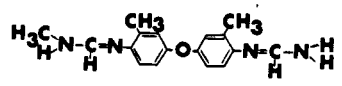
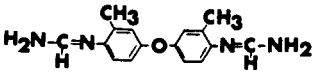
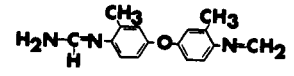
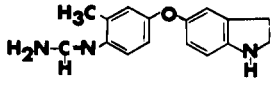
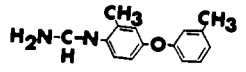
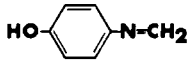
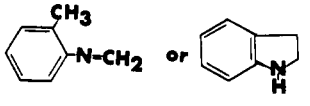


Figure 1. Mass spectrum of Compound VI

Table II. Mass Spectral Fragments of Compound VI

m/e	Molecular formula	Suggested fragments, ⊕	Abundance, % of base peak
338	$C_{20}H_{26}N_4O$		1·2
324	$C_{19}H_{24}N_4O$		2·9
310	$C_{18}H_{22}N_4O$		4·6
296	$C_{17}H_{20}N_4O$		3·6
282	$C_{16}H_{18}N_4O$		1·4
267	$C_{16}H_{17}N_3O$	 or 	11
266		267 - H	36
240	$C_{15}H_{16}N_2O$		90
121	C_7H_7NO		95
120		120 - H	100
119	C_8H_9N		21
118		119 - H	22

days at room temperature (~25°C) with constant stirring. Between 4 and 12 days, there was no detectable difference in percent reaction or product ratio as a function of time.

Aliquots of 500 ml of the reaction products of I were extracted twice each with 50 ml of benzene. The benzene fractions were combined, dried with anhydrous magnesium sulfate, and vacuum evaporated at room temperature. The dried products weighed 0.85 g or ~100% of the theoretical yield based on the nonvolatile products IV and VI.

After irradiation of II, the reaction mixture was recovered simply by vacuum evaporation. No products other than the starting material were detected.

Control "dark reactions," and a 0.5-hr photolysis of I were subjected to the same procedures, but showed no reaction.

Separation and Purification. After it had been ascertained by tlc that there were at least three components, R_f's 0.74, 0.61, and 0 in the photolyzate of I, 0.3 g of the mixture was chromatographed on a preparative silica gel G plate. The separated products were extracted from the silica gel with methanol, and each was rechromatographed in the same solvent system. Another solvent system, benzene–diethylamine (95:5 v/v) was used to verify the uniformity of the isolated products.

Product Identification. Mass spectrometry and ir were the principle tools employed for product analyses. These spectral techniques confirmed the integrity of the tlc isolations procedures.

RESULTS AND DISCUSSION

The identified photoproducts of I for both distilled water and "natural water" were IV (R_f 0.61) and VI (R_f 0.74) with respective yields estimated at approximately 95 and 5% of the total residue. Unidentified product(s) (R_f 0) were estimated at less than 1%. No detectable reaction was observed for the control "dark reaction" under the same conditions. There was no apparent difference in percent reaction or product ratio, regardless of whether I was photolyzed for 4, 8, or 12 days.

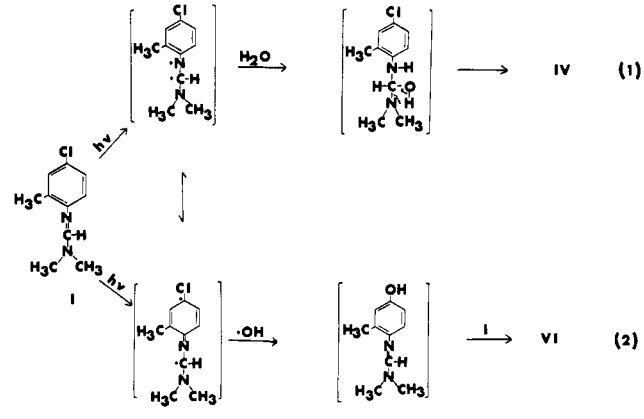
The hydrochloride salt II showed no detectable reaction even after 12 days of irradiation. The tlc behavior and ir spectrum of the photolyzate and the starting material were identical.

The uv spectrum of II was different than that of I. In the 330–350 nm region, I has a significant extinction coefficient (*e.g.*, ϵ_{340} 106). In the same wavelength region, II has virtually no absorption (*e.g.*, ϵ_{340} ~1). This should be the reason that II is unreactive under our reaction conditions.

The mass spectrum of photoproduct IV has a molecular ion at *m/e* 169 and was found to be identical to that of an authentic sample of *N*-(4-chloro-*o*-tolyl)formamide. The major mass spectral fragments are given in Table I. Comparison of their ir spectra again showed them to be the same compound.

The highest mass fragment of VI was at *m/e* 338, which corresponds to the molecular weight of VI. No M + 2, characteristic of the ^{37}Cl isotope was present (Figure 1). The major fragments are listed in Table II. The ir spectrum (Figure 2) showed no carbonyl absorption, but did show a peak at 1245 cm^{-1} which is characteristic of aromatic ethers.

Equations 1 and 2 represent probable reaction schemes that will give rise to the observed products. Formation of ethers when irradiated in like manner have been reported (Pape and Zabik, 1970).



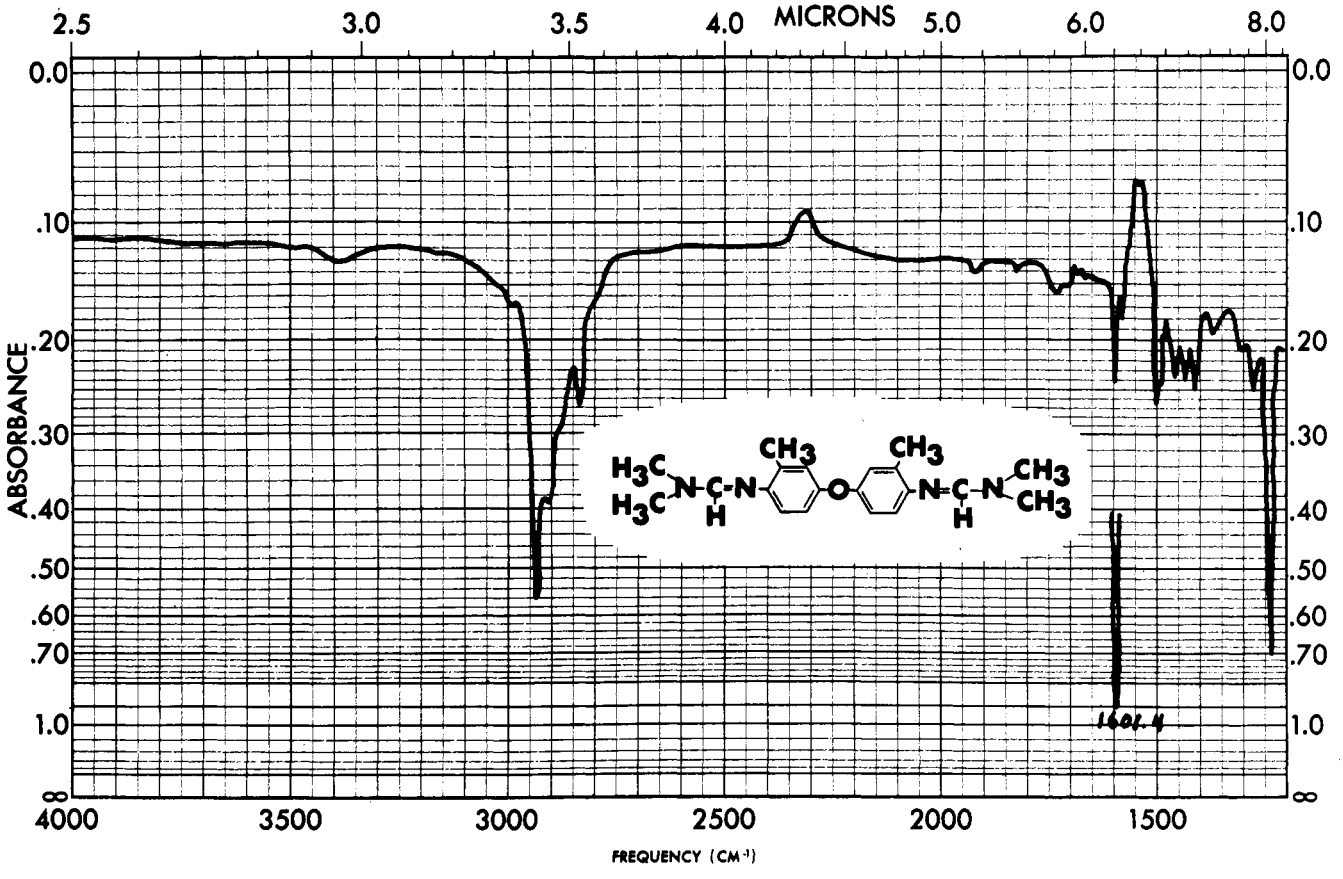


Figure 2. Infrared spectrum of Compound VI

SUMMARY AND CONCLUSIONS

Photolyses of compounds I and II were carried out in water in a manner similar to that in the environment. The photoproducts identified were IV (95%) and VI (5%). Compound VI, never before reported in photochemical studies, has been characterized by detailed analyses of mass spectral fragmentation patterns and infrared spectroscopy.

The practical significance of this study lies in the widespread large-scale use of these pesticides in the United States. We believe this study is an important step toward understanding the photochemical fate of these compounds in the environment.

ACKNOWLEDGMENT

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