Photolysis of 3-(p-Chlorophenyl)-1,1-dimethylurea (Monuron) and 3-Phenyl-1,1-dimethylurea (Fenuron)

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The herbicide 3-(p-chlorophenyl)-1,1-dimethylurea (monuron) was photolyzed under anaerobic conditions in methanol and was found to react cleanly to form the dechlorinated herbicide 3-phenyl-1,1-dimethylurea (fenuron). Methyl p-chlorophenylcarbamate was obtained as a minor product.

Photolysis of 3-phenyl-1,1-dimethylurea (fenuron) afforded aniline, o-amino-N,N-dimethylbenzamide, and p-amino-N,N-dimethylbenzamide. All products were isolated and identified by comparison with authentic materials.

The photodecomposition of herbicides has received much attention recently (Plimmer, 1971; Crosby and Li, 1969). Most of these studies have been carried out in the laboratory under conditions designed to approximate those found in the field, i.e., they were carried out with ultraviolet light sources in water solution in the presence of oxygen. Such a study of the photodecomposition of monuron (Crosby and Tang, 1969) showed that a mixture of products was formed but, exceptionally, the hydration product 1-(p-hydroxyphenyl)-3,3-dimethylurea was absent. In a similar investigation (Rosen et al., 1969), however, this product was obtained. Since many of the products isolated and identified in these studies were obviously the result of photooxidation, we decided to reinvestigate the photochemistry of monuron in the absence of oxygen. Although these conditions are not comparable to those found in the field, we hoped that this simplification might result in some clarification of the photochemical processes involved.

EXPERIMENTAL

Methods. Infrared spectra were measured on a Perkin-Elmer 337 spectrophotometer; nmr spectra were measured on a Varian A-60 spectrometer in deuteriochloroform.

Irradiations were carried out by placing the sample in a quartz tube sealed with a serum cap in the center of a circular bank of 10 GE-G15t^8 low pressure mercury lamps. The samples were purged with a stream of nitrogen and irradiated under a nitrogen atmosphere. Aliquots were removed from the photolysis sample during the reaction via a hypodermic syringe.

A preparative scale reaction on I was run under a nitrogen atmosphere using a 450 W Hanovia type L medium pressure lamp in a quartz immersion well with a Vycor filter.

Glc analyses were carried out using a Varian Aerograph 1200 gas chromatograph with a flame ionization detector. Injector and detector were maintained at 220°. A 2 ft × $^1/_8$ in. column (A) packed with 20% UCON LB 1715 on Chromosorb W, 60-80 mesh, and a 6 ft × $^1/_8$ in. column (B) packed with 15% silicone DC550 on Chromosorb W, 80-100 mesh, were used.

Thin-layer chromatography was carried out on Brinkmann MN-Polygram silica gel G plates using ethyl acetate-hexane (5:1). Under these conditions I had R_f = 0.36, with each respective R_f for II = 0.36, III = 0.67, VI = 0.63,

VIII = 0.12, X = 0.22, and an unidentified material from I had R_f = 0.56.

Materials. 1,1-Dimethyl-3-phenylurea was prepared by the addition of an excess of dimethylamine to phenylisocyanate in chloroform. One recrystallization gave product mp 133–134° [Crosby and Niemann (1954), report 127.5–128°].

1,1-Dimethyl-3-(p-chlorophenyl)urea was prepared similarly from p-chlorophenyl isocyanate. One recrystallization from methanol gave product mp 173–174° [Todd (1953), reports 170.5–171.2°]. p-Amino-N,N-dimethylbenzamide was prepared by the reduction of p-nitro-N,N-dimethylbenzamide with tin and hydrochloric acid according to the procedure of Vogel (1957). Recrystallization from ethyl acetate gave product mp 151–152.5° [Johnston et al. (1966), report 153°].

o-Amino-N,N-dimethylbenzamide was prepared from isatoic anhydride and dimethylamine. Recrystallization from xylene gave product mp 58–59° (Staiger and Miller, 1959).

Irradiation and Product Isolation. MONURON. A solution of monuron (9 g) in methanol (450 ml) was irradiated for a period of 84 hr. Solvent was evaporated from a 100-ml portion of the photolysate and the concentrate (15 ml) was diluted with 50 ml of ether. The ether solution was extracted with two 10-ml portions of 10% HCl. The acid extract was treated with cold 30% NaOH to pH 11 and filtered. The solid appeared to be (nmr) a mixture of fenuron and monuron. Extraction of the basic solution with ether gave a yellow solid on evaporation. Recrystallization from ether–hexane gave white crystals which were identified as fenuron.

The ether solution was evaporated and unreacted I was obtained by recrystallization of the residue from carbon tetrachloride. Addition of hexane to the mother liquors gave a second crop of brown crystals. Recrystallization of these from hexane gave white crystals, mp 114–116°, identical in all respects with authentic methyl p-chlorophenylcarbamate (III).

The photolysis solution gave a voluminous precipitate of silver chloride with silver nitrate.

The solution also gave a positive test for formaldehyde with carbazole–sulfuric acid.

QUANTITATIVE RUN. A 0.100 M solution (9.932 g in 500 ml) of I in methanol was irradiated and aliquots were removed at various times. Titration of 5-ml samples against 0.0198 N NaOH indicated that HCl was generated rapidly in the initial stages of the reaction but tailed off dramatically after about 40 hr of irradiation. Under these conditions 49.5% of the starting material was converted after 28 hr; 70.1% was converted after 49 hr.

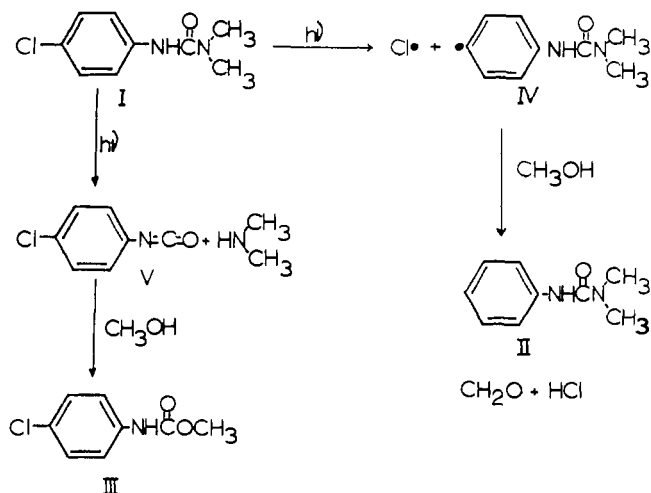Department of Chemistry, University of Maryland, College Park, Maryland 20742.

Figure 1. Photolysis of monuron

Figure 2. Photolysis of fenuron

A sample of the photolysate was treated with an equimolar amount of acetanilide, the solution was evaporated, and the nmr spectrum was obtained. The integral ratio of N–CH₃ (from I and II) to CH₃C peaks (of acetanilide) was 1.96 after 28 hr irradiation (theoretical = 2.0) but this value dropped to 1.52 after 75 hr, indicating that extensive secondary decomposition was taking place.

Nmr analysis of the photolysate indicated that urethane formation was a minor process (<5%).

FENURON. A solution of 10 g of II in 500 ml of absolute methanol was irradiated for a period of 13 days. Tlc indicated that some starting material still remained. Half of the reaction mixture was removed and concentrated in vacuo to ca. 20 ml, and 125 ml of ether was added. The clear solution was decanted and extracted with three 25-ml portions of 10% HCl. The acid extract was cooled in an ice bath, brought to pH 10 by the careful addition of 20% NaOH, and the precipitated solid was filtered. Tlc indicated that the solid and the ether solution consisted of starting material.

The aqueous filtrate was extracted with ether and the extract was concentrated to a brown liquid which was purified by preparative glc and identified as aniline (VI) by comparison of its ir and nmr spectra and glc retention time with those of an authentic sample.

The aqueous alkaline solution was further extracted with ethyl acetate and the dried extract was evaporated to a brown semisolid. The semisolid was crystallized from ethyl acetate–hexane to give a solid, mp 151–153°, after one recrystallization from benzene. The solid was identified as p-amino-N,N-dimethylbenzamide (X) by comparison of its ir, nmr, and uv spectra with those of an authentic sample.

The mother liquor from the above crystallization was evaporated and the residue was subjected to bulb-to-bulb distillation. The distillate (100°/1 mm) was recrystallized once from p-xylene to give white crystals, mp 56–58°, which were identified as o-amino-N,N-dimethylbenzamide (VIII) by comparison their ir, nmr, and uv spectra with those of an authentic sample.

A similar reaction was carried out in a sealed quartz tube in isoamyl alcohol. A sample of the gaseous phase was withdrawn into a gas infrared cell. The infrared spectrum clearly showed the characteristic bands of carbon monoxide at 2040 and 2010 cm⁻¹.

QUANTITATIVE RUN. A solution of fenuron (2.043 g), tetradecane (0.115 g), and hexadecane (0.0996 g) in methanol (100 ml) was irradiated in the usual manner. Samples were
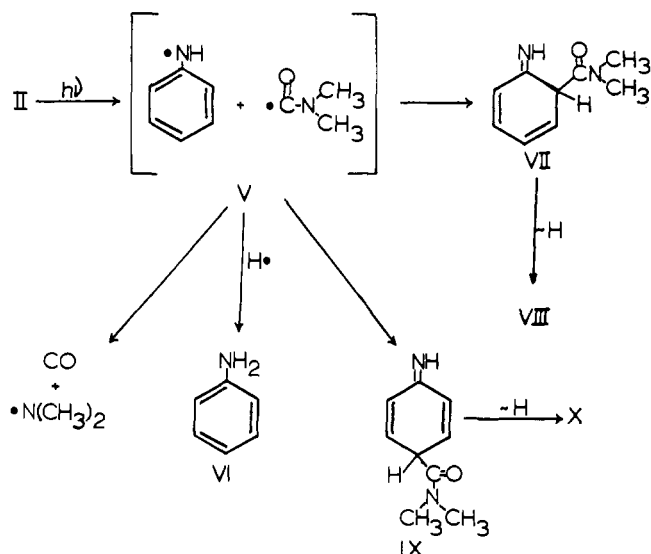
removed at various times and analyzed by glc. Aniline was determined vs. tetradecane using column A at 70°, while VIII and X were determined vs. hexadecane internal standard using column B at 180°. Application of the appropriate response factors gave product yields. The products increased essentially monotonically until after 162 hr; the yields of VI, VIII, and V were 13.3, 14.2, and 12.7%, respectively.

RESULTS AND DISCUSSION

The irradiation of monuron under nitrogen in methanol with 2537 Å light proceeded with the generation of hydrogen chloride as evidenced by a decrease in pH and a copious precipitate of silver chloride on treatment of the reaction mixture with silver nitrate solution. The major organic product was isolated and identified as 1-phenyl-3,3-dimethylurea. In addition, a minor product, methyl p-chlorophenyl carbamate (III), was also isolated. These results suggest the route outlined in Figure 1 for this reaction.

The formation of III via reaction of isocyanate V with solvent is analogous to the route proposed for the formation of 1,3-di-(p-chlorophenyl)urea and p-chloroaniline in aqueous solution by Crosby and Tang (1969).

The generation of the major product, II, clearly arises via intermediate radical IV, as in the case of the chlorobenzoic acids (Plimmer, 1971) and is the obvious precursor of 1-(p-hydroxyphenyl)-3,3-dimethylurea on photodecomposition of I in aqueous solution (Rosen et al., 1969). In fact, the photolysate gave a positive spot test for formaldehyde which would result from methanol acting as a hydrogen donor.

In order to obtain qualitative information on the efficiency of the dehalogenation process, we followed the generation of HCl by titration with standard sodium hydroxide. The reaction was initially quite rapid, but after ca. 50% conversion the rate of formation of hydrogen chloride decreased and the solution discolored, suggesting that I was no longer cleanly photolyzing to II (fenuron).

The decrease in the rate of disappearance of I is reasonable in view of the absorption spectra of I (247 nm, ε 1.92 × 10⁴) and II (240 nm, ε 1.86 × 10⁴). Thus, as II is formed, it efficiently competes with I for available light.

Since fenuron (II) is the major product from I, its photochemistry was investigated. Irradiation of II in methanol solution under nitrogen afforded three products: aniline (VI),

o-amino-N,N-dimethylbenzamide (VIII), and p-amino-N,N-dimethyl benzamide (X). The products are similar to those obtained from acetanilide (Elad et al., 1965; Rao and Lambreti, 1967), suggesting that the reaction takes place via a mechanism similar to that suggested for the photoanilide rearrangement (Figure 2). The initial formation of radical pair V would lead, via migration in a solvent cage, to VII and IX. Alternatively, hydrogen abstraction would account for aniline formation. Analysis of the gaseous product indicated that carbon monoxide was produced, in accord with expectations for the decomposition of an N,N-dimethylformyl radical.

An approximate comparison of the rates of photodegradation of I and II indicates that I reacts about four times as fast as II. Thus the photodegradation of II should not be an important process in irradiation of I.

Clearly then the initial process involved under these conditions is cleavage of a carbon–nitrogen bond in II to give the radical pair V. All stable photoproducts are due to subsequent reactions of these radicals.

In the case of I, by far the major process is cleavage of a carbon-chlorine bond followed by hydrogen abstraction from solvent to afford the reduced product fenuron (II). It has been shown in other cases (Kharasch and Sharma, 1966; Plimmer et al., 1970) that the presence of oxygen in photo-

degradation reactions strongly influences the nature of the products formed. The differences between the results reported here and those of the previous investigators are most logically ascribed to the presence of oxygen in those studies.

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Semiautomated Analysis of Granular Organophosphorus Pesticide Formulations

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The determination of Dasanit [O,O-diethyl O-[4-(methylsulfinyl)phenyl] phosphorothioate] and Di-Syston [O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate] in 10 and 15% clay granular formulations is now carried out on a semiautomated basis. The procedure involves an extraction of the granular samples with an acetic acid bromine mixture and subsequent colorimetric phosphorus determination using an AutoAnalyzer. The method produced significant savings in analytical time and decreased the precision standard deviation by about 50% over previous manual methods.

Dasanit (Bay 25141 or fensulfothion) [O,O-diethyl O-[4-(methylsulfinyl)phenyl] phosphorothioate] is a product of Farbenfabriken Bayer AG, licensed in the U. S. and Canada to Chemagro Division of Baychem Corp. It exhibits both insecticidal and nematicidal activity and its formulations are used to control parasitic, sedentary, and free-living nematodes. The most commonly used formulations are impregnated granules and a spray concentrate.

Di-Syston (thiodemeton or disulfoton) [O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate] is also a product of Farbenfabriken Bayer AG, licensed to Chemagro in the U.S. and Canada. It is a systemic insecticide and its formulations are used for control of sucking insects and mites on

plants. As with Dasanit, the most commonly used formulations are a spray concentrate and impregnated granules.

Granular formulations of both compounds are produced by a number of manufacturers under contract to Chemagro. This practice effects freight savings but produces severe demands on analytical control because of the many individual batches involved.

Prior to the 1968-1969 season, the active ingredient content of both Dasanit and Di-Syston granular production was monitored by use of conventional manual methods of analysis. These consisted of extracting the active ingredient, followed by acidimetric back-titration of hydrolyzed Di-Syston or reductimetric titration of Dasanit with titanous chloride. The thousands of samples resulting from a month's production imposed a severe burden on the analytical laboratory, since the analyst times required for Dasanit and Di-Syston were 45 and 40 min, respectively. Therefore a method more suitable for mass production of data was required.

During the 1968-1969 season, the present semiautomated

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