

Solution Phase Photolyses of Substituted Diphenyl Ether Herbicides under Simulated Environmental Conditions

Jae Koo Lee

Department of Agricultural Chemistry, Chungbuk College, Chongju, Korea

(Received April 5, 1974)

模造 環境條件下에서의 置換 Diphenyl Ether 除草劑의 光分解에 關한 研究

李 載 球

忠北大學 農化學科

(1974, 4, 5 受理)

要 約

八種의 置換 diphenyl ether 除草劑를 Rayonet 光化學 反應器를 使用한 模造環境條件下에서 溶液相 光分解시켜 그 分解產物에 關하여 研究하였다. 試料로 使用된 化合物들은 300 nm 에서 光化學反應을 일으키기에 充分한 energy 를 吸收하였으며 分解產物은 tlc, glc, ir, ms, 그리고 nmr 等에 依하여 確認하였다. 그 結果를 要約하면

C-6989의 溶液相 光分解: *p*-nitrophenol 이 多量 生成됨을 보아 ether 結合의 결렬이 主反應이며 置換基 $\text{NO}_2 \rightarrow \text{NH}_2$ 의 光化學的 還元反應과 $\text{CF}_3 \rightarrow \text{COOH}$ 의 酸化反應도 관찰되었다.

***p*-Nitrophenol 의 水中 光分解:** quinone(0.28%), hydroquinone(0.66%) 및 *p*-aminophenol(0.42%)과 比較의 少量의 未知化合物이 生成됨을 確認하였고 母化合物은 大部分 作用을 받지 않은 채로 存在하였다. 이들 分解產物의 形成機構는 $n \rightarrow \pi^*$ 勵起를 거친 nitro-nitrite 再配列 및 自由基에 依한 水素脫取를 통한 光還元으로 推測되었다.

Nitrofen 의 溶液相 光分解: *n*-hexane 中에서는 NO_2 基의 光還元이 主反應이었고 水溶液 中에서는 光還元 및 hydroxylation 이 ether 結合 결렬 보다 현저하였다. hydroxide ion 에 의한 親核的 置換, hydroxyl 基 및 少量이긴 하지만 水素에 의한 鹽素의 置換도 다소 관찰되었다.

MO-338의 溶液相 光分解: *n*-hexane 용액中 nitro 基의 光還元 反應과 水溶液中에서의 光還元 및 hydroxylation 이 主反應이었으며 hydroxyl 基와 水素에 依한 鹽素의 置換 및

ether 결합의 결렬도 볼 수 있었다.

n-Hexane 과 cyclohexane 中에서의 MC-4379, MC-3761, MC-5127, MC-6063 및 MC-7181의 光分解: nitro 基의 光還元反應과 水素에 依한 halogen 의 置換反應이 主로 일어났다.

MC-4379의 水中 光分解: ether 결합의 결렬, hydroxyl 基에 의한 carboxymethyl 基의 置換, hydroxylation, hydroxyl 基에 의한 nitro 基의 置換이 主로 일어났고 光還元 및 脫鹽素化反應도 약간 일어났다.

MC-3761의 水中 光分解: ether 결합의 결렬, hydroxyl 基에 의한 carboxymethyl 基의 置換 및 hydroxylation 이 主로 되는 光還元이 主反應이었다.

MC-5127의 水中 光分解: 水素에 의한 carboxyethyl 基의 置換이 현저하였고 ether 결합의 결렬, 光還元 및 脫鹽素化反應도 약간 관찰되었으며 decarboxyethylation 은 decarboxymethylation 보다 용이함을 볼 수 있었다.

MC-6063의 水中 光分解: ether 결합의 결렬과 脫鹽素化反應이 主로 관찰되었다.

MC-7181의 水中 光分解: 水素에 의한 carboxymethyl 基의 置換과 monodechlorination 이 현저하였고 ether 결합 결렬과 hydroxylation 도 약간 일어났다.

3-Carboxymethyl-4-nitrophenol의 水中 光分解: 芳香族 ester 에서 흔히 볼 수 있는 光誘導 Fries rearrangement 는 이 化合物의 carboxymethyl 基에서는 볼 수 없었고 nitro→nitroso 反應이 主로 일어났다.

Introduction

Herbicides, like other pesticide chemicals, constitute one of the indispensable tools in modern agriculture. Their ultimate fate and persistence in the environment after use, however, are of great concern to the public as a whole especially in terms of environmental pollution and public health, as well as agricultural practices. Pesticides released into the environment can be chemically changed not only by microbiological, plant, insect, and animal metabolism, but also by chemical reactions on soil surfaces and physical forces. Among other factors, solar radiation can comprise one of the most powerful factors affecting the fate of these chemicals. Knowledge of pesticide photolysis will be important for the effective use, environmental safety, and potential for intentional destruction of residues of these chemicals. Sufficient energy is supplied by the ultraviolet light (290-450 nm) to permit a number of types of reactions involving oxidation, reduction, polymerization, isomerization, and displacement.

Theoretically, a compound, on absorbing sunlight, will acquire excess energy to be in an excited electronic state. Once a molecule becomes excited, it may lose this excess energy to

convert the excitation energy into translational and vibrational energy by losing it to the surroundings. Secondly, the excited molecule can emit through fluorescence or phosphorescence depending on the nature of the excited states of singlet or triplet, respectively. And, finally, it can undergo chemical reactions. Grotthuss and Draper⁽⁵⁸⁾ state that only radiation absorbed in a system, directly or indirectly, is effective in producing a chemical change. In addition, as the lowest recorded wavelength of sunlight reaching the earth's surface is 286.3 nm^(28,87) and solar radiation may probably be considered negligible below about 295 nm,⁽⁴⁸⁾ it is, in practice, extremely significant to adopt wavelengths greater than 286.3 nm of wavelength in simulating the environmental conditions in laboratory experiments. Photochemical approaches to pesticide degradation were not begun until about 1960. Ever since, numerous research papers have appeared in various journals.

It has been well known that substituted diphenyl ether compounds have excellent herbicidal activity when applied as a preemergence or as an early postemergence applications to a wide variety of annual broad leaf and grass weeds. C-6989 was reported to be especially suitable for use in rice,

cotton, and many large-seeded legumes⁽²⁵⁾. Nitrofen was the first compound of this type developed as a herbicide, and is used for selective, postemergence weed control in Brassica crops in Western Canada, and for preemergence weed control in transplanted rice in Oriental countries. The other MC-compounds are now being developed by the Mobil Chemical Company for the same purpose. The diphenyl ethers are reported to function essentially as inhibitors of chloroplast noncyclic electron transport and ranked in the following decreasing order of inhibitory effectiveness: MC-1478 (MO-338) \geq C-6989 \gg Nitrofen. The main site of action appeared to be associated with light reaction II and the oxygen evolution pathway⁽⁴⁷⁾.

Walter et al.⁽⁵⁹⁾ treated two types of soils with C-6989. Less than 10% of the herbicide remained 6 months after application. Its decomposition was believed to be rapid at the soil surface, suggesting that volatility or photodecomposition is an important means of dissipation. After one year of application, only traces of parent compound were detected. This herbicide persisted 3-6 weeks at phytotoxic concentrations based on weed counts. Ebner et al.⁽²⁵⁾ reported that C-6989 was active for 8-12 weeks. Eastin⁽²¹⁾ also adopted ultraviolet light (254 nm) and phytotron light to investigate photolysis of C-6989 in a solid state. He detected *p*-nitrophenol, *p*-aminophenol, 2-nitro-4-trifluoromethyl phenol, 2-amino-4-trifluoromethyl-phenol, *p*-nitrophenyl- α,α,α -trifluoro-2-amino-*p*-tolyl ether, *p*-aminophenyl- α,α,α -trifluoro-2-amino-*p*-tolyl ether, and *p*-aminophenyl- α,α,α -trifluoro-2-nitro-*p*-tolyl ether.

Gutenmann et al.⁽²⁹⁾ reported that 2,4-dichloro-4'-amino-diphenyl ether (amino-Nitrofen) was rapidly detected in rumen fluid as a metabolite of Nitrofen, and this metabolite was absent in the chromatograms of milk, urine, and feces. Aromatic amines may undergo ring hydroxylation followed by elimination as a conjugate⁽⁶¹⁾. Crosby et al.⁽⁴⁷⁾ demonstrated that Nitrofen was rapidly photolyzed in water to 2,4-dichlorophenol and *p*-nitrophenol, and the nitro group also underwent

both reduction (to 2,4-dichlorophenyl-4'-aminophenyl ether) and nucleophilic displacement by hydroxide ions to give the corresponding phenol and nitrite ion. Ichihashi⁽³²⁾ et al. compared the residual effects in soil of CNP (MO-338), Nitrofen, and X-52 (2,4-dichloro-3'-methoxy-4'-nitro-diphenyl ether) by bioassay with barnyard grass and other weeds. They found that X-52 had a long residual effect and that in enriched soil solution, the reduced amino derivatives formed from all these diphenyl ethers. CNP(MO-338), Nitrofen, X-52, and MO-500 (2,4-dichloro 6-fluorophenyl-4'-nitrophenyl ether) were compared by Kuwatsuka⁽³⁸⁾ as to their degradation in soils under flooded and upland conditions. It was pointed out that amino compounds of the diphenyl ethers were detected only in flooded soils treated with diphenyl ethers, that degradation was much slower under upland conditions than under flooded ones, and that no amino derivatives were detected in soils under upland conditions. It is also shown that under flooded conditions, Nitrofen and MO-500 were degraded much faster than CNP and X-52, and amino derivatives were the major metabolites in the earlier stages of incubation, whereas later, amino compounds were also metabolized to other compounds. The fate of Nitrofen in the foliage of rape, redroot pigweed, and green foxtail was investigated by Hawton et al.⁽³⁰⁾ with the aid of C¹⁴-Nitrofen. They concluded that at least two of the metabolites were lipid-Nitrofen conjugates or Nitrofen polymers and others may be formed by cleavage of Nitrofen at the ether linkage.

The test compounds contain a *p*-nitro substituent on one phenyl ring and Matsunaka^(44,45) found that diphenyl ether herbicides could be classified into two groups depending upon their requirement for light and other properties. One group, such as Nitrofen or CNP having ortho-substituent(s) on one benzene ring, required light energy to kill the plant. This group is inactive in the dark. Meanwhile, the other group with a meta-substituent on one benzene ring was not thought to require light for herbicidal

activity.

Water represents a rather general solvent, is important in the environment, and it also is essentially transparent to sunlight. Many classes of pesticides, including the chlorobenzoic acids^(12,49), chloro-phenylacetic acids⁽¹³⁾, halogenated phenylureas^(14,51), chlorinated phenoxyacetic acids^(11,16), chloroanilines⁽⁵²⁾, 1-naphthalene acetic acid⁽¹⁵⁾, and Diquat⁽⁵³⁾ were photolyzed as aqueous solutions or suspensions.

In this experiment, water was used as one of the main solvents and 300 nm wavelength (95.3 Kcal/mole) of artificial ultraviolet light was used as a light source to simulate the environmental conditions. Photoproducts resulting from each compound in various solvents were isolated, purified, and characterized in order to evaluate its importance in the formation or degradation of a toxic residue in the environment.

Materials and Methods

1. Substituted diphenyl ether herbicides

Skeletal structure and designations of these compounds are presented in Fig. 1 and Table I.

C-6989 (2,4'-Dinitro-4-trifluoromethyl-diphenyl ether) was obtained from CIBA Agrochemical Company, Division of CIBA Corp., Vero Beach, Fla. It was recrystallized from ethanol until gas-

liquid chromatography (glc) and thin-layer chromatography (tlc) showed no impurities. Chemical authenticity was supported by observed melting point (mp), infrared (ir) spectrum, nuclear magnetic resonance (nmr) spectrum, and mass spectrum (ms).

TOK E-25 (Nitrofen, NIP, 2,4-Dichloro-4'-nitro-diphenyl ether) was supplied by the Rohm and Haas Chemical Company, Independence Mall West, Philadelphia, Pa., 19105, as a technical grade and was purified by dissolving in ethanol and filtering by suction, the residue being discarded. The filtrate was evaporated to dryness on a rotary evaporator and the residue was dissolved in acetone and recrystallized from *n*-hexane. This compound was dissolved again in a mixture

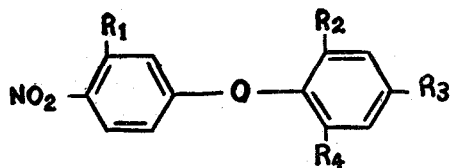


Fig. 1. Skeletal structure of substituted diphenyl ether herbicides

- I: $R_1=H$, $R_2=NO_2$, $R_3=CF_3$, $R_4=H$
- II: $R_1=H$, $R_2=Cl$, $R_3=Cl$, $R_4=H$
- III: $R_1=H$, $R_2=Cl$, $R_3=Cl$, $R_4=Cl$
- IV: $R_1=COOCH_3$, $R_2=Cl$, $R_3=Cl$, $R_4=H$
- V: $R_1=COOCH_3$, $R_2=Cl$, $R_3=Cl$, $R_4=Cl$
- VI: $R_1=COOCH_2CH_3$, $R_2=Cl$, $R_3=Cl$, $R_4=H$
- VII: $R_1=COOCH_3$, $R_2=Cl$, $R_3=F$, $R_4=H$
- VIII: $R_1=COOCH_3$, $R_2=Cl$, $R_3=Cl$, $R_4=F$

Table I. Substituted diphenyl ether herbicides

Common name	Designation	Chemical name
C-6989, Preforan, Fluorodifen	I	2,4'-dinitro-4-trifluoromethyl-diphenyl ether
TOK E-25, Nitrofen, NIP	II	2,4-dichloro-4'-nitro-diphenyl ether
MO-338, MC-1478, CNP	III	2,4,6-trichloro-4'-nitro-diphenyl ether
MC-4379	IV	2,4-dichloro-3'-carboxymethyl-4'-nitro-diphenyl ether
MC-3761	V	2,4,6-trichloro-3'-carboxymethyl-4'-nitro-diphenyl ether
MC-5127	VI	2,4-dichloro-3'-carboxyethyl-4'-nitro-diphenyl ether
MC-6063	VII	2-chloro-4-fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether
MC-7181	VIII	2,4-dichloro-6-fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether

of benzene-chloroform (1 : 1 v/v) and column chromatographed using the benzene-chloroform as eluting solvent (Silica gel : 0.2-0.5 mm, 30-70 mesh ASTM for Column Chromatography, Merck, Germany). With this column most of the colored material was removed.

The eluates were collected, evaporated on a rotary evaporator and passed again through aluminum oxide column (Activity II-III, according to Brockmann, M. Woelm Eschwege, Germany). The eluates were evaporated on a rotary evaporator, dissolved in acetone, recrystallized from *n*-hexane, and washed with dilute hydrochloric acid and distilled water and finally with *n*-hexane. More than 99% purity was obtained. The purity was confirmed by tlc, glc, nmr, and ms.

MO-338 (MC-1478, CNP, 2,4,6-Trichloro-4'-nitro-diphenyl ether) was obtained from the Mobil Chemical Company, Edison, N.J. The compound dissolved in a mixture of chloroform-benzene (1 : 1 v/v) was passed through the aluminum oxide column with the chloroform-benzene mixture as eluting solvent. The eluates were concentrated on a rotary evaporator, dissolved in acetone, and recrystallized from *n*-hexane. The resulting crystals were washed with *n*-hexane. The purity was confirmed by tlc, glc, nmr, and ms.

MC-6063 (2-Chloro-4-fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether) was obtained from the Mobil Chemical Company, Edison, N.J. The compound was dissolved in the chloroform-benzene mixture (1 : 1 v/v), passed through the aluminum oxide column and eluted with chloroform-benzene. Eluates were concentrated to dryness on a rotary evaporator, dissolved in acetone, and recrystallized from *n*-hexane. The crystals were washed successively with 1N-HCl, distilled water, and *n*-hexane. The purity was confirmed by the chromatographic and spectrometric methods mentioned above.

MC-4379 (2,4-Dichloro-3'-carboxymethyl-4'-nitro-diphenyl ether), **MC-3761** (2,4,6-Trichloro-3'-carboxymethyl-4'-nitro-diphenyl ether), **MC-5127** (2,4-Dichloro-3'-carboxyethyl-4'-nitro-diphenyl ether), and **MC-7181** (2,4-Dichloro-6-

fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether) were also obtained from the Mobil Chemical Company and used with no further purification. Ir, nmr, and ms (direct probe, 70 eV ionizing voltage) all gave spectra consistent with these compounds.

2. Analytical methods

Ultraviolet (uv) spectra were obtained in spectrophotometric grade solvents (Mallinckrodt Chemical Works, St. Louis, Mo.), and were recorded with a Beckman DB-G grating spectrophotometer (Beckman Instruments, Inc., Fullerton, Calif.).

The ir spectra were determined as potassium bromide disc (or micropellet) with a Perkin-Elmer 337 grating spectrophotometer (Perkin-Elmer Corp., Norwalk, Conn.).

Nmr spectra were recorded using a Varian T-60 NMR Spectrometer (Varian Associates, Palo Alto, Calif.). Samples were dissolved in carbon tetrachloride and deuterated chloroform-d (Mallinckrodt). Tetramethylsilane was used as an internal standard.

Gas-liquid chromatographic analyses were performed with a Beckman GC-65 instrument equipped with a flame ionization detector. The column packing was a mixture of 15% QF-1 and 10% DC-200 (by weight) liquid phases on 80-100 mesh Gas Chrom Q (Applied Science Laboratories, Inc., State College, Pa.)⁽⁶⁾. Operating parameters were generally as follows: Stainless steel column of 4 mm i.d., 2 ft in length (Column A) and pyrex glass tube of 2 mm i.d., 6 ft in length (Column B); Column flow of 20 ml prepurified helium (99.997% purity) per min. in column A and 120 ml per min. in column B, respectively. These columns were conditioned at 250°, with a helium flow, for 5 days.

Injection temp. of 210°; Detector temp. of 310°; All analyses were made by temperature-programming from 70° (2min.) to 230° at a rate of a linear temperature increase of 7.5° per min. for column A and from 100° to 240° at a rate of temp. increase of 10° per min. for column B,

Thin-layer chromatography was accomplished on precoated analytical plates of silica gel HF-254 with fluorescent indicator containing zinc silicate phosphor (Brinkmann Instruments, Inc., Westbury, N.Y.) using solvent systems consisting of (A) benzene-chloroform (1:1 v/v), (B) chloroform-ethyl acetate-acetic acid (6:3:1 v/v), (C) chloroform-ethanol-acetic acid (90:5:5 v/v), and (D) chloroform-methanol-acetic acid (95:5:1 v/v). The separated substances were detected by means of light absorption and fluorescence at 254 nm.

Mass spectra were obtained using a 21-490 gas chromatograph-mass spectrometer (CEC/Analytical Instruments Division, Bell & Howell) and an LKB 9000 gas chromatograph-mass spectrometer. Spectra were determined using the direct probe and gc inlet system at an ionizing potential of 70 electron volts (eV).

Column chromatography was accomplished with a 1×75 cm column of 0.2–0.5 mm (30–70 mesh ASTM) silica gel, chloroform-ethanol-acetic acid (90:5:5 v/v) and n-butanol-water-acetic acid (100:50:20 v/v) eluents, and an automated fraction collector.

Diazomethane was prepared from Diazald (Aldrich Chemical Co., Inc., Milwaukee, Wis.) according to Kirkland.⁽⁸⁶⁾

3. Photolysis

Photochemical equipment: Samples were irradiated in a Rayonet Photochemical Reactor (The southern N.E. Ultraviolet Co., Middletown, Conn.). This reactor was equipped with filtered medium pressure lamps having a peak output of 300 nm (Cat. No. N.P.R. -3000). Photolysis was carried out at approximately 30° to 40° with constant stirring. Unless otherwise stated, the irradiations were carried out in a 2-liter borosilicate glass round-bottomed flask surrounded by aluminum foil to increase the photochemical efficiency of the radiation. A borosilicate filter (2 mm. thick) effectively absorbed all radiation below 290 nm. As there is very little radiation in sunlight with a wavelength below 300 nm and

none below 290 nm, it was assumed that the photochemical breakdown in solution would be similar to that occurring in sunlight.

Solvents: The solvents used in the photochemical experiments were glass-distilled methanol (Burdick and Jackson Laboratories, Inc., Muskegon, Mich.), acetone (Mallinckrodt Chemical Works, St. Louis, Mo. 63160, Analytical Reagent), n-hexane and cyclohexane (Burdick and Jackson Laboratories, Inc., Muskegon, Mich.). All water used as a solvent in photolysis was distilled and deionized, having a pH of approximately 7.

Photolysis of C-6989 in distilled water: Half a gram of C-6989 was suspended in two liters of distilled water with the aid of a small amount of methanol. This suspension was irradiated in a Rayonet photochemical reactor. The photoreaction mixture was evaporated to dryness on a rotary evaporator. The residue was dissolved in acetone and applied on column and tlc plates, successively, to isolate photoproducts. Each band on tlc plates was scraped off, extracted with acetone or methanol, depending on the polarity of photoproducts, and concentrated by bubbling with nitrogen gas. The "dark control" held in the dark was also checked in order to test the possible decomposition of the compound without light. The duration includes 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 30-days, 6 months, and 9 months.

Photolyses of C-6989 in other solvents:

In an attempt to investigate the ether linkage breakdown and the possible photosensitizing activities of organic solvents used for dissolving pesticides in formulating emulsion concentrates, C-6989 was dissolved in xylene, cyclohexane-acetone (5:5 v/v), toluene, acetone, cyclohexane-acetone (8:2 v/v), methanol, and benzene, respectively, to give a solution of 2,000 ppm. These solutions were irradiated for 24 hrs. The reaction mixtures were concentrated to dryness by bubbling with nitrogen gas. The residues were dissolved again in a small amount of acetone. Gas chromatography was performed to analyze the photoproducts.

Photolysis of Nitrofen in distilled water:

One gram of Nitrofen was suspended evenly with magnetic stirrer in 2 liters of distilled water (500 ppm) and photoreacted for 2 and 10 days. After photolysis, the mixture was evaporated to dryness on a rotary evaporator and the residue dissolved in acetone. The acetone solution was applied on tlc plates as a band and developed using chloroform-benzene (1 : 1 v/v) mixture as solvent. The developed bands were scraped off separately and eluted with acetone. Each portion was concentrated in the same manner as before.

Photolysis of MO-338 in distilled water: One gram of MO-338 was dispersed evenly in distilled water with the aid of magnetic stirrer to make a 500 ppm suspension. This suspension was photolyzed in a magnetically stirred and cooled system. After photolysis, the same procedures were adopted for the isolation of photolysis products. The products were identified by means of glc-ms, tlc, and ir spectrometry.

Photolysis of MC-4379 in distilled water:

Two grams of MC-4379 were dispersed in 4 liters of distilled water contained in each of the two pyrex round-bottomed flasks with the aid of a small amount of methanol. The suspensions were irradiated for 2 and 10 days, respectively. After photolysis, the reaction mixtures were evaporated to dryness on a rotary evaporator, redissolved in acetone, and concentrated by bubbling with purified nitrogen gas. This concentrated acetone solution was applied as a band on 20×20 cm precoated tlc plates 2.5 cm from one edge and developed in a solvent mixture of chloroform-ethanol-acetic acid (90 : 5 : 5 v/v). Each band was scraped off the plates separately, extracted with acetone, and concentrated to a small volume or to dryness for ir, ms, glc, and tlc.

Photolyses of 3-carboxymethyl-4-nitrophenol in methanol and distilled water:

Since 3-carboxymethyl-4-nitrophenol is one of the main products of the photolyses of MC-4379 and its related compounds in distilled water, it will be of significance to pursue its photolysis

behavior in order to elucidate the photochemical reaction. Prior to photolysis, the 3-carboxymethyl-4-nitrophenol was purified on precoated tlc plates using solvent C.

(1) Photolysis in methanol

One 10^{-3} M methanol solution of the standard compound was irradiated in a screw-capped vial for the following periods : 30 hrs, 2, 3, 5, 9, 12, 15, 16, 20, and 33 days. After each photolysis period, a small aliquot was subjected to glc analysis using column A. For further identification, an aliquot of 20 day photolysis was applied on tlc plates as a band and developed in the solvent B for about 2 hrs. After development, each band was scraped off, extracted with acetone, and concentrated to a small volume or to dryness for the analyses of glc, ms, ir, tlc, and nmr.

(2) Photolysis in distilled water

Another 10^{-3} M aqueous solution of the compound was irradiated in a screw-capped vial for the following periods : 24, 58, 90, 136, 218, and 336 hrs. After photolysis, the products were identified by glc-ms.

Photolyses of MC-3761, MC-5127, MC-6063, and MC-7181 in distilled water:

Half a gram of each of the compounds was suspended in distilled water by magnetic stirrer and irradiated for 2 and 10 days, respectively, in a magnetically cooled system. The subsequent workup procedures were the same as the above.

Photolyses of C-6989, Nitrofen, MO-338, MC-4379, MC-3761, MC-5127, MC-6063, and MC-7181 in methanol:

Each of the compounds was dissolved in 25 ml of methanol, respectively, to be the concentration of 10^{-3} M. These solutions were irradiated for 48 hrs. The photoproducts were identified by glc-mass spectrometry.

Photolyses of MC-4379, MC-3761, MC-5127, MC-6063, and MC-7181 in cyclohexane:

Each of the 10^{-3} M cyclohexane solutions of the above compounds was irradiated for 48 hrs and the photoproducts therefrom were identified by glc-mass spectrometry.

Photolysis of *p*-nitrophenol:

Since *p*-nitrophenol is the predominant photoproduct of C-6989 resulting from the ether linkage cleavage, it seems quite significant to pursue the fate of *p*-nitrophenol under the environmental conditions. The following photolysis periods were checked: 10, 30 min., 1, 2, 4, 8 hr., 1, 2, 3, 4, 5, 15, 20, and 25 days. All the photoproducts were identified by means of tlc, glc, ms, and ir.

Photolysis of C-6989 in ethanol:

In order to check the formation of *p*-nitrophenol from C-6989 photolysis as a function of time, 5×10^{-4} M C-6989 solution in ethanol was photolyzed for the following periods: 0, 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 48, 72, 96, 120, and 144 hrs, respectively.

Photolyses of C-6989, Nitrofen, MO-338, MC-4379, MC-3761, MC-5127, MC-6063, and MC-7181 in n-hexane:

In order to compare the photolysis behaviors of the above structurally similar compounds as affected by different substituents, each of the compounds was dissolved in n-hexane at 10^{-3} M concentrations, respectively. Two milli-liters of each solution were irradiated in screw-capped vials. Photolysis periods were 24, 48, and 72 hrs. The photoproducts were analyzed by means of the temperature-programming on glc. Identifications were made by ms.

Results and Discussion

Photoproducts of C-6989 in distilled water:

Products of 2- and 10-day photolyses are pre-

sented at Table II and Table III.

The period of irradiation did not affect the formation of photoproducts. The predominant amount of *p*-nitrophenol strongly indicates the readiness of the ether linkage cleavage. Photoreduction of one or both of the nitro groups occurred as minor reactions. This reaction is supposed to proceed by way of $-\text{NO}_2 \rightarrow -\text{NO} \rightarrow -\text{NHOH} \rightarrow -\text{NH}_2$.^(2,38) Formation of 2,4'-diamino-4-carboxy-diphenyl ether and 4-hydroxy-3-nitro-benzoic acid proves

Table II. Photoproducts of C-6989 in distilled water (glc)

Photoproducts	Retention time (min.)	
	Column A	Column B
1) undecomposed C-6989	41	13.1
2) <i>p</i> -nitro-phenyl- α, α, α -trifluoro-2-amino- <i>p</i> -tolyl ether	34.75	12
3) <i>p</i> -amino-phenyl- α, α, α -trifluoro-2-nitro- <i>p</i> -tolyl ether	32.25	11.3
4) <i>p</i> -amino-phenyl- α, α, α -trifluoro-2-amino- <i>p</i> -tolyl ether	28.5	10
5) <i>p</i> -nitrophenol	22.5	5.6
6) 2-amino-4-trifluoromethyl phenol	18.25	2.96
7) 2-nitro-4-trifluoromethyl phenol	14.5	1.36
8) 2,4'-diamino-4-carboxy-diphenyl ether	—	13.8
9) 4-hydroxy-3-nitrobenzoic acid	—	8.99
10) hydroquinone	16.8	2.36

* Column A: Stainless steel column of 4 mm i.d., 2 ft in length

Column B: Pyrex glass tube of 2 mm i.d., 6 ft in length

Table III. Photoproducts of C-6989 in distilled water(tlc)

Photoproducts	Rf			
	Solvent A	B	C	D
1) undecomposed C-6989	0.37	0.66	—	—
2) <i>p</i> -nitro-phenyl- α, α, α -trifluoro-2-amino- <i>p</i> -tolyl ether	0.24	0.64	—	—
3) <i>p</i> -amino-phenyl- α, α, α -trifluoro-2-nitro- <i>p</i> -tolyl ether	0.09	0.42	—	—
4) <i>p</i> -amino-phenyl- α, α, α -trifluoro-2-amino- <i>p</i> -tolyl ether	0.04	0.27	—	0.46
5) <i>p</i> -nitrophenol	—	0.55	0.50	0.37
6) 2-amino-4-trifluoromethyl phenol	—	—	—	0.28
7) 2-nitro-4-trifluoromethyl phenol	—	—	—	0.49
8) 2,4'-diamino-4-carboxy-diphenyl ether	—	0.13	—	0.17

- 9) 4-hydroxy-3-nitrobenzoic acid
 10) hydroquinone

— 0.51 — —
 — — 0.44 —

** Solvent A: benzene-chloroform (1:1 v/v)

C: chloroform-ethanol-acetic acid (90:5:5 v/v)

B: chloroform-ethyl acetate-acetic acid (6:3:1 v/v)

D: chloroform-methanol-acetic acid (95:5:1 v/v)

the oxidation of $-CF_3$ to $-COOH$ group during aqueous photolysis. Hydroquinone detected in a trace amount is thought to be formed from *p*-nitrophenol by the mechanism as shown later. Besides the compounds appearing in Table II, III, more than eight unknown compounds were also detected in small amounts. All the carboxyl-containing compounds were treated with ethereal diazomethane solution to give corresponding methyl esters, because these carboxyl compounds do not elute from the glc column. The ir spectra of undecomposed parent compound and *p*-nitrophenol were identical with those of authentic compounds, respectively. Fig. 2 shows the ir spectra of the authentic *p*-nitrophenol and the

isolated photoproduct. The strong $-OH$ stretches are remarkable in the region of $3,000-3,500\text{ cm}^{-1}$ in both spectra, the rest being identical with each other. The ir spectra of the other photoproducts could not be measured because of the paucity of amounts.

Photoproducts of C-6989 in ethanol:

In order to check the amount of *p*-nitrophenol formation from C-6989 as a function of time, its $5 \times 10^{-4}\text{ M}$ ethanolic solution was photolyzed for various time intervals and the absorbance of the photolyzed solution was measured with spectrophotometer at 400 nm. The absorbance plotted against irradiation time is shown in Fig. 3.

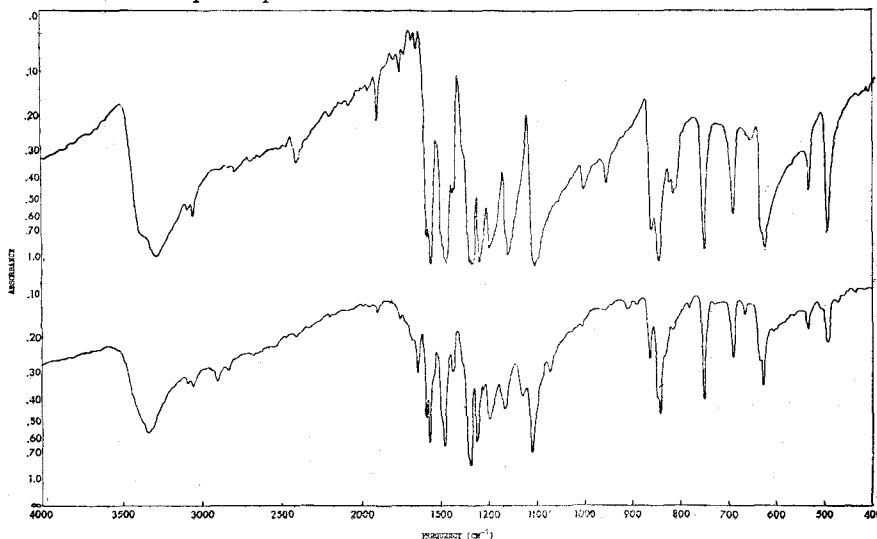


Fig. 2. Infrared spectra of the authentic *p*-nitrophenol (upper line) and the isolated photoproduct (lower line)

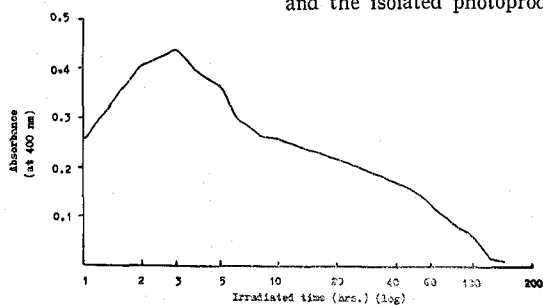


Fig. 3. *p*-Nitrophenol formation from C-6989 photolysis as a function of time ($5 \times 10^{-4}\text{ M}$ ethanol solution)

As seen in the figure, the largest amount of *p*-nitrophenol was formed at 3 hr. irradiation. This fact suggests that C-6989 undergoes rapid cleavage at the ether linkage.

Photoproducts of *p*-nitrophenol in distilled water:

As shown in Fig. 4, in order to check light absorption of *p*-nitrophenol in water, the absorbance of a $1 \times 10^{-3}\text{ M}$ aqueous solution was measured against the wavelengths of 300 to 480 nm. It is obvious from this spectrum that this compound absorbs sufficient light energy at 300 nm.

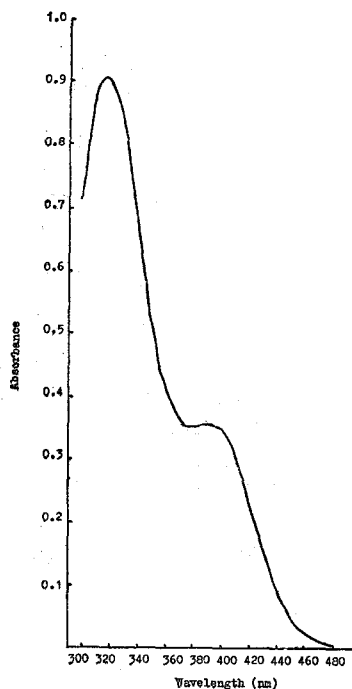


Fig. 4. Ultraviolet absorption spectrum of an aqueous solution of 10^{-8} M *p*-nitrophenol

to undergo photolysis. Gas chromatogram of *p*-nitrophenol photoproducts from aqueous solution photolysis of 30-day irradiation is presented in Fig. 5. The photoproducts include quinone (0.28%), hydroquinone (0.66%), *p*-aminophenol (0.42%), unchanged *p*-nitrophenol (98.6%), and a relatively small amount of an unidentified product. As time goes on, these photoproducts increased in amounts, but not sharply. The quantitation was performed on glc by measuring the peak areas with a planimeter, normalizing, and expressing as a percentage of the total peak area. The retention times of quinone, hydroquinone, *p*-aminophenol, and *p*-nitrophenol were 11.25, 16.8, 19.25, and 22.5 min, respectively, on column A by the above-mentioned temperature programming.

On tlc (Fig. 6), the R_f 's in solvent C of quinone, hydroquinone, *p*-aminophenol, and *p*-nitrophenol were 0.79, 0.23, 0.04, and 0.55, respectively. The postulated mechanisms for the photolysis of an aqueous *p*-nitrophenol solution are presented in Fig. 7 and 8.

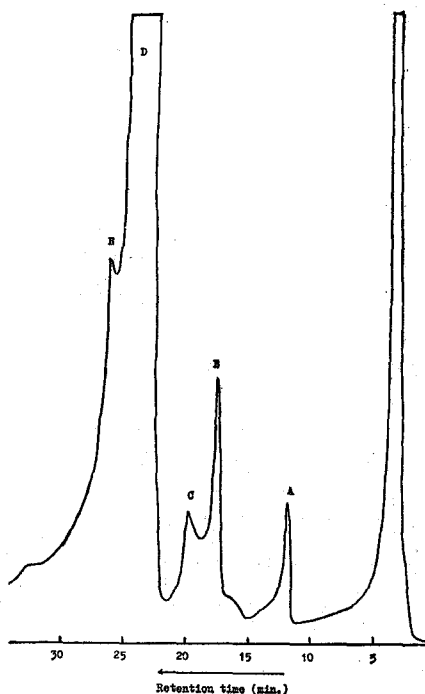


Fig. 5. Gas chromatogram of *p*-nitrophenol photoproducts from aqueous solution photolysis for 30 days (7.5°/min., temperature programmed from 70° to 230°)

A : Quinone (0.28%), B : Hydroquinone (0.66%), C : *p*-Aminophenol (0.42%), D : *p*-Nitrophenol (98.6%), E : An unknown compound

In Fig. 7, the mechanism of photochemical formation of quinone and hydroquinone from *p*-nitrophenol can be rationalized by the following scheme^(9,10,34). The key feature of the $n \rightarrow \pi^*$ excited state of a nitro group is the overlap of the half-vacant nonbonding orbital with the adjacent orbital of the aromatic ring. This overlap, which is a result of the out-of-plane nitro group, leads to the formation of an oxaziridine ring which collapses to a nitrite thermally. The process of the nitrite formation may be accelerated by a polar solvent, water. The resulting aryl nitrite is very labile and is solvolyzed by water to yield the *p*-semiquinone radical, which has been shown to be produced from hydroquinone and quinone by flash photolysis work^(3,28,38,39,40). This intermediate radical, instead of

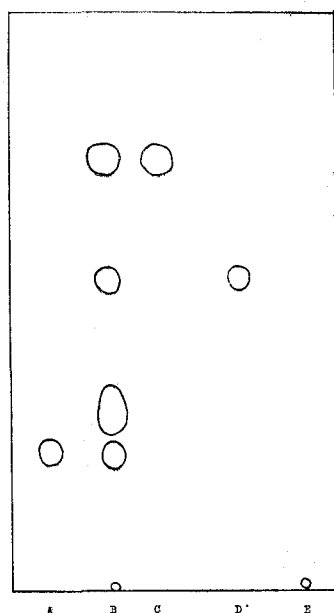


Fig. 6. Thin-layer chromatogram of photoproducts of an aqueous *p*-nitrophenol solution
 A: Hydroquinone, B: Photoproducts of aqueous photolysis of *p*-nitrophenol for 20 days, C: Quinone, D: *p*-nitrophenol, E: *p*-aminophenol, Developing solvent: C

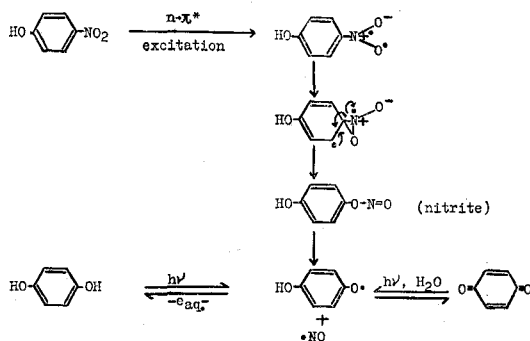


Fig. 7. Proposed mechanism of nitro-nitrite rearrangement leading to the formation of hydroquinone and quinone from the aqueous *p*-nitrophenol photolysis

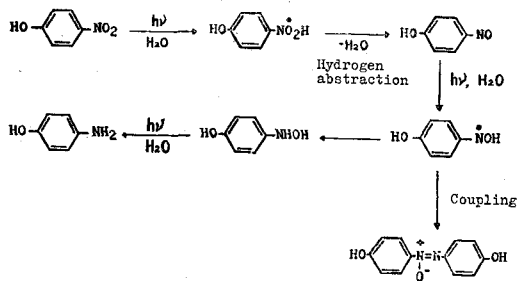


Fig. 8. Postulated pathway of the formation of *p*-aminophenol from the aqueous photolysis of *p*-nitrophenol

combining, may disproportionate rapidly⁽⁸⁾ ($K = 4.6 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$) to hydroquinone and quinone as presented.

In a hydrogen donating solvent, a competition reaction between nitro-nitrite rearrangement and photoreduction obviously occurs, and the competition may depend on the degree of steric hindrance of a nitro group and probably on the polarity of the solvent⁽³⁶⁾.

In addition, it has been known that the ultra-violet irradiation of easily oxidized aromatics in rigid media leads to electron ejection and the stabilization of the resulting free-radical products^(18,41,42). More recent work has shown that photolysis of aromatics in aqueous solution produces radical products and the same hydrated electron species that is generated by the action of ionizing radiation on water^(19,27,56). Grossweiner and Joschek⁽²³⁾ showed that e^-_{aq} optical generation correlates with low gas-phase photoionization potential (PIP), negative Hammett σ_p constants, and low reactivity of the parent molecules with e^-_{aq} . Joschek and Grossweiner⁽³³⁾ also observed that in the disubstituted benzenes which have been studied the substituents with $\sigma_p > 0$ suppress e^-_{aq} generation even when combined with those with $\sigma_p < 0$. According to them, nitrophenol did not produce any radical product, presumably due to the positive Hammett σ_p constant of the nitro group irrespective of the negative one of the OH substituent. This fact indicates that the *p*-aminophenol resulting from the aqueous photolysis of *p*-nitrophenol will be formed by some mechanisms other than the above hydrated electron mechanism. Fig. 8 gives the proposed pathway of *p*-aminophenol formation from the aqueous photolysis of *p*-nitrophenol⁽³⁶⁾. Hydrogen abstraction of the excited nitro compound from water leads to a radical intermediate^(4,7,60). This further abstracts hydrogen from water followed by dehydration to give nitrosophenol. The latter undergoes photochemical hydrogen abstraction to give a *p*-hydroxyphenyl nitroxide radical^(1,31,46,50) which will also couple to give 4,4'-dihydroxy-azoxybenzene. Mostly the *p*-hydroxy-

phenyl nitroxide radical abstracts hydrogen to form *p*-hydroxyphenyl hydroxylamine. The latter will be reduced slowly to *p*-aminophenol.

Photolyses of the eight herbicides in *n*-hexane:

In the cases of 24 and 48 hr. photolyses, C-6989 produced *p*-nitrophenol and 1-nitro-3-trifluoromethyl benzene as the main photoproducts on glc.

Meanwhile, Nitrofen showed 4-amino-2',4'-dichloro-diphenyl ether (amino-Nitrofen) in a small amount as its main photoproduct. MO-338 also exhibits 4-amino-2', 4', 6'-trichloro-diphenyl ether (amino-MO-338) as the predominant photoproduct in somewhat a larger amount than in the case of Nitrofen. In 72 hr. photolyses, they showed all the same decomposition patterns as in the cases of 24 and 48 hr. photolyses, except that some fragments resulting from *n*-hexane photolysis were produced. While in the photolysis of C-6989, it is likely that the ether linkage will be cleaved before the reduction of 4-nitro group of one benzene ring to amino group, the nitro groups of Nitrofen and MO-338 are reduced to amino groups before the ether linkages are broken. In the cases of photolyses of MC-4379, MC-3761, MC-5127, MC-6063, and MC-7181, decarboxymethylation or decarboxyethylation depending on the substituent of each compound dominates over the other various reactions irrespective of the irradiation time.

Ultraviolet spectrometry:

In order to check the ultraviolet absorptions of the test compounds, C-6989 was dissolved in ethanol to give the concentration of 5×10^{-5} M and the rest were dissolved in *n*-hexane to the concentration of 1×10^{-5} M. All these compounds exhibit the same absorption curves as shown in Fig. 9. The photochemical behavior of organic nitro compounds is of interest because of the comparative similarity of their absorption characteristics to carbonyl compounds. As seen in Fig. 9, organic nitro compounds display short and long wavelength absorptions assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The molar absorptivities (ϵ 300) of the compounds at 300 nm wavelength are

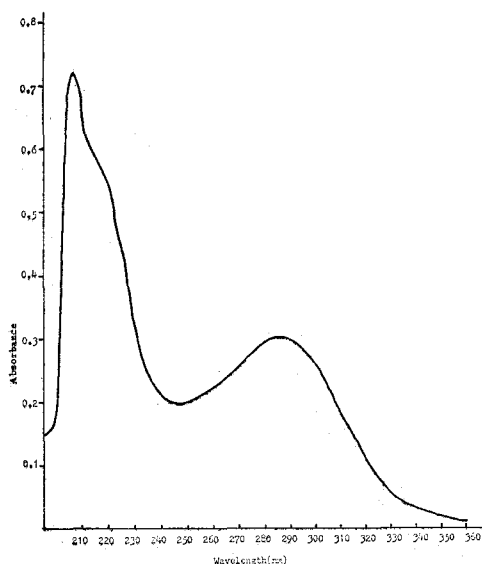


Fig. 9. Ultraviolet absorption of C-6989 (5×10^{-5} M in ethanol)

shown in Table IV.

Table IV. Molar absorptivities of the test compounds

Compound	Solvent	Concentration	Molar absorptivity
C-6989	ethanol	5×10^{-5} M	5,720
Nitrofen	<i>n</i> -hexane	1×10^{-5} M	20,000
MO-338	<i>n</i> -hexane	1×10^{-5} M	9,000
MC-3761	<i>n</i> -hexane	1×10^{-5} M	5,000
MC-4379	<i>n</i> -hexane	1×10^{-5} M	6,500
MC-5127	<i>n</i> -hexane	1×10^{-5} M	7,500
MC-6063	<i>n</i> -hexane	1×10^{-5} M	4,400
MC-7181	<i>n</i> -hexane	1×10^{-5} M	5,500

As seen in Fig. 9, λ max appears to be around between 218 nm and 220 nm. These data indicate that the compounds absorb enough ultraviolet energy to undergo some photochemical reactions under the experimental conditions.

Photoproducts of C-6989 in other organic solvents:

The results of glc analyses are as follows:

Xylene solution: C-6989 (Unchanged), *p*-nitrophenol, 1-nitro-3-trifluoromethyl benzene, *p*-nitro-*p*-phenyl- α, α, α -trifluoro-2-amino-*p*-tolyl ether, 2,2'-dinitro-4,4'-bis(trifluoromethyl) biphenyl (dimer

of 1-nitro-3-trifluoromethyl benzene radical), and 5 unknowns.

Cyclohexane-Acetone (5 : 5 v/v): C-6989, *p*-nitrophenol, 1-nitro-3-trifluoromethyl benzene, *p*-nitrophenyl- α, α, α -trifluoro-2-amino-*p*-tolyl ether, 1-amino-3-trifluoromethyl benzene, 2,2'-dinitro-4,4'-bis-(trifluoromethyl) biphenyl, and about 14 unknown peaks.

Toluene solution: C-6989, *p*-nitrophenol, 1-nitro-3-trifluoromethyl benzene, and about 5 unknown peaks.

Acetone solution: C-6989, *p*-nitrophenyl- α, α, α -trifluoro-2-amino-*p*-tolyl ether, *p*-nitrophenol, 1-nitro-3-trifluoromethyl benzene, and four unknowns.

Methanol solution: C-6989, *p*-nitrophenol, 1-methoxy-2-nitro-4-trifluoromethyl benzene, 1-methoxy-2-amino-4-trifluoromethyl benzene, and about five unknowns.

Benzene solution: C-6989, *p*-nitrophenol, *p*-nitrophenyl- α, α, α -trifluoro-2-amino-*p*-tolyl ether, 1-nitro-3-trifluoromethyl benzene, 2,2'-dinitro-4,4'-bis-(trifluoromethyl) biphenyl, and two unknowns. There is little difference between solvents in which the compound is dissolved in producing photoproducts, except that acetone-cyclohexane mixture exhibited quite a few unidentifiable products, indicating that there is some possibility of photosensitization.

In the light of the metabolic studies carried out by some others,^(20,21,22,23,24,59) it will be reasonable to mention that the C-6989 photolysis in an aqueous solution undergoes a similar chemical change to the metabolism in plants.

In the present experiment, 2,4'-dinitro-4-carboxyl-diphenyl ether, 2-nitro-4-carboxyl-phenol, 2,4'-diamino-4-carboxyl-diphenyl ether, 2-amino-4-carboxyl-phenol, and hydroquinone were detected, in addition to the compounds identified in the Eastin's work of metabolism and photolysis.^(20,21,22,23,24)

Products of Nitrofen photolysis in distilled water:

By means of a combination of glc and ms, the following photoproducts were identified:

(1). Unaltered Nitrofen: the parent peak occurred at m/e 283. Isotopic abundances at P+2 and P+4 were in good agreement with those expected for a compound containing two chlorines⁽⁵⁴⁾. Ions at P-30 and P-81 indicate P-NO and P-NO, Cl, and O, successively, consistent with the expected fragmentation.

(2). 2,4-Dichloro-4'-amino-diphenyl ether: the parent ion appeared at m/e 253. The P+2 and P+4 peaks indicate the presence of two chlorines. Ions at P-70 and P-145 are consistent with the expected fragmentation.

(3). 2,4-Dichloro-4'-hydroxy-diphenyl ether: the parent ion occurred at m/e 254. The P+2 and P+4 ions comply with the isotopic abundances of two chlorines. The P-1 ion indicates the presence of the hydroxyl substituent. The P-70 and P-145 peaks support the structure.

(4). 4-Chloro-4'-nitro-diphenyl ether: the parent ion occurred at m/e 249. The P-35 and P-111 peaks comply with the expected fragmentation pattern.

(5). 2-Hydroxy-4-chloro-4'-nitro-diphenyl ether: the parent ion occurred at m/e 265. The P+2 peak indicates the presence of one chlorine. The P-47 and P-82 peaks support the expected fragmentation pattern.

(6). 2,4,6-Trihydroxy-4'-nitro-diphenyl ether: the parent ion appeared at m/e 263.

(7). Hydroxylated Nitrofen: the parent ion appeared at m/e 299. Two chlorines are indicated by the P+2 and P+4 ions. The P-1 ion suggests the presence of hydroxy group. The P-17, P-47, P-82, and P-191 peaks comply with the expected fragmentation pattern.

(8). Hydroxylated amino-Nitrofen: the parent peak appeared at m/e 269. The spectra are characterized by the P-1, P-33, and P-92 peaks.

(9). 2,4-Dichloro-diphenyl ether: the parent ion occurred at m/e 238, the P+2 and P+4 ions indicating the presence of two chlorines. Prominent ions occurred at P-35 and P-70, which will mean the loss of one or two chlorines.

(10). *p*-Nitrophenol: the parent ion appeared at m/e 139. The P-30 and P-47 peaks indicate

the loss of NO and OH groups. The spectrum is consistent with that of the authentic compound.

(11). 2,4-Dichlorophenol: the parent ion occurred at m/e 162. The P+2 and P+4 peaks prove the presence of two chlorines. The P-35 peak supports the expected fragmentation pattern.

(12). Hydroxylated 2,4-dichlorophenol: the parent peak occurred at m/e 178. The spectra are characterized by the P+2, P+4, P-1, and P-17 ions, being consistent with the expected fragmentation.

As indicated above, amino-Nitrofen is the predominant photoproduct of Nitrofen photolysis. *p*-Nitrophenol and 2,4-dichlorophenol resulting from the ether linkage cleavage are also found in small amounts. Gas chromatography showed the retention times of Nitrofen and amino-Nitrofen to be 34.7 min. and 28.5 min., respectively, on column A. The retention times of the other products were not measured. The IR spectra of authentic amino-Nitrofen and the isolated product are identical, showing the characteristic $-NH_2$ absorption in the 3,300-3,400 cm^{-1} region.

In the present experiments, 12 compounds including undecomposed parent were identified. For the most part, photochemical reduction leading to the *p*-amino derivatives and hydroxylation predominate over the ether linkage cleavage contrary to C-6989 photolysis. Photodechlorination and photodenitration reactions were also observed. The complete displacement of chlorines on benzene ring by hydroxyl groups will suggest the possibility of forming polymeric humic acid in the long run⁽¹¹⁾. All these kinds of reactions will be competitive depending on the actual environmental conditions. The photodecomposition pattern of Nitrofen in aqueous suspension is quite similar to the corresponding metabolism in animals and plants. In the course of photolysis, some tarry products were formed and precipitated, increasing in amounts with time. The fact that these products were insoluble in organic solvents is probably suggestive of the formation of polymers. This kind of polymerization was also observed on thin-layer chromatograms. Black materials always

remained at the origin after the development.

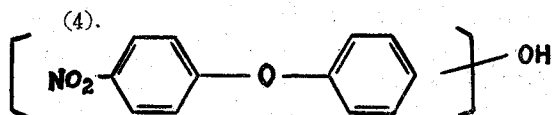
No basic difference was observed between 2 and 10 day photolyses, except that more tarry products were formed in 10 day photolysis and the amounts of products increased with time. **Products of MO-338 photolysis in distilled water:**

By the same method as the above, the following products were identified.

(1). Unaltered MO-338: the parent ion occurred at m/e 317. The isotopic abundances at P+2, P+4, and P+6 were consistent with those of the authentic compound. The P-30 and P-81 peaks support the expected fragmentation pattern.

(2). 2,4,6-Trichloro-3-hydroxy-4'-nitro-diphenyl ether: the parent ion appeared at m/e 333. The P+2, P+4, and P+6 peaks indicate the presence of three chlorines. The P-17, P-87, and P-138 peaks are in good agreement with the expected fragmentation, strongly indicating the hydroxylated product. This is thought to be the main product of the aqueous photolysis of MO-338.

(3). Chlorinated MO-338: the parent peak occurred at m/e 351. The isotopic abundances at the P+2, P+4, P+6, and P+8 peaks indicate the presence of four chlorines, which will mean the substitution of a hydrogen on the ring by a chlorine atom during the aqueous photolysis. The position of the substitution was not known. The P-30 and P-81 peaks show the losses of NO, O, and Cl from the structure, successively.



The parent ion occurred at m/e 231. The P-17, P-93, and P-123 peaks are consistent with the expected fragmentation. The absence of the characteristic P+2, P+4, and P+6 peaks indicates the loss of the three chlorines, one of which was probably replaced by a hydroxyl group.

(5). 2-Hydroxy-4,6-dichloro-4'-amino-diphenyl ether: the parent ion appeared at m/e 269. The presence of two chlorines is characterized by the isotopic abundances of the P+2 and P+4 peaks. The P-35, P-70, and P-161 peaks are

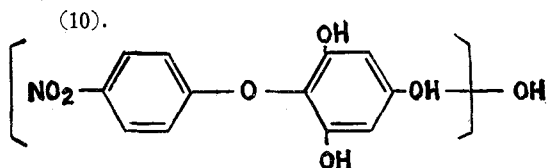
also indicative of the expected fragmentation pattern. This compound was found in a trace amount.

(6). *p*-Nitrophenol: the parent peak occurred at *m/e* 139. The P-30 peak indicates the loss of NO from the rearranged nitro group.

(7). 2,4,6-Trichlorophenol: the parent ion appeared at *m/e* 196. The isotopic abundances at the P+2, P+4, and P+6 peaks indicate the presence of three chlorines. The P-35 peak shows the loss of one of the three chlorines.

(8). 2,4,6-Trichloro-4'-amino-diphenyl ether: the parent peak appeared at *m/e* 287. The fragmentation pattern was not distinct to characterize.

(9). 2,4-Dichloro-4'-nitro-diphenyl ether: the parent peak occurred at *m/e* 283. It is most likely that one of the ortho chlorines will be readily lost during irradiation.



The parent peak appeared at *m/e* 279. The P-17, P-64, P-97, and P-114 peaks indicate the successive losses of OH, NO, OH, O, OH, and OH from the structure. The fragmentation is consistent with what is expected. This product will arise from the replacement of chlorines by hydroxyl groups.

Besides those compounds identified, some other products were also present. Identification of those products was not possible due to their poor resolution on glc and the paucity of the amounts. As photolysis proceeds, some polymerized products appeared. In addition, in an attempt to confirm the identities of the products, the 10-day irradiated mixture dissolved in a small amount of acetone was applied as a band on pre-coated tlc plates and developed in solvent C for about 1.5 hrs.

Quite a large amount remained at the origin, comprising black-colored material. Four bands were scraped off the plates, extracted with acetone, and concentrated to a small volume by bubbling with purified nitrogen, separately. Only one band could be characterized by ir, glc, and ms (direct probe). This product turned out to

be the above-mentioned 2,4,6-trichloro-3-hydroxy-4'-nitro-diphenyl ether. The ir spectrum exhibits the characteristic OH stretching absorption in the 3,200-3,600 cm^{-1} region. The glc analyses on column A show the retention times of 2,4,6-trichloro-3-hydroxy-4'-nitro-diphenyl ether, MO-338, 2,4-dichloro-4'-nitro-diphenyl ether, and 2,4,6-trichloro-phenol to be 49.9 min., 39 min., 34.4 min., and 17.6 min., respectively.

Basically, no difference was recognized between 2- and 10-day photolyses. However, it seems likely that more hydroxylated products will be formed in the 10-day photolysis.

Products of MC-4379 photolysis in cyclohexane:

Gas chromatogram of these products is shown in Fig.10. The following compounds were identified by a combination of glc and ms.

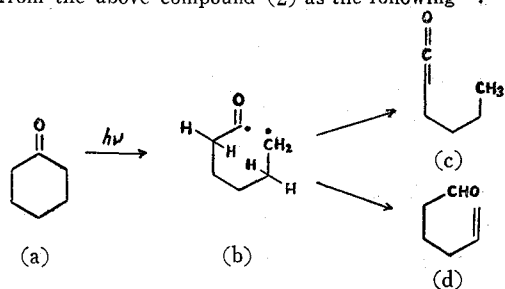
(1). Cyclohexanol (): the molecular ion occurred at *m/e* 100.

(2). Cyclohexanone (): the molecular ion appeared at *m/e* 98.

(3). 1-Hexenone or 1-hexenal: the molecular ion appeared at *m/e* 98.



It is known that these structures are formed from the above compound (2) as the following⁽⁸⁾.



The α -cleavage may be viewed as a homolytic fission to formula (b) which can undergo intramolecular abstraction of a hydrogen atom from the carbon adjacent to the acyl radical giving the ketene (c) or from the carbon adjacent to the alkyl radical giving the unsaturated aldehyde (d).

(4). Dicyclohexyl ether ():

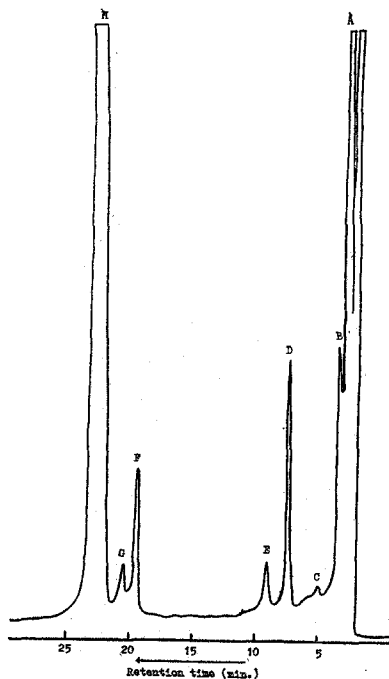


Fig. 10. Gas chromatogram of products from MC-4379 photolysis for 48 hrs in cyclohexane, temperature programmed from 110° to 230°, 7.5°/min.

A: Cyclohexanol, B: Cyclohexanone, C: Unknown, D: 1-Hexenone or 1-Hexenal, E: Dicyclohexyl ether, F: 2,4-dichloro-3'-carboxymethyl-4'-amino-diphenyl ether, G: Monodechlorinated MC-4379, H: Unchanged MC-4379

the parent ion occurred at m/e 182. The P-83 ($P-C_6H_{11}$), P-99 ($P-C_6H_{11}O$), and P-113 ($P-C_6H_{11}$, O, CH_2) peaks were in good agreement with the expected fragments⁽⁶⁾. It seems likely that this product will arise from the condensation of two molecules of cyclohexanol by irradiation.

(5). 2,4-Dichloro-4'-nitro-diphenyl ether: the parent ion occurred at m/e 283. It is possible that the decarboxymethylation from the parent compound and hydrogen abstraction from cyclohexane will occur to give the above structure. The amount was too small to be further characterized.

(6). 2,4-Dichloro-3'-carboxymethyl-4'-amino-diphenyl ether (amino-MC-4379): the isotopic abundances of the P+2 and P+4 peaks are consistent with those of the authentic compound. The P-31 peak indicates the loss of OCH_3 .

(7). Monodechlorinated MC-4379: the parent ion appeared at m/e 307. The P+2 peak is in good agreement with the expected isotopic abundance, indicating the loss of one chlorine.

(8). Unchanged MC-4379 (parent compound): the parent peak occurred at m/e 341. The isotopic abundances of the P+2 and P+4 peaks are well indicative of the presence of two chlorines. The P-31 peak is also consistent with the expected fragmentation. One product having the molecular ion at m/e about 100 could not be identified. Amino-MC-4379 is the predominant product. The above results indicate that photoreduction of nitro to amino group and photodechlorination are the main processes in cyclohexane solution phase photolysis.

Products of MC-4379 photolysis in methanol:

The following products were identified by the glc-ms method.

(1). Unchanged MC-4379: the parent ion occurred at m/e 341. The P+2 (67% relative to the parent peak) and P+4 peaks are in good agreement with the isotopic abundances. The P-31 and P-101 peaks indicate the successive losses of OCH_3 and two chlorines from the parent compound.

(2). Methyl formate: the parent peak appeared at m/e 60. The P-15 and P-31 peaks indicate $P-CH_3$ and $P-OCH_3$, respectively.

(3). 2,4-Dichlorophenol: the parent peak occurred at m/e 162. The P+2 (67% relative to the parent ion) and P+4 peaks indicate the presence of two chlorines. The P-35 ($P-Cl$) peak was also observed.

(4). 2,4-Dichloro-6-methoxy-phenol: the parent peak appeared at m/e 192. The P+2 and P+4 peaks were recognized, but not distinct.

(5). 2,4-Dichloro-3'-carboxymethyl-4'-amino-diphenyl ether (amino-MC-4379): the parent ion appeared at m/e 311. The P+2 (about 80% relative to the parent ion) and P+4 peaks were observed. The P-31 peak represents $P-OCH_3$.

(6). 2-Methoxy-4-chloro-3'-carboxyl-4'-nitro-diphenyl ether: the parent peak occurred at m/e 323. The P+2 peak indicates the presence of one

nlorine. The P-31, P-61, and P-112 peaks correspond to P-OCH₃, P-OCH₃, NO, and P-OCH₃, NO, O, Cl, respectively.

Products of MC-4379 photolysis in distilled water:

Products isolated from tlc plates and identified by the combined glc and ms include the following.

(1). 3-Carboxymethyl-4-nitrophenol: in the direct probe mass spectrum, the parent ion occurred at m/e 197. The P-31 peak represents P-OCH₃, the other fragments being indistinct. On tlc, the R_f values of this product in solvents B and C were 0.508 and 0.549, respectively. These values are identical with those of the authentic compound. The ir spectrum is consistent with that of the authentic compound, exhibiting the strong OH stretch at 3,000 to 3,500cm⁻¹, carbonyl stretch at 1670 cm⁻¹, and almost the same finger print region.

(2). 2,4-Dichloro-3'-hydroxy-4'-nitro-diphenyl ether: in ms(direct probe), the parent ion appeared at m/e 299. The isotopic abundances at the P+2 and P+4 peaks indicate the presence of two chlorines. The P-30 peak amounts to P-NO from the rearranged nitro group.

On tlc, the R_f values of this product in solvents B and C are 0.255 and 0.58, respectively. For comparison, the R_f values of 2,4-dichloro-3'-carboxyl-4'-amino-diphenyl ether in the same solvents were shown to be 0.448 and 0.55, respectively. Under an ultraviolet lamp, these two compounds phosphoresce brightly, but they are completely different from each other based on the R_f values. The ir spectrum shows the OH stretching absorption in the 3,000 to 3,500 cm⁻¹ region.

(3). 2,4-Dichloro-6-hydroxy-3'-carboxymethyl-4'-nitro-diphenyl ether: the mass spectrum of direct probe shows the parent ion to occur at m/e 357. The isotopic abundances at the P+2 and P+4 peaks prove the presence of two chlorines. The P-17 and P-31 peaks represent P-OH and P-OCH₃, respectively. The ir spectrum shows the OH stretch in the region of 3,100 to 3,500 cm⁻¹ and the characteristic carbonyl absorption at

1,700 cm⁻¹,

(4). 2,4-Dichloro-3'-carboxymethyl-4'-hydroxy-diphenyl ether: in the direct probe mass spectrum, the parent ion occurred at m/e 312. The P+2 and P+4 peaks were enough to support the presence of two chlorines. The P-1, P-17, and P-31 peaks correspond to P-H, P-OH, and P-OCH₃, respectively. The ir spectrum was not distinct enough to show the OH stretch, but the carbonyl absorption occurred at 1,650 cm⁻¹. This product was isolated from the undecomposed MC-4379 band which was scraped off the tlc plates, extracted with *n*-hexane, and concentrated to a small volume by bubbling with nitrogen gas. This concentrated hexane solution was applied on 20×20 cm precoated tlc plates as a band and developed in solvent A. The predominant band was collected as the above product by the same procedures. This compound was first considered to be amino-MC-4379. However, the ir, ms, and glc confirmed that they are completely different. For comparison, the R_f values of this product and amino-MC-4379 in solvent A were 0.44 and 0.17, respectively.

(5). Undecomposed MC-4379: in the direct probe ms, the fragmentation behavior was all the same as the above mentioned, the parent ion occurring at m/e 341.

(6). 2,4-Dichloro-3'-carboxymethyl-4'-amino-diphenyl ether (amino-MC-4379): this was identified as a minor product with the parent ion occurring at m/e 311 in ms.

(7). 2,4-Dichlorophenol: the parent peak occurred at m/e 162. This compound was detected as a minor product, presumably due to the loss resulting from its high volatility.

(8). *p*-Nitrophenol: the parent peak appeared at m/e 139. This must be formed from the decarboxymethylation, ether linkage cleavage of the parent compound, and hydrogen abstraction from water. It was detected only in a trace amount.

(9). 2,3'-Dihydroxy-4-chloro-4'-nitro-diphenyl ether: the parent peak appeared at m/e 281. It was detected only as a trace product, still indicating the possibility of decarboxymethylation

and dechlorination. It is likely that the radicals formed will abstract hydrogen from water.

(10). 2,3',4-Trihydroxy-4'-amino-diphenyl ether: the parent ion occurred at m/e 233. Only a trace amount was detected. This product shows the possibility of the nitro group reduction, decarboxymethylation, and dechlorination, followed by the replacement by hydroxyl groups.

(11). 2,4-Dichloro-4'-nitro-diphenyl ether (Nitrofen): the parent peak appeared at m/e 283. It shows the possibility of decarboxymethylation by irradiation. This turned out to be a minor product. Besides the above, some trace products could not be identified. In this aqueous photolysis, compound (4) was the predominant product, indicating the readiness of the nitro group replacement by hydroxyl group. Quite a large amount of methyl formate will prove the decarboxymethylation. The ether linkage cleavage was also thought to be one of the main reactions.

Products of 3-carboxymethyl-4-nitrophenol photolysis in methanol:

(1). Methyl phenyl ether (anisole): on ms, the parent ion occurred at m/e 108. The P-31 peak corresponding to P-OCH₃ is in good agreement with the fragment species of the authentic compound. This product strongly indicates the possibility that the denitration, decarboxymethylation, and replacement of hydroxyl group by methoxy group can occur in methanol solution. On glc, the retention time (temperature programming on column A) was 3.7 min., being consistent with that of the authentic compound.

(2). 3-Methoxy-4-nitrophenol: on ms, the parent ion appeared at m/e 169. The P-31 peak corresponds to P-OCH₃. On glc, the retention time was 23 min., representing one of the main products.

(3). 3-Carboxymethyl-4-nitrophenol (Unchanged parent compound): the ms shows that the parent ion occurred at m/e 197, giving the P-31 (P-OCH₃), P-48 (P-OCH₃, OH), and P-61 (P-OCH₃, NO) peaks as fragment species. The retention time on glc (on column A) was 26.1 min., being identical with that of the authentic

compound.

(4). 1-Methoxy-3-carboxymethyl-4-nitrobenzene: the parent ion occurred at m/e 211, showing the P-30 (P-NO), P-31 (P-OCH₃), and P-62 (P-OCH₃, OCH₃) peaks as the prominent fragment species. The glc exhibits the retention time to be 28.75 min.

(5). *p*-Nitrophenol: the parent ion appeared at m/e 139, representing a minor product. This will indicate the possibility of decarboxymethylation in methanol.

(6). 1,5-Dimethoxy-3-carboxymethyl-4-nitrobenzene: the parent ion appeared at m/e 241, but had an indistinct fragmentation pattern. It is considered to be a trace amount. In the photolysis of methanol solution, the decarboxymethylation followed by methoxylation and the replacement of hydroxy group by methoxy group were the predominant reactions, resulting in products (2) and (4), respectively.

Products of 3-carboxymethyl-4-nitrophenol photolysis in distilled water:

The following compounds were identified as products.

(1). 3-Hydroxy-4-nitrosophenol: on ms, the parent ion occurred at m/e 139, showing P-31 (P-NO, H, weak) and P-32 (P-NO, H, H, strong) peaks as noticeable fragment species⁽⁵⁾. On glc, the retention time was 20.25 min. This was recognized as a trace product.

(2). 3-Hydroxy-4-nitrophenol: the parent ion appeared at m/e 155. The prominent fragment species correspond to the P-17 (P-OH), P-30 (P-NO), and P-46 (P-NO₂) peaks. The retention time on glc was 21.75 min.

(3). Undecomposed parent compound: the parent ion occurred at m/e 197, having the prominent P-31 peak (P-OCH₃). The retention time on glc was 25.7 min.

(4). 3-Carboxymethyl-4-nitrosophenol: the parent ion appeared at m/e 181. The strong P-31 peak corresponds to the loss of OCH₃ group. On glc, the retention time was 27.75 min. In the cases of 24 and 58 hr. irradiations, compound (2) was the main product. However, as the photolysis

proceeded after 90 hr. irradiation, the compound (4) increased remarkably, predominating over all the other products including parent compound especially in 336 hr. photolysis.

In aqueous solution, the parent compound undergoes decarboxymethylation followed by hydroxylation by hydroxyl group stemming from water. However, the nitroso compound formation was the predominant reaction at the later stages of irradiation. Gas chromatogram of products from aqueous solution photolysis of this compound is presented in Fig. 11. Photoproduct D, 3-carboxymethyl-4-nitrosophenol is most remarkable. Fig. 12, 13 present the nmr spectra in deuterated chloroform (60 MHz) of 3-carboxymethyl-4-nitrosophenol and 3-carboxymethyl-4-nitrosophenol (photoproduct), respectively. It is seen from these data that the OCH_3 group was still intact

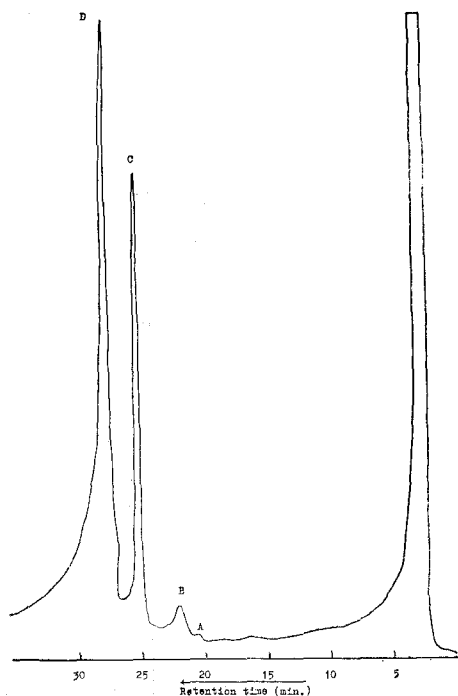


Fig. 11. Gas chromatogram of photoproducts from aqueous solution photolysis of 3-carboxymethyl-4-nitrosophenol for 90 hrs, temperature programmed from 70° to 230°
 A: 3-Hydroxy-4-nitrosophenol, B: 3-Hydroxy-4-nitrosophenol, C: Undecomposed parent compound, D: 3-Carboxymethyl-4-nitrosophenol

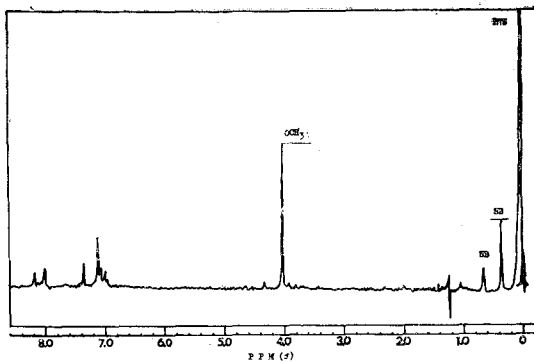


Fig. 12. Nmr spectrum of 3-carboxymethyl-4-nitrosophenol in chloroform-d

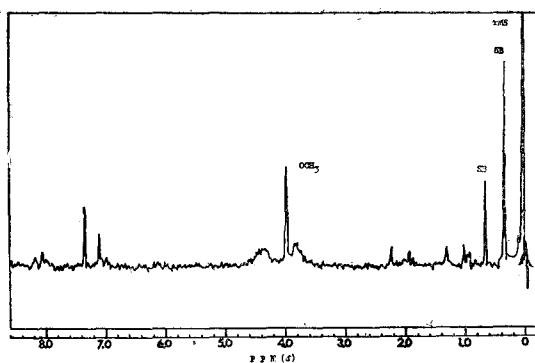


Fig. 13. Nmr spectrum of 3-carboxymethyl-4-nitrosophenol (21.5 day photoproduct) in chloroform-d

(δ 4.0) during photolysis and both spectra are identical, which supports the fact that the carboxymethyl group in the parent compound did not undergo the Fries rearrangement known to a variety of aromatic esters, only to cause the conversion of nitro to nitroso group in this type of ester compounds. The decarboxymethylation is suggestive of the possibility that MC-compounds with the carboxymethyl group as one of the substituents on one of the benzene rings will undergo such reaction in an aqueous solution.

Products of MC-5127 photolysis in cyclohexane:

- (1). Cyclohexanol (2). Cyclohexanone (3). 1-Hexenone or 1-hexenal (4). Dicyclohexyl ether:

the parent ion occurred at m/e 182, giving the P-83 ($P-C_6H_{11}$), P-99 ($P-C_6H_{11}O$), and P-113 ($P-C_6H_{11}, O, CH_2$) peaks as the characteristic fragment species. This product is thought to arise from the condensation of two molecules of cyclohexanol by irradiation.

(5). 2,4-Dichloro-4'-nitro-diphenyl ether: the parent ion appeared at m/e 283. The isotopic abundances at the P+2 and P+4 peaks indicate the presence of two chlorines. The P-30 (P-NO) and P-81 (P-NO, O, Cl) peaks were suggestive of the expected fragmentation. It can be observed that decarboxyethylation more readily occurs than decarboxymethylation in other MC-compounds.

(6). 2,4-Dichloro-3'-carboxyethyl-4'-amino-diphenyl ether: the parent ion occurred at m/e 325, also having the P+2 and P+4 peaks. The P-31 ($P-OCH_3$) peak was recognized. From the intensity of the parent ion, it is likely that the photoreduction predominates over the other reactions in cyclohexane solvent.

(7). 4-Chloro-3'-carboxyethyl-4'-nitro-diphenyl ether: the parent ion occurred at m/e 321. The P+2 peak indicates the loss of one chlorine. The P-45 peak corresponds to $P-OCH_2CH_3$. The dechlorination is thought to occur in a trace amount based on the observed spectrum.

(8). 2,4-Dichloro-3'-carboxyethyl-4'-nitro-diphenyl ether (unchanged parent compound): the parent ion occurred at m/e 355. The P+2 and P+4 peaks and the P-30 and P-46 peaks were in characteristic features.

Products of MC-5127 photolysis in methanol:

(1). 2,4-Dichloro-4'-nitro-diphenyl ether: the parent ion occurred at m/e 283. The P+2 and P+4 peaks indicate the presence of two chlorines. The P-30 (P-NO), P-46 (P-NO, O), and P-81 (P-NO, O, Cl) peaks were typical of the fragmentation. The strong spectrum is indicative of the readiness of decarboxyethylation followed by the hydrogen abstraction from solvent methanol more readily than the decarboxymethylation in other MC-compounds to form Nitrofen.

(2). 4-Chloro-3'-carboxyethyl-4'-nitro-diphenyl ether: the parent ion occurred at m/e 323, giving

the P-27 ($P-C_2H_3\cdot$) and P-45 ($P-OCH_2CH_3$) peaks as fragment species⁽⁶⁾. The P+2 peak represents the loss of one chlorine. Only a trace amount of dechlorination is thought to occur based on the weak spectrum.

(3). 2,4-Dichlorophenol: the parent ion occurring at m/e 162 has the P+2 and P+4 peaks indicating two chlorines based on the isotopic abundances. The P-35 peak exhibits the loss of one chlorine. The cleavage of ether linkage in the parent compound is suggested by this product.

(4). *p*-Nitrophenol (m/e : 139): only a trace amount was recognized, resulting from the decarboxyethylation and ether linkage cleavage, followed by hydrogen abstraction from methanol in both cases. The fragmentation was not distinct enough to read due to the paucity of the amount.

(5). 1,3-Dimethoxy-4-nitrobenzene: the parent ion occurred at m/e 183, giving the P-30 (P-NO) and P-46 (P-NO, O) peaks consistent with the expected fragments. This product is considered to arise from the decarboxyethylation and ether linkage cleavage, followed by the methoxyl abstraction from solvent methanol.

(6). Unchanged parent compound: the parent ion occurred at m/e 355. The P-27 ($P-C_2H_3\cdot$) and P-45 ($P-OCH_2CH_3$) peaks were recognized as fragment species.

(7). Methyl formate: the parent ion occurred at m/e 60. The P-29 peak indicates the loss of H and CO to form $(HOCH_2)^+$ (m/e 31) ion⁽⁶⁾. This product suggests the possibility that methyl formate can be formed from ethyl formate by irradiation in methanol solution. Besides the above products, three spectra could not be identified.

Products of MC-5127 photolysis in distilled water:

(1). 2,4-Dichlorophenol (m/e 162): the same spectrum as that of the product in methanol. On glc, the R_t was 13.8 min. consistent with that of the authentic compound.

(2). 3-Carboxyethyl-4-aminophenol: the parent ion occurred at m/e 181. The P-17 peak indicates the loss of OH group. The R_t on glc was 22.8

min.

(3). 2,4-Dichloro-4'-nitro-diphenyl ether (m/e 283): the same spectrum as in the methanol case. On glc, the Rt was 33.7 min. consistent with that of Nitrofen. It is suggested that decarboxymethylation followed by hydrogen abstraction is one of the predominant reactions.

(4). 2,4-Dichloro-3'-carboxyethyl-4'-amino-diphenyl ether: the parent ion occurred at m/e 325. Only a weak spectrum was recognized. The P-108 peak indicates P-Cl, COOCH₂CH₃. On glc, the Rt was 41.5 min.

(5). 4-Chloro-3'-carboxyethyl-4'-nitro-diphenyl ether (m/e 321): only a trace was detected on ms. On glc, the Rt was 44.5 min.

(6). 4-Chloro-3'-hydroxy-4'-amino-diphenyl ether (m/e 235): only a trace was recognized.

(7). Unchanged parent compound (m/e 355)

Products of MC-3761 photolysis in cyclohexane:

The following were identified as products by the combined glc-ms method.

(1). Cyclohexanol (m/e 100) (2). Cyclohexanone (m/e 98)

(3). 1-Hexenone or 1-hexenal (m/e 98)

(4). Dicyclohexyl ether (m/e 182)

(5). 4,6-Dichloro-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent peak appeared at m/e 341. The P+2 and P+4 peaks indicate the presence of two chlorines resulting from the loss of one chlorine from the parent compound. The strong P-31 peak corresponding to P-OCH₃ suggests the presence of the carboxymethyl group.

(6). 2,4,6-Trichloro-3'-carboxymethyl-4'-amino-diphenyl ether (amino-MC-3761): the parent peak occurred at m/e 345, giving the intense fragment at the P-31 (P-OCH₃). The isotopic abundances at the P+2, P+4, and P+6 peaks indicate the presence of three chlorines.

(7). Undecomposed parent compound: the parent ion occurred at m/e 375. The intense P-31 peak and P+2, P+4, and P+6 peaks support the structure.

From the above observations, it is obvious that the photoreduction of nitro substituent and

the dechlorination, as well as the ether linkage cleavage can occur on a competitive basis.

Products of MC-3761 photolysis in methanol:

Photoproducts identified include the following:

(1). 2,4-Dichloro-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent peak occurred at m/e 341, giving an intense fragment at the P-31 corresponding to P-OCH₃. The P+2 and P+4 peaks indicate the presence of two chlorines. This turned out to be one of the major products, indicating photodechlorination from the benzene ring.^(48,57,58)

(2). Unchanged parent compound: the parent peak at m/e 375. An intense P-31 (P-OCH₃) peak and P+2, P+4, and P+6 peaks were the main features.

(3). 2,4,6-Trichlorophenol: the parent ion appeared at m/e 196, giving an intense P-35 (P-Cl) fragment. The isotopic abundances of the P+2, P+4, and P+6 peaks are indicative of the presence of three chlorines. This material arises from the ether linkage cleavage and abstraction of the hydrogen from the solvent, methanol.

(4). 1-Methoxy-3-carboxymethyl-4-nitrobenzene: the parent ion occurred at m/e 211. The P-31 peak (P-OCH₃) and the strong base peak at P-77 (P-NO₂, OCH₃) support the expected fragmentation of the structure. This product arises from the ether linkage cleavage, followed by the OCH₃ abstraction from methanol, comprising one of the predominant products.

(5). 2,4,6-Trichloro-3'-methoxy-4'-amino-diphenyl ether: the parent peak occurred at m/e 317, giving the P-31 (P-OCH₃) peak as an intense fragment. The P+2, P+4, and P+6 peaks were recognized in support of the structure. It will be conceivable that the photoreduction of the nitro to amino group and the decarboxymethylation followed by the OCH₃ abstraction from solvent methanol can occur in an appreciable amount.

(6). 2,6-Dimethoxy-4-chloro-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent ion appeared at m/e 367. The P+2 and P-31 (P-OCH₃) peaks suggest the structure. Only a trace amount

was detected.

(7). Methyl formate: the parent peak appeared at m/e 60. The P-15 and P-31 peaks corresponding to the P-CH₃ and P-OCH₃ respectively fit the expected fragmentation. This product implies the possibility of decarboxymethylation from the parent compound followed by the hydrogen abstraction from methanol. An appreciable amount was detected.

(8). 2,4,6-Trichloro-3'-carboxymethyl-4'-aminodiphenyl ether: the parent ion occurred at m/e 345, exhibiting the P-31 (P-OCH₃) peak as a fragment. The presence of three chlorines was recognized by the isotopic abundances of the P+2, P+4, and P+6 peaks. It is seen that the nitro group can be reduced to amino group in methanol.

Products of MC-3761 photolysis in distilled water:

(1). Methyl formate: the parent ion appeared at m/e 60, giving the P-15 (P-CH₃) and P-31 (P-OCH₃) peaks as fragment species. On glc, the retention time was 8.6 min., being identical with that of the authentic compound. It is obvious that this product was most readily formed during irradiation, based on the observed peak height of the gas chromatogram.

(2). 2,4-Dichlorophenol: the parent ion appeared at m/e 162. The isotopic abundances at the P+2 and P+4 peaks indicate the presence of two chlorines. The fragmentation pattern was not distinct, because of its trace formation. However, it is suggested that the ether linkage cleavage and dechlorination from the benzene ring can occur. The Rt on glc was 14.25 min.

(3). 2,4,6-Trichlorophenol: on ms, the parent peak appeared at m/e 196, exhibiting the P-35 (P-Cl) as an intense fragment. The P+2, P+4, and P+6 peaks support the three chlorine substituents. On glc, the rather large peak, the Rt of which was 17.25 min., supports the readiness of the photochemical cleavage of the ether linkage, followed by the hydroxyl abstraction from water.

(4). 3-Carboxymethyl-4-nitrosophenol: the pa-

rent ion occurred at m/e 181, the fragment species being indistinct because of the paucity of its formation during irradiation. The Rt on glc was 22.2 min., only a small peak area being recognized.

(5). 3-Hydroxy-4-nitrophenol: the parent ion occurring at m/e 155 has the P-17 peak as a fragment suggestive of P-OH. Only a trace amount was detected. The Rt was 24.05 min. on glc.

(6). 3-Carboxymethyl-4-nitro-6-hydroxyphenol: the parent peak occurred at m/e 213, giving the P-30 (P-NO) and P-31 (P-OCH₃) fragment species. Only a trace amount was recognized. The Rt on glc was 25.1 min.

(7). 2,4,6-Trichloro-3',6'-dihydroxy-4'-aminodiphenyl ether: the parent ion occurred at m/e 319. The P-34 (P-OH, OH) and P-62 (P-OH, OH, HCN, H \cdot) fragment species are in good agreement with what were expected⁽⁶⁾. The P+2, P+4, and P+6 peaks support the presence of three chlorines. The Rt on glc was 32 min. Based on the rather large peak, this must be one of the main products arising from the reduction of nitro to amino group, the decarboxymethylation followed by the hydroxyl abstraction, and the replacement of hydrogen by hydroxyl group from water.

(8). 2,4,6-Trichloro-3'-hydroxy-4'-nitrosodiphenyl ether: the parent ion appeared at m/e 317. The isotopic abundances at the P+2, P+4, and P+6 peaks indicate the presence of three chlorines. The P-30 (P-NO) and P-82 (P-NO, OH, Cl) peaks are consistent with the expected fragment species. On glc, the rather large peak corresponding to this product, the Rt of which is 36.6 min., represents the readiness of the decarboxymethylation followed by the immediate hydroxyl abstraction from water and the photoreduction mechanism leading to the nitroso group formation (see Fig. 8).

(9). 2,4-Dichloro-3'-carboxymethyl-4'-nitrodiphenyl ether: the parent ion occurring at m/e 341 indicates the loss of one chlorine. Because of the modicum of this product, the fragmentation pattern was not distinct. On glc, the Rt was

47.25min.

(10). The unchanged parent compound: the parent ion occurring at m/e 375 has the same fragmentation pattern as before. On glc, the Rt was 55.25 min.

Products of MC-6063 photolysis in cyclohexane:

(1). Cyclohexanol (m/e 100)
(2). Cyclohexanone (m/e 98)
(3). 1-Hexenone or 1-hexenal (m/e 98)
(4). Dicyclohexyl ether (m/e 182)
(5). 2-Chloro-4-fluoro-3'-carboxymethyl-4'-amino-diphenyl ether: the parent ion occurred at m/e 295. The isotopic abundance at the P+2 peak indicates the presence of one chlorine. The P-35 (P-F, NH₂), P-101 (P-F, NH₂, Cl, OCH₃), and P-129 (P-F, NH₂, Cl, OCH₃, CO) peaks were in good agreement with the expected fragment species. The photoreduction of nitro to amino group was indicated by this product.

(6). 4-Fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent ion occurred at m/e 291. The absence of the P+2 peak proves the loss of the chlorine. The P-31 (P-OCH₃) peak was noticeable. This product shows the preferential loss of chlorine in photolysis.

(7). Unchanged parent compound (2-Chloro-4-fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether): the P+2 peak is indicative of the presence of one chlorine. The P-31 (P-OCH₃) and P-59 (P-COOCH₃) peaks were characteristic features. The decarboxymethylation product was not detected based on the spectrum.

Products of MC-6063 photolysis in methanol:

(1). Methyl formate (m/e 60): the P-31 peak appeared as a fragment.

(2). 4-Fluoro-4'-nitro-diphenyl ether: the parent ion occurred at m/e 233. The P-19 (P-F) peak was noticeable as a fragment.

(3). 4-Fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent ion appeared at m/e 291. The absence of the P+2 peak exhibits the loss of the chlorine. The P-31 peak corresponds to P-OCH₃.

(4). 2-Chloro-4-fluorophenol: the parent peak

appeared at m/e 146. The fragmentation was indistinct due to its small amount.

(5). 1-Methoxy-3-carboxymethyl-4-nitrobenzene: the parent ion occurred at m/e 211. The P-59 peak indicates the loss of the carboxymethyl group.

(6). The unchanged parent compound: the parent ion appeared at m/e 325. The isotopic abundance of the P+2 peak indicates the presence of one chlorine. The P-31 (P-OCH₃) and P-59 (P-OCH₃, CO) peaks are agreeable. Besides these products, one compound could not be identified due to its weak spectrum (m/e : about 279).

Products of MC-6063 photolysis in distilled water:

(1). Methyl formate (m/e 60): the P-31 peak corresponds to the P-OCH₃ ion. On glc, the Rt was 8.7 min.

(2). 2-Chloro-4-fluorophenol: the parent ion occurred at m/e 146. The isotopic abundance of the P+2 peak confirms the presence of one chlorine. The P-35 (P-Cl) and P-54 (P-Cl, F) peaks are in good agreement with the actually expected fragments. This compound turned out to be one of the predominant products resulting from the ether linkage cleavage of the parent MC-6063. On glc, the Rt was 10 min.

(3). 3-Carboxymethyl-4-nitrophenol: the parent ion appeared at m/e 197, showing an indistinct fragmentation largely due to its small quantity. On glc, the Rt was 28 min.

(4). 2-Chloro-3',4'-dihydroxy-4'-nitro-diphenyl ether: the parent ion appeared at m/e 281. Only a trace spectrum was obtained, indicating the possibility of the decarboxymethylation and defluorination, followed by hydroxyl abstractions from water. The Rt on glc was 31.8 min.

(5). 4-Fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent ion appeared at m/e 291. The absence of the characteristic P+2 peak proves the photodechlorination. The P-31 peak (P-OC H₃) was noticeable. Based on the observed intense spectrum, it seems likely that this will be one of the main photoproducts. On glc, the Rt was 33.5 min.

(6). 2-Chloro-3'-carboxymethyl-4'-nitro-diph-

enyl ether: the parent ion occurred at m/e 307, giving the characteristic $P+2$ peak. The $P-35$ peak exhibits the loss of chlorine as a fragment species. The photochemical defluorination was indicated by this spectrum.

(7). The unchanged parent compound (m/e 325): On glc, the R_t was 38 min.

Products of MC-7181 photolysis in cyclohexane:

- (1). Cyclohexanol
- (2). Cyclohexanone
- (3). 1-Hexenone or 1-hexenal
- (4). Dicyclohexyl ether

(5). 2,4-Dichloro-6-fluoro-3'-carboxymethyl-4'-amino-diphenyl ether: the parent ion occurred at m/e 329, giving the $P-31$ ($P-OCH_3$) peak as a fragment species. The isotopic abundances at the $P+2$ and $P+4$ peaks prove the presence of two chlorines.

(6). 4-Chloro-6-fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent ion occurring at m/e 325 shows the $P-31$ ($P-OCH_3$) peak as a fragment. The $P+2$ peak indicates the loss of one chlorine.

(7). 2,4-Dichloro-6-fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether (Unchanged parent compound): the parent peak appeared at m/e 359. The presence of two chlorines was indicated by the isotopic abundances at the $P+2$ and $P+4$ peaks. The $P-31$ ($P-OCH_3$) and $P-59$ ($P-COOCH_3$) or $P-30$ ($P-NO$) and $P-46$ ($P-NO_2$) peaks were consistent with the expected fragments. In this case, the decarboxymethylation product was not recognized.

Products of MC-7181 photolysis in methanol:

- (1). Unchanged parent compound
- (2). 2,4-Dichloro-4'-nitro-diphenyl ether: the parent ion occurred at m/e 283. Two chlorines were indicated by the isotopic abundances at the $P+2$ and $P+4$ peaks. The $P-30$ ($P-NO$) and $P-46$ ($P-NO_2$) peaks were in good agreement with the expected fragments. This product is thought to arise from the decarboxymethylation and defluorination, followed by the hydrogen abstraction from solvent methanol.

(3). 4-Chloro-6-fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent peak appeared at m/e 325. The $P+2$ peak indicates the loss of one chlorine. The $P-31$ ($P-OCH_3$) peak was recognized.

(4). 6-Fluoro-4'-nitro-diphenyl ether: the parent ion occurred at m/e 233. The $P-19$ ($P-F$) peak was remarkable. The m/e 138 ion was present as a fragment species. This product will result from the decarboxymethylation and dechlorination, followed by the hydrogen abstraction from the solvent. This was one of the main products.

(5). 2,4-Dichloro-6-fluoro-4'-nitro-diphenyl ether: the parent ion occurred at m/e 301. The presence of two chlorines was indicated by the isotopic abundances at the $P+2$ and $P+4$ peaks. The $P-19$ ($P-F$) peak was shown as a fragment. The m/e 108 ion was indicative of the *p*-nitro-phenoxy ion as a fragment. This product is thought to result from the decarboxymethylation followed by the hydrogen abstraction. Only a small amount was recognized.

(6). 2,4-Dichloro-6-fluorophenol: the parent peak appeared at m/e 180. The isotopic abundances at the $P+2$ and $P+4$ peaks prove the presence of two chlorines. The $P-19$ ($P-F$) peak was remarkable as a fragment. This compound is thought to arise from the ether linkage cleavage by irradiation.

(7). 4-Nitroanisole: the parent ion occurred at m/e 153. The fragmentation was not able to read due to the paucity of the amount. Only a trace was recognized, indicating the possibility of decarboxymethylation followed by the hydrogen abstraction and ether linkage cleavage followed by the methoxyl abstraction from the solvent.

(8). Methyl formate (m/e 60): the $P-31$ ($P-OCH_3$) peak was remarkable.

(9). The unchanged parent compound

Products of MC-7181 photolysis in distilled water:

(1). Methyl formate: the parent ion occurred at m/e 60. The $P-31$ ($P-OCH_3$) peak was prominent. On glc, the R_t was 8.5 min.

(2). 2,4-Dichloro-6-fluorophenol: the parent ion appeared at m/e 180. The same fragmentation

was observed as the above. The Rt on glc was 22.2 min. Only a small amount was shown to be formed.

(3). 3-Hydroxy-4-nitrophenol: the parent ion occurred at m/e 155. The P-17 ion indicates the loss of one hydroxyl group. Only a trace amount was thought to be formed based on the weak spectrum. On glc, the Rt was 24 min.

(4). 2,4-Dichloro-6-fluoro-4'-nitro-diphenyl ether: the parent ion appeared at m/e 301. The presence of two chlorines was exhibited by the isotopic abundances of the P+2 and P+4 peaks. The P-30 (P-NO) and P-46 (P-NO₂) peaks were consistent with the expected fragments. This compound is shown to be one of the main products. On glc, the Rt was 30.6 min.

(5). 4-Chloro-6-fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent ion occurred at m/e 325. The P-31 (P-OCH₃) peak was noticeable. An appreciable amount was formed, indicating the preferential dechlorination in photolysis. On glc, the Rt was 40 min.

(6). Mono-hydroxylated MC-7181: the parent ion occurred at m/e 375. The P-17 peak indicates the loss of hydroxyl group. The presence of two chlorines was shown by the P+2 and P+4 peaks. Only a trace amount was recognized.

(7). 2,4-Dichloro-3,6'-dihydroxy-6-fluoro-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent ion appeared at m/e 391. The noticeable P-17 peak indicates the loss of hydroxyl group. Only a trace amount was detected.

(8). 2,4-Dichloro-6,6'-dihydroxy-3'-carboxymethyl-4'-nitro-diphenyl ether: the parent ion appeared at m/e 373. The presence of two chlorines was indicated by the isotopic abundances at the P+2 and P+4 peaks. It is thought to be a minor product.

(9). Unchanged parent compound

Summary

Eight substituted diphenyl ether herbicides and some of their photoproducts were studied in terms of solution phase photolysis under simulated

environmental conditions by using a Rayonet photochemical reactor. The test compounds absorbed sufficient light energy at the wavelength of 300 nm to undergo various photoreactions. All the photoproducts were confirmed by means of tlc, glc, ir, ms, and/or nmr spectrometry. The results obtained are summarized as follows:

Solution phase photolysis of C-6989:

An exceedingly large amount of *p*-nitrophenol formed strongly indicates the readiness of the ether linkage cleavage of this compound as the main reaction in all solvents used. Photoreduction of nitro to amino group(s) and photooxidation of trifluoromethyl to carboxyl group were recognized as minor reactions.

Aqueous photolysis of *p*-nitrophenol:

Quinone(0.28%), hydroquinone (0.66%), and *p*-aminophenol (0.42%) were confirmed as photoproducts, in addition to a relatively small amount of an unknown compound. The mechanisms of formation of these products were proposed to be the nitro-nitrite rearrangement via $n \rightarrow \pi^*$ excitation and the photoreduction through hydrogen abstractions by radicals, respectively.

Solution phase photolysis of Nitrofen:

Photochemical reduction leading to the *p*-amino derivative was the main reaction in *n*-hexane. In aqueous solution, the photoreduction of nitro to amino group and hydroxylation predominated over the ether linkage cleavage. Nucleophilic displacement of the nitro group by hydroxide ion and replacement of chlorine substituents by hydroxyl group or, to a lesser extent, hydrogen were also observed as minor reactions.

Solution phase photolysis of MO-338:

Photoreduction of the nitro to amino group was marked in the *n*-hexane solution photolysis. In the aqueous solution, photoreduction of the nitro substituent and hydroxylation were the main reactions with replacement of chlorine substituents by the hydroxyl group and hydrogen, and cleavage of the ether linkage as minor reactions.

Photolyses of MC-4379, MC-3761, MC-5127, MC-6063, and MC-7181 in *n*-hexane and cyclohexane:

Photoreduction of the nitro group leading to the

corresponding amino derivative and replacement of one of the halogen substituents by hydrogen from the solvent used were the key reactions in each compound.

Aqueous photolysis of MC-4379:

Cleavage of the ether linkage, replacement of the carboxymethyl by hydroxyl group, hydroxylation, and replacement of the nitro by hydroxy group were prominent with photoreduction and dechlorination as minor reactions.

Aqueous photolysis of MC-3761:

Cleavage of the ether linkage, replacement of the carboxymethyl by hydroxyl group, and photoreduction followed by hydroxylation were the main reactions.

Aqueous photolysis of MC-5127:

Replacement of carboxyethyl by hydrogen was predominant with ether linkage cleavage, photoreduction, and dechlorination as minor reactions. It was obvious that the decarboxyethylation proceeded more readily than decarboxymethylation occurring in the other compounds.

Aqueous photolysis of MC-6063:

Cleavage of the ether linkage and photodechlorination were the main reactions.

Aqueous photolysis of MC-7181:

Replacement of the carboxymethyl group by hydrogen and monodechlorination were the remarkable reactions. Cleavage of the ether linkage and hydroxylation were thought to be the minor reactions.

Aqueous photolysis of 3-carboxymethyl-4-nitrophenol:

The photo-induced Fries rearrangement common to aromatic esters did not appear to occur in the carboxymethyl group of this type of compound. Conversion of nitro to nitroso group was the main reaction.

Acknowledgment

The author wishes to give his thanks to FAO for financial support throughout this work. Dr. Matthew J. Zabik, acting director of Pesticide Research Center, Michigan State University, is

hereby gratefully acknowledged for the helpful guidance and assistance with all this investigation. Special appreciation is also cordially expressed to Dr. Chun Yung Lee, Dr. C. K. Park, and all the faculty members of the Department of Agricultural Chemistry, College of Agriculture, Seoul National University, for invaluable advice and suggestions.

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