

Photolysis of Amiben (3-Amino-2,5-dichlorobenzoic Acid) and Its Methyl Ester

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The products of irradiation of amiben (3-amino-2,5-dichlorobenzoic acid) and its methyl ester have been investigated. Under conditions in which oxidation is prevented these compounds undergo selective loss of the 2-chloro substituent to give 3-

amino-5-chlorobenzoic acid and methyl 3-amino-5-chlorobenzoate, respectively. Irradiation of amiben in the presence of air or oxygen affords a complex mixture of oxidation products.

Rapid decomposition of the herbicide, amiben (3-amino-2,5-dichlorobenzoic acid) [1] by light has been reported (Plimmer, 1967; Sheets, 1963). A number of unidentified products were separated by chromatography. The identification of amiben photolysis products has been undertaken as part of a comprehensive study of the irradiation of chlorinated aromatic compounds. Investigations of the liquid phase photolysis of halogenated aromatic compounds have been reported previously (Szyclinski and Litwin, 1963; Walczak and Szyclinski, 1963; Wolf and Kharasch, 1965). The evidence for a free-radical mechanism for the photochemically induced reactions of aromatic iodo-compounds is supported by the observation that facile hydrogen transfer took place in hydrogen donor solvents and reductive deiodination occurred.

The rate of photolytic dechlorination of isomeric monochlorobenzoic acids in methanol has been determined by measurement of liberated Cl^- (Walczak and Szyclinski, 1963). This reaction and the photolysis of a number of polychlorinated aromatic compounds are being investigated in this laboratory to determine the influence of substituents on the course of the reaction. Elimination of chlorine from a polychlorinated aromatic compound occurs stepwise by the consecutive loss of single chlorine atoms, and it is therefore of interest to study the electronic and steric factors influencing the selective release.

EXPERIMENTAL

Amiben (3-amino-2,5-dichlorobenzoic acid) was greater than 98% pure and had m.p. 207.5–208.0° C. Methyl 3-amino-2,4-dichlorobenzoate had m.p. 56.5–57.0° C.,

and was shown to be homogeneous by gas chromatography.

Gas chromatography was carried out on a Research Specialties 600 Series instrument equipped with a hydrogen flame detector. The column used (glass 0.25 inch \times 6 feet) was packed with 5% SE 30 on Chromosorb W (60- to 80-mesh, acid washed, DMCS treated) and was operated at a temperature of 210° C.

The NMR spectra were obtained in CDCl_3 solution with TMS as internal standard on a Varian HA-100 spectrometer. Infrared spectra were obtained on a Perkin-Elmer 620 infrared spectrophotometer.

Thin layer chromatography was performed on silica-coated glass plates (20 \times 20 cm.) by using the solvent systems specified. Compounds were detected by exposure to iodine or visualization by ultraviolet light. Column chromatography was carried out using silica-gel (E. Merck A. G., 0.05 to 0.20 mm. as purchased). Solvents were distilled before use in irradiation experiments.

The light-source used was a 450-watt Hanovia quartz mercury vapor lamp (Hanovia Catalog No. 679-A-36) housed in a water-cooled, double-walled quartz immersion well, immersed in the solution to be irradiated contained in a vessel fitted with a standard joint and equipped with a side arm for withdrawal of samples.

Irradiation of Methyl 3-Amino-2,5-dichlorobenzoate and 3-Amino-2,5-dichlorobenzoic Acid. Methyl 3-amino-2,5-dichlorobenzoate (0.50 gram) was irradiated for 2 hours in methanol (1 liter). A borosilicate glass filter sleeve was used to exclude radiation of wavelength less than 2800 Å. Nitrogen was bubbled through the solution. The volume of the solution was reduced and the crude product (0.51 gram) obtained by chromatography on a silica column eluting with 20% ether in benzene. The solid was converted to the N-acetyl derivative (0.57 gram) which was crystallized twice from benzene to give pure methyl 3-acetamido-5-chlorobenzoate, m.p. 143–143.5° C.

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Analysis: Calculated for $C_{10}H_{10}NO_3Cl$: (227.6) C, 52.76; H, 4.43; N, 6.15; Cl, 15.57%. Found: C, 53.00; H, 4.35; N, 6.19; Cl, 15.59%.

The infrared spectrum (KBr disk) showed the expected absorption bands for N-acetyl and ester groups.

The NMR spectrum was consistent with the above structure.

This compound was also obtained by irradiation of 3-amino-2,5-dichlorobenzoic acid (0.70 gram) in water (4 liters) containing sodium bisulfite (1 gram) for 9 hours as previously described. The yellow solution was evaporated to dryness to afford a crude solid which was converted to the N-acetyl derivative. The crude N-acetyl derivative (0.35 gram) was methylated and purified by chromatography on a silica column eluting with a mixture of benzene and ethyl acetate (4 to 1). The purity of the solid obtained as major product was confirmed by gas chromatography. The retention time (8 minutes) was the same as that of methyl 3-acetamido-5-chlorobenzoate described in the previous section. The infrared spectra of the two compounds were identical and there was no depression of melting point on admixture.

In a subsequent experiment the yield of the irradiation product of 3-amino-2,5-dichlorobenzoic acid (0.217 gram) in water (1 liter) containing sodium bisulfite was obtained by gas chromatography following conversion to methyl 3-acetamido-5-chlorobenzoate. The photolysis product contained 31% of the theoretical amount of this compound. A small peak due to a compound with the same retention time as the methyl ester of *m*-acetamidobenzoic acid was also present.

An 82% yield of methyl 3-acetamido-5-chlorobenzoate was obtained by irradiation for 1 hour (and subsequent acetylation) of methyl 3-amino-2,5-dichlorobenzoate (0.50 gram) in methanol (1 liter). Less than 1% of the starting material remained after 1 hour of irradiation.

Irradiation of 3-Amino-2,5-dichlorobenzoic Acid in Water Alone. 3-Amino-2,5-dichlorobenzoic acid was dissolved in water and irradiated. A range of concentrations from 2 to 4 grams per liter was used and irradiation at wavelengths greater than 2800 Å. was carried out for periods of 2 to 20 hours. The solution rapidly became brown in color. Products were separated by thin-layer chromatography on silica coated plates in the solvent system: ammonia-methanol-ethanol-isopropanol (10:20:25:45). A large number of spots were visible, both fluorescent and absorbing, when the developed plate was viewed in ultraviolet light. The presence of free chloride ion in the solution was demonstrated by the color developed by mercuric thiocyanate-ferrous iron reagent (Iwasaki *et al.*, 1952). An infrared spectrum of the residue obtained by evaporating a solution irradiated for 1 hour showed major changes in absorption in the $-\text{NH}_2$ stretching region. The identity of these products has not been fully established but studies of the photochemistry of amiben and some of its derivatives are continuing.

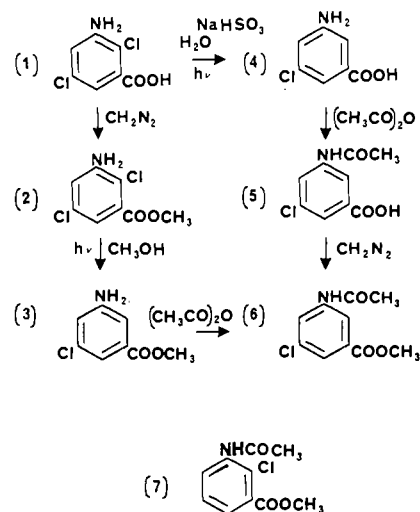
RESULTS AND DISCUSSION

Methyl 3-amino-2,5-dichlorobenzoate [2] and 3-amino-2,5-dichlorobenzoic acid [1] on photolysis react predominantly by loss of the 2-chloro substituent. The

reductive loss of chlorine from *o*-chlorobenzoic acid in methanol is much more rapid than the loss of chlorine from *m*-chlorobenzoic acid (Plimmer and Hummer, 1968). This also appears to hold if two chlorine atoms are substituted in the same aromatic ring, as in 2,5-dichlorobenzoic acid—i.e., the products of irradiation are benzoic acid and *m*-chlorobenzoic acid. The preferred loss of a chlorine atom ortho to the carboxylic acid group rather than a meta chloro substituent appears to be a general feature of reductive dechlorination.

Methyl 3-amino-2,5-dichlorobenzoate was irradiated in methanolic solution and the product was characterized as the N-acetyl derivative. The analysis and infrared spectrum were consistent with the formulation of the product as a chloro-substituted methyl 3-acetamidobenzoate [6] or [7]. The evidence for the orientation of the substituents rests on the NMR spectrum. The NMR spectrum showed the following signals: 2.20 ($\text{CH}_3\text{CO}\cdot\text{N}$); 3.87 ($\text{CH}_3\cdot\text{CO}\cdot\text{O}$); 7.69, 7.89, 7.98 (three aromatic protons), and 8.30 p.p.m. (NH). It was clear from the spacing of the signals due to the aromatic protons (three triplets $J \sim 1$ c.p.s.) that these protons are located at the 2, 4, and 6 positions of the ring. A much larger splitting would be expected if ortho protons were present (Bhacca and Williams, 1964) as in structure [7]; therefore structure [6] has been allocated to the final product.

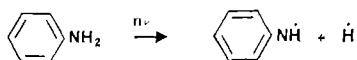
Irradiation of 3-amino-2,5-dichlorobenzoic acid in aqueous sodium bisulfite solution under nitrogen afforded a product identical with [6] after acetylation and methylation. A trace of 3-aminobenzoic acid was also detected. Some replacement of chlorine by hydroxyl would also be expected, since *o*-chlorobenzoic acid gives both benzoic acid and salicylic acid on irradiation in water (Crosby, 1966; Plimmer and Hummer, 1968). It is likely that the aminophenol thus formed may polymerize or oxidize during subsequent manipulation. Photolytic hydroxylation of aromatic compounds in water has been reported in a number of cases (Crosby, 1966; Joschek and Miller, 1966) but hydrogen abstraction is not without precedent (Bridge and Porter, 1958; Crosby, 1966). Scheme I shows the reactions discussed.



Scheme I

Irradiation of the free acid in aqueous solution in the absence of sodium bisulfite effects rapid darkening. This change takes place readily in daylight. Chloride ion is liberated and the solution contains a complex mixture of products. Thin-layer chromatography was used to separate a number of fractions after treatment of the irradiation product with diazomethane. Fractions thus obtained were shown by infrared to lack a primary amino group. In the presence of sodium bisulfite, the photo-oxidation of the amino group is repressed and loss of the chlorine atom is the preferred route of photodecomposition. Products arise by hydrogen abstraction and possibly by hydroxylation, and it is of interest that the former process occurs to a considerable extent in an aqueous medium.

In the absence of sodium bisulfite or other inhibitor it seems likely that the following process dominates the course of photodecomposition:



The amino radical is free to react further and may polymerize or participate in abstraction of chlorine atoms. The latter appear ultimately as chloride ions. Thus, the irradiation of amiben in aqueous solution produces a complex mixture of colored products which arise by polymerization and oxidative processes analogous to those involved in the production of polymeric humic acid by phenol oxidation (Crosby and Tutass, 1966).

ACKNOWLEDGMENT

Amiben (98%) was generously supplied by Amchem Products, Inc., Ambler, Pa. The NMR spectrum was determined by E. L. Gooden, Entomology Division, ARS, U. S. Department of Agriculture, Beltsville, Md.

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Received for review May 17, 1968. Accepted September 20, 1968. Mention of a trademark name or a proprietary product does not constitute a guarantee or warranty of the product by the USDA, and does not imply its approval to the exclusion of other products that may also be suitable.