

## Photochemistry of Bioactive Compounds

### Photochemistry of Selected 2-Chloro- and 2-Methylthio-4,6-di-(Alkylamino)-*s*-Triazine Herbicides

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Atrazine (I), Propazine (II), and Simazine (III) irradiated in methyl alcohol at 253.7 nm. formed their 2-methoxy analogs: Atraton (IV), Prometon (V), and Simeon (VI), respectively, in yields ranging from 85–95%. Irradiation of I, II, and III in water at 253.7 nm. formed hydroxy-Atrazine (VII), hydroxy-Propazine (VIII), and hydroxy-Simazine (IX), respectively, in good yield. The photolysis of I in ethanol or *n*-butanol yielded the respective 2-ethoxy or 2-*n*-butoxy analog. Ametryne (X), Prometryne (XI), and Simeetryne (XII) photolyzed in methyl, ethyl, or *n*-butyl alcohol, or in

water or benzene at 253.7 nm. formed 4-ethylamino-6-isopropylamino-*s*-triazine, 4,6-bis(isopropylamino)-*s*-triazine, and 4,6-bis(ethylamino)-*s*-triazine, respectively. Yields ranged from 85–95%. Photolysis did not occur under laboratory conditions at wavelengths greater than 300 nm. Spectroscopic studies indicate that these photoreactions occur in natural sunlight. Atraton, Simeon, Prometon, and their respective 2-hydroxy analogs did not undergo photochemical reaction when irradiated in methanol, ethanol, or in water at 253.7 nm.

Ultraviolet light causes the chemical alteration of many pesticides under laboratory conditions (Mitchell, 1961). If such photodecompositions were to occur under field conditions, the result(s) might be of major importance in determining the environmental stability and agricultural use of these compounds. Evaluation of such naturally occurring photoproducts and the investigation of their chemistry, toxicology, and pharmacology would be necessary to evaluate the merit of their continued use.

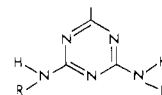
The effects of ultraviolet light on herbicides have been investigated by several researchers. Crosby and Tutass (1966) reported that 2,4-dichlorophenoxyacetic acid (2,4-D) decomposed rapidly in the presence of water and natural sunlight to yield 2,4-dichlorophenol, 4-chlorocatechol, 2-hydroxy-4-chlorophenoxyacetic acid, 1,2,3-benzenetriol, and polymeric humic acids. Rosen and Strusz (1968) found that 3-(*p*-bromophenyl)-1-methoxy-1-methylurea underwent a photolysis reaction when exposed to natural sunlight in aqueous solution. The major product was 3-(*p*-hydroxy-phenyl)-1-methoxy-1-methylurea.

Two objectives stimulated this investigation of the photochemistry of these symmetrical triazine herbicides.

First, a thorough study of the photolysis of these compounds was undertaken to determine the chemical and physical nature of the isolated photoproducts, solvent effect, correlation between the ultraviolet absorbance characteristics of reactants and products and their respective photochemical behavior, and whether or not photodecomposition might be expected to occur under natural conditions. The second objective was to consider any correlation(s) between molecular structure and the nature of these photochemical transformations, and the reported metabolic fate(s) of these compounds in plant and animal systems.

Four groups of the 2-substituted-4,6-di(alkylamino)-*s*-triazine analogs were investigated (Table I). Although all

have some phytotoxicity, the 2-chloro-*s*-triazine analogs are the most widely used group (Neumeyer *et al.*, 1969).



No definitive work has been reported in the literature on the photodecomposition of these compounds (Comes and Timmons, 1965; Jordan *et al.*, 1963, 1965). Several investigators, however, have reported the metabolism of triazine compounds by both enzymatic and nonenzymatic systems in plants and micro-organisms. These investigators found that several plants metabolized the 2-chloro-*s*-triazines to their respective 2-hydroxy analogs (Freed *et al.*, 1961; Montgomery and Freed, 1961; Funderburk and Davis, 1963; Castelfranco *et al.*, 1961; Roth and Knuesli, 1961; Hamilton and Moreland, 1961; Shimabukuro, 1967).

Because of their very low solubility in water, the photolysis of these *s*-triazines was first investigated in methanol solutions. The purposes were to determine what type(s) of photochemical processes occurred upon irradiation and what products were formed. Photodecomposition in aqueous solution was studied in order to evaluate its potential importance in the formation or degradation of a toxic residue in the environment.

#### EXPERIMENTAL

**Material and Methods.** HERBICIDES. The *s*-triazines were obtained from Geigy Agricultural Chemicals, Division of Geigy Chemical Corporation, Ardsley, N. Y. They were received as technical grade (95% purity) and were recrystallized from the appropriate solvent until gas-liquid chromatography (GLC) and thin-layer chromatography (TLC) showed no impurities. Chemical authenticity was supported by infrared spectra (IR) and nuclear magnetic resonance (NMR) spectra.

**SOLVENTS.** Alcohols used in photochemical reactions were glass distilled (Burdick and Jackson Laboratories, Inc.,

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Table I. Substituted Triazine Herbicides

Common Name	Designation	Chemical Name
Atrazine	I	2-Chloro-4-ethylamino-6-isopropylamino- <i>s</i> -triazine
Propazine	II	2-Chloro-4,6-bis(isopropylamino)- <i>s</i> -triazine
Simazine	III	2-Chloro-4,6-bis(ethylamino)- <i>s</i> -triazine
Atraton	IV	2-Methoxy-4-ethylamino-6-isopropylamino- <i>s</i> -triazine
Prometone	V	2-Methoxy-4,6-bis(isopropylamino)- <i>s</i> -triazine
Simetone	VI	2-Methoxy-4,6-bis(ethylamino)- <i>s</i> -triazine
Hydroxy-Atrazine	VII	2-Hydroxy-4-ethylamino-6-isopropylamino- <i>s</i> -triazine
Hydroxy-Propazine	VIII	2-Hydroxy-4,6-bis(isopropylamino)- <i>s</i> -triazine
Hydroxy-Simazine	IX	2-Hydroxy-4,6-bis(ethylamino)- <i>s</i> -triazine
Ametryne	X	2-Methylthio-4-ethylamino-6-isopropylamino- <i>s</i> -triazine
Prometryne	XI	2-Methylthio-4,6-bis(isopropylamino)- <i>s</i> -triazine
Simetryne	XII	2-Methylthio-4,6-bis(ethylamino)- <i>s</i> -triazine

Muskegon, Mich.). At all other times, analytical grade solvents (Mallinckrodt Chemical Works, St. Louis, Mo.) were used. All water used as a solvent in photolysis reactions was distilled, deionized, degassed, and had a pH of 6.90.

**PHOTOCHEMICAL EQUIPMENT.** Reaction vessels were of borosilicate glass, and fitted with Teflon stopcocks and accessories. Standard taper (60/50) Asco Quorn Sleeves (Arthur F. Smith Co., Inc., Pampano Beach, Fla.) were used as seals between the ground glass tapers of the reaction vessel and the inserted immersion well. There was a usable volume of 220–550 ml. after the standard reaction vessels were fitted with an immersion well. Some large-scale reactions in water were photolyzed in a 5000-ml. round bottom flask, fitted with a standard taper (60/50) ground glass joint. Photochemical lamps, immersion wells, and absorption sleeves were obtained from Hanovia Lamp Division, Engelhard Hanovia Inc., Newark, N. J. In all experiments, clear, fused quartz immersion wells (water cooled) were used to hold the light source inside the reaction vessel. Combinations of 200 watt-type S, 450 watt-type L, and 550 watt-type A laboratory photochemical lamps were used as the ultraviolet (UV) radiation sources. These lamps emitted a continuous spectrum from 1367.3 nm. in the IR to at least 222.4 nm. in the near UV region, with a primary UV emission at 253.7 nm. Absorption sleeves consisted of three types of glass: 7910 Vycor, 9700 Corex, and 7740 Pyrex (with UV cutoffs at 210, 250, and 280 nm., respectively).

Water-cooled, quartz immersion wells were used to maintain a constant solution temperature during photolysis reactions. Solution temperature was maintained at approximately 22° C.

**ANALYTICAL EQUIPMENT.** All melting points were determined with an electrothermal melting point apparatus and were uncorrected.

Infrared spectra were determined as potassium bromide disks using a Perkin-Elmer 337 grating spectrophotometer, with a reference beam attenuator (Perkin-Elmer Corporation, Norwalk, Conn.).

Ultraviolet spectra were obtained in analytical solvents, and recorded with a Beckman DB-G grating spectrophotometer (Beckman Instruments, Inc., Fullerton, Calif.).

Nuclear magnetic resonance spectra were recorded using a Varian A-60 high resolution instrument (Varian Associates, Palo Alto, Calif.). Samples were dissolved in spectrophotometric grade carbon tetrachloride, deuterated chloroform-*d*<sub>1</sub>, or methanol-*d*<sub>4</sub>.

Gas-liquid chromatographic analyses were accomplished with a Beckman GC-4 instrument, equipped with a rotary fraction collector and with flame ionization and thermal

conductivity detectors. The column (6-foot × 1/4-inch) used in all analyses was a 5% Carbowax-20 M liquid phase on 60/80 mesh Gas-Chrom Q (Applied Science Laboratories, Inc., State College, Pa.). Operating parameters were generally as follows: column flow of 40 ml. prepurified helium (99.997% purity) per minute; column temperature of 150–230°; detector temperature of 250°.

Thin-layer chromatography was accomplished on precoated analytical plates of silica gel F-254 with fluorescent indicator (Brinkmann Instruments, Inc., Westbury, N. Y.). The solvent system was chloroform–acetone (9:1).

A combination of GLC and TLC was used to determine if samples underwent thermal or catalytic decomposition and/or rearrangement under chromatographic conditions.

Column chromatography was accomplished using 0.8- and 1.5-m. glass chromatographic columns with an inside diameter of 2 cm., and fitted with a coarse porosity fritted glass disk and Teflon stopcock (Fischer and Porter Co.). The column was packed using a slurry of 100 mesh silicic acid (Mallinckrodt) in chloroform–acetone (9:1). All samples were dissolved in a minimal amount of chloroform–acetone, added to the column, and eluted with chloroform–acetone (9:1).

Mass spectra were obtained using an LKB 9000 gas chromatograph-mass spectrometer (LKB Instruments, Inc., Rockville, Md.). Samples were introduced *via* a direct probe into the ionization source, or indirectly by means of a gas chromatograph. Gas chromatographic introduction was accomplished using an SE-30 column (1% by weight on 60/80 mesh Gas-Chrom Q), with a column temperature ranging from 125–175°. Isotopic abundances were calculated according to Silverstein and Bassler, 1967.

The spectral data reported were obtained at an ionization voltage of 70 electron volts (eV).

Elemental analyses for carbon, hydrogen, and nitrogen were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

**Photochemical Procedures.** PHOTOLYSIS OF 2-CHLORO-4,6-DI(ALKYLAMINO)-*S*-TRIAZINES (I, II, AND III) IN METHYL ALCOHOL. Triazine solutions ranged in concentration from 0.2–1.0 g. per 100 ml. of solvent. A 550-watt photochemical lamp having a primary UV emission at 253.7 nm. was used as the irradiation source. In general, reactions took six to 10 hours for complete disappearance of the starting material. During the reaction, no HCl evolution was observed. After irradiation, the solvent was removed using a rotoevaporator under partial vacuum at 40°–55° C. The viscous material remaining after evaporation was taken up in a small volume of chloroform–acetone (9:1) and chromatographed on a silicic acid column using the same solvent system. Column fractions were analyzed by GLC and TLC. The fractions

Table II. Elemental Analyses and Melting Points of Photoproducts

Photoproduct Analysis	Carbon		Hydrogen		Nitrogen		( $^{\circ}$ C)	
	Calcd	Found	Calcd	Found	Calcd	Found	Lit. <sup>a</sup>	Determined
C <sub>9</sub> H <sub>17</sub> N <sub>5</sub> O (IV)	51.16	50.91	8.11	8.15	33.16	33.04	95	94
C <sub>10</sub> H <sub>19</sub> N <sub>5</sub> O (V)	53.31	53.41	8.50	8.62	31.09	30.97	91	91
C <sub>8</sub> H <sub>15</sub> N <sub>5</sub> O (VI)	48.71	48.75	7.67	7.59	35.51	35.58	93	88
C <sub>8</sub> H <sub>15</sub> N <sub>5</sub> O (VII)	48.70	48.66	7.68	7.32	35.51	35.87		decomp. <sup>b</sup>
C <sub>9</sub> H <sub>17</sub> N <sub>5</sub> O (VIII)	51.15	51.06	8.13	8.07	33.15	32.99		decomp. <sup>b</sup>
C <sub>7</sub> H <sub>13</sub> N <sub>5</sub> O (IX)	45.88	45.79	7.17	7.07	38.23	38.07		decomp. <sup>b</sup>
C <sub>8</sub> H <sub>15</sub> N <sub>5</sub> (XIII)	53.01	53.01	8.34	8.35	38.65	38.60		180
C <sub>9</sub> H <sub>17</sub> N <sub>5</sub> (XIV)	55.35	55.20	8.78	8.83	35.87	35.64		215
C <sub>7</sub> H <sub>13</sub> N <sub>5</sub> (XV)	50.27	50.30	7.84	7.87	41.89	41.78		203

<sup>a</sup> Literature values taken from patent information and confirmed with authentic standard.

<sup>b</sup> Decomposition without melting above 250 $^{\circ}$ .

which contained a pure, major photoproduct were pooled. Solvent was removed under vacuum, and final drying was done in a drying pestle.

**PHOTOLYSIS OF 2-METHYLTHIO-4,6-DI(ALKYLAMINO)-S-TRIAZINES (X, XI, XII) IN METHYL ALCOHOL.** Five to 20 g. of X, XI, and XII were reacted in 550 ml. of glass distilled methanol. Irradiation conditions were standard—a 550 watt lamp, emitting at 253.7 nm. Reactions took from 12 to 24 hours for completion. The reaction solutions showed a progressive color change during irradiation, with the final solution being yellowish brown. Evaporation of the photolytic solution yielded a yellow-brown solid material. Successive recrystallizations from methyl alcohol yielded a fine, white crystalline product. Product was dried as previously described.

**PHOTOLYSIS OF 2-METHYLTHIO- AND 2-CHLORO-4,6-DI(ALKYLAMINO)-S-TRIAZINES IN WATER.** The appropriate 2-SCH<sub>3</sub> and 2-Cl analogs were added to 4900 ml. of water at the level of approximately 0.1 g. per 1000 ml. and stirred until a dispersed, flocculent mixture was formed. The solutions were photolyzed for 24 hours in a 5000-ml. round bottom flask, using a standard UV source. Water was removed with an evacuated, roto-evaporator, at 55 $^{\circ}$ . The major photoproducts of X, XI, and XII were purified by recrystallization from methanol. The major products of I, II, and III proved, in each case, to be quite insoluble in chloroform-acetone, which permitted the selective removal of any remaining starting material by repeated extraction. The GLC analysis of the final extracts of this insoluble precipitate showed no starting material. All products were dried as previously described.

**INVESTIGATION OF PHOTOCHEMISTRY OF 2-METHOXY- AND 2-HYDROXY-4,6-DI(ALKYLAMINO)-S-TRIAZINES IN METHANOL, ETHANOL, AND WATER.** The appropriate 2-methoxy and 2-hydroxy-*s*-triazines (IV, V, VI, and VII, VIII, IX, respectively) were irradiated in solution with 253.7 nm. After irradiation, solvent removal yielded a white, crystalline material in each case. Analysis by GLC, TLC, and IR indicated that the recovered material was the original 2-OCH<sub>3</sub> or 2-OH starting material.

**PHOTOCHEMICAL INVESTIGATIONS IN OTHER SOLVENTS.** The photochemistry of X, XI, and XII in ethanol, *n*-butanol, and in benzene was investigated under conditions similar to that in methanol. In each case, photolysis occurred with the formation of major photoproducts with identical chromatographic properties to those obtained in methanol.

Atrazine(I) was photolyzed in ethanol, and in *n*-butanol under similar conditions. The product of I irradiated in

*n*-butanol was partially purified by column chromatography on silicic acid, using a solvent system of chloroform-acetone (9:1).

Photolysis of I in ethanol-water (1:1) apparently proceeded with the formation of two major products. Concentration of the final reaction solution resulted in the precipitation of a white, flocculent material that was quite insoluble in chloroform-acetone and in short-chain alcohols. The other major product, remaining in solution, could be detected by GLC; but the flocculent precipitate was not eluted from a Carbowax-20M column, even at 230 $^{\circ}$ . The precipitate was partially purified by repeated washings with ethanol.

**ULTRAVIOLET SPECTROSCOPY OF PHOTOLYSIS REACTIONS.** Ultraviolet spectroscopy was used to follow the rate and the spectral changes of photolysis reactions under study. A solution containing 1.25 mg. of a particular *s*-triazine in 300 ml. of methanol or water was irradiated for 30 minutes, using a 250-watt photochemical lamp. A Vycor absorption sleeve was used to eliminate the occurrence of any primary photochemical process(es) involving the solvent (Calvert and Pitts, 1966). Aliquots were analyzed with time, and irradiation was continued until GLC showed the total disappearance of the starting material.

## RESULTS AND DISCUSSION

**Elemental Analyses and Melting Points.** Elemental analyses and melting points of photoproducts are reported in Table II.

**Thin-Layer Chromatography.** The *R<sub>f</sub>*'s of I, II, III, and their respective photoproducts formed by irradiation in methanol showed that these products were chromatographically distinct. Each product cochromatographed with its respective 2-methoxy-*s*-triazine analog of the starting material. Likewise, the photoproducts of I, II, and III in water are distinct, and have *R<sub>f</sub>*'s identical to those of the respective 2-hydroxy-*s*-triazine analogs. Chromatography of X, XI, and XII and of the respective products gave distinct spots with different *R<sub>f</sub>*'s (Table III).

**Gas-Liquid Chromatography.** Quantitative analyses indicated that all major photoproducts were formed in 85–95% yields. Reaction conditions did influence the level of primary product formation. Under conditions of increased solute dilution and/or restricted irradiation (the use of a Vycor absorption sleeve), product yield increased. Formation of polymer(s) under such conditions was apparently reduced.

Thin-layer chromatography of the GLC effluent of authentic triazines and their photoproducts showed that no thermal

decomposition occurred under these conditions. Such GLC-TLC combination also showed that the major and minor products (except in the case of the 2-hydroxy-*s*-triazine compounds) were resolved by both GLC and TLC, and that they were thermally stable under such chromatographic procedures.

Retention times of authentic triazines and their products were determined at a column temperature of 220° (Table IV). The retention times of the respective photolysis products of I, II, and III when methanol was used as the solvent during photolysis were identical to those of the authentic 2-methoxy analogs of the starting materials. The photoproducts formed when I, II, and III were irradiated in water, as well as authentic samples of their 2-hydroxy analogs, were not eluted from the GLC column. This was consistent with the increased polarity of an enol-keto tautomer at C-2. Gas chromatography of the photolysis reactions of I in methanol, ethanol, and in *n*-butanol showed that the major products were distinct and had an increased elution time, in the order of the methanol, ethanol, and *n*-butanol photoproducts.

The GLC retention times of the respective photolysis products of X, XI, and XII irradiated in methanol, ethanol, *n*-butanol, benzene, and in water were the same for each analog. The short retention times obtained for these products indicated a significant decrease in the polarity of the C-2 substituent.

**Mass Spectral Analyses.** Product spectra after the photolysis of I, II, and III in methanol and in water were consistent with the respective 2-OCH<sub>3</sub> or 2-OH substitution. The spectra were characterized by: (1) P + 2 abundance indicating the loss of chlorine at C - 2; (2) abundant ions representing P minus alkyl-group fragmentations (P - CH<sub>3</sub>, P - C<sub>2</sub>H<sub>5</sub>, P - C<sub>3</sub>H<sub>6</sub>); and (3) strong peaks at *m/e* 43, 44, and 58 (assigned to the appropriate alkylamine ions). Calculated and found isotopic abundances were consistent with empirical assignments.

The photoproduct isolated after the irradiation of I in *n*-butanol had a mass spectrum which supported its assignment as the 2-*n*-butoxy-*s*-triazine analog. The molecular ion occurred at *m/e* 253 (relative to *m/e* 215 for atrazine). The P + 2 isotopic abundance indicated the loss of chlorine. The P minus alkyl-group fragmentation pattern at the high mass end of the spectrum was consistent with the increased chain length of a linear, four-carbon butoxy substituent at C - 2. Ions at *m/e* 43, 44, and 58 indicated that the C - 4 and C - 6 alkylamino substituents were intact.

Products isolated after the photolysis of X, XI, and XII had spectra which showed a strong parent peak 46 mass units below the molecular ion of the respective starting material. The P + 2 abundance suggested the loss of the C - 2 sulfur atom of the -SCH<sub>3</sub> substituent. Such an elimination of sulfur, with a mass decrease of 46 is consistent with a hydrogen substitution. Calculated and found isotopic abundances were in good agreement. Fragmentation at the high mass end of the spectra was characteristic of alkyl-group eliminations. Ions at P - CH<sub>3</sub>, P - C<sub>2</sub>H<sub>5</sub>, and P - C<sub>3</sub>H<sub>6</sub> were prominent. The prominent ion fragments at the lower end of the spectra were assigned to fragments of the C - 4 and C - 6 alkylamino substituents (*m/e* 43, 44, and 58).

**Infrared Spectroscopy.** Comparison of the infrared spectra of I, II, III, and their products obtained by photolysis in methanol showed no great change in the 3 to 8- $\mu$  region. This similarity is due to the retainment of the triazine ring and the secondary amine substituents on C - 4 and C - 6. Comparison of the triazine "spike" (12- to 13- $\mu$  region) showed that this strong absorbance in the product's spectrum

**Table III. Thin-Layer Chromatography Data for S-Triazines and Their Photoproducts**

Authentic S-Triazines		Relative R <sub>f</sub> (Simazine = 1)	
S-Triazine			
I			1.47
II			1.57
III			1.00
IV			1.07
V			1.23
VI			0.735
VII			0.00
VIII			0.00
IX			0.00
X			1.47
XI			1.67
XII			1.20

Photolysis Products			
Reactant	Photolysis Solvent	Product	Product Relative R <sub>f</sub> (Simazine = 1)
I	Methanol	(IV)	1.07
II	Methanol	(V)	1.23
III	Methanol	(VI)	0.735
I	Water	(VII)	0.00
II	Water	(VIII)	0.00
III	Water	(IX)	0.00
X	Methanol	(XIII)	0.167
X	Water	(XIII)	0.167
XI	Methanol	(XIV)	0.266
XI	Water	(XIV)	0.266
XII	Methanol	(XV)	0.133
XII	Water	(XV)	0.133

Solvent system of chloroform-acetone (9:1).

**Table IV. Gas-Liquid Chromatography Data for S-Triazines and Their Photoproducts**

Authentic S-Triazines		Photolysis Products			
S-Triazine	Retention Time, Sec.	Reactant	Photolysis Solvent	Product	Retention Time, Sec.
I	138	I	Methanol	IV	100
II	100	II	Methanol	V	80
III	169	III	Methanol	VI	127
IV	100	I	Water	VII	...
V	79	II	Water	VIII	...
VI	129	III	Water	IX	...
VII	...	X	Methanol	XIII	39
VIII	...		Water	XIII	
IX	...	XI	Methanol	XIV	30
X	192		Water	XIV	
XI	163	XII	Methanol	XV	49
XII	245		Water	XV	

was shifted to shorter wavelengths, relative to that of their starting material. This shift indicated a C - 2 substituent less electron-withdrawing than chlorine (Padgett and Hamner, 1958). The IR spectra of authentic 2-methoxy-*s*-triazines and the respective photoproducts isolated after the photolysis of I, II, and III in methanol were identical.

Starting materials and products formed after the irradiation of I, II, and III in water had IR spectra which showed little difference in the primary absorbances ascribed to their amine and alkyl groupings. The photolysis products did, however, show a new and distinct absorbance in the region of 3.8  $\mu$  (ascribed to an enol-keto tautomer of the C - 2 hydroxy

substituent). The triazine "spike" was shifted to even longer wavelengths, relative to the 2-chloro analogs. This shift to 12.7  $\mu$  is expected, because of the greater electro-negativity of the tautomer. The spectra of each product and the authentic 2-hydroxy-*s*-triazine analog of the starting material were identical.

The photoproduct isolated after the photolysis of I in *n*-butanol showed all the characteristics of the *s*-triazine system: N—H stretch at 2.9–3.2  $\mu$ ; internal deformation in the 6- $\mu$  region; appropriate C—H stretching and skeletal vibrations; and the diagnostic triazine spike was shifted to shorter wavelengths, relative to I, supporting an alkoxy substitution.

The IR spectra of X, XI, and XII, and their respective products have similar spectra in the region of 3 to 8  $\mu$ . The spike absorbance was shifted to shorter wavelengths in the product's spectrum, supporting the proposed hydrogen substitution at C — 2.

**Nuclear Magnetic Resonance Spectroscopy.** The NMR data added further evidence to the structural assignments of the photoproducts of X, XI, and XII, and of those products isolated after the photolysis of I, II, and III in methanol.

Products isolated after photolysis of I, II, and III in methanol had spectra which differed from those expected for the respective starting material. These product spectra differed in the appearance of a singlet in the region of 6.25–6.30  $\tau$ . Integration indicated three hydrogens.

This new singlet was assigned as the methoxy methyl of the C — 2 substituent, having no adjacent hydrogens. All other chemical shifts of these product spectra were consistent with the data expected for the hydrogens of the C — 4 and C — 6 alkylamino substituents.

Comparison of NMR spectra of X, XI, and XII to the respective photoproduct supported the hydrogen substitution at C — 2. Product spectra did not show the three hydrogen singlet at the 7.5- to 7.7- $\tau$  region, which was assigned to the methyl group of SCH<sub>3</sub>. These products did show a singlet at 2.2  $\tau$ , which was assigned to a hydrogen on C — 2 of the triazine ring. Other absorbances were assigned to appropriate hydrogens on the C — 4 and C — 6 alkylamino substituents.

**Ultraviolet Spectroscopy.** The UV spectra of I, II, and III showed a  $\lambda_{\max}$  at 220 nm. An additional, minor absorption was also present with a maximum intensity at about 260 nm. No definitive studies were made to determine the molar absorptivity (extinction coefficient) at 260 nm., the nature of the electronic transition (*i.e.*, an  $n$  to  $\pi^*$ ,  $\pi$  to  $\pi^*$  transition), or the nature of the chromophore involved in the absorbance.

The spectra of X, XI, and XII also showed the characteristic  $\lambda_{\max}$  in the 220-nm. region. These compounds also had the absorbance in the 260-nm. region that was characteristic of their 2-chloro analogs.

The UV spectra of the isolated photoproducts of I, II, and III, and also of X, XI, and XII (the 2-methoxy, 2-hydroxy, and 2-H analogs) were quite similar to each other. They all showed the  $\lambda_{\max}$  absorbance in the 220-nm. region and little or no absorbance at 260 nm. Comparison of the spectra of the 2-methoxy and 2-hydroxy photoproducts with their authentic standards (IV, V, VI, and VII, VIII, and IX, respectively) showed them to be identical. None of the nine isolated photolysis products showed the minor UV absorption at 260 nm., characteristic of their starting materials.

The nature of the electronic transition responsible for the  $\lambda_{\max}$  absorbance of these authentic triazines I–XII and their products was a  $\pi$  to  $\pi^*$  transition of the C=N of the triazine ring. This assignment was based on expected similarities

between the  $\lambda_{\max}$  and the extinction coefficient (calculated to be in the range of 35,000 to 43,000) of these analogs, and similarities between this ring system and data reported by Rao (1961) for other heterocyclic systems. The  $\lambda_{\max}$  of technical grade Atrazine in *n*-hexane, methanol, and water were determined as 218.0, 220.75, and 221.5 nm., respectively (literature values of 221.5 and 222.0 nm. in methanol and water, respectively). Such a shift of  $\lambda_{\max}$  to longer wavelengths in solvents of increasing polarity is characteristic of  $\pi$  to  $\pi^*$  transitions. Solvent effect on the minor absorbance at 260 nm. could not be measured.

Ultraviolet spectroscopy was also used to qualitatively follow the course of the photolysis reactions as reflected in change(s) in the absorbance characteristics.

The UV spectra of I, II, and III showed a time-dependent decrease in the 260-nm. absorbance when photolyzed in methanol or water. Final reaction solutions showed no absorbance at 260 nm., which was consistent with the formation of their 2-methoxy and 2-hydroxy analogs. The same loss of the 260-nm. absorbance was seen when X, XI, and XII were photolyzed in methyl alcohol or water. Again, this change at 260 nm. was consistent with the data expected for the formation of the 2-H analogs.

**Cursory Investigations.** Photolysis of Atrazine(I) in ethanol–water (1:1) resulted in the formation of two major photoproducts. Concentration of the final reaction solution resulted in the precipitation of a relatively insoluble material that had a mass and IR spectra identical to that of the product (VII) isolated after the photolysis of I in water. The other major product had a GLC retention time identical to that of the material isolated after the irradiation of I in absolute ethanol.

Cursory rate studies were done on photolysis reactions at different wavelengths. Rates decreased when a Vycor absorption sleeve was used. A Corex filter resulted in even greater decreases in reaction rates. In all cases, photolysis carried out at greater than 300 nm. (Pyrex absorption sleeve) resulted in no chemical reaction. Products isolated after irradiation at wavelengths between 210 and 300 nm. (irradiation through Vycor and Corex filters, respectively) were identical to those obtained at 253.7 nm.

**Photochemical Mechanism.** Considerations of a photochemical mechanism must be based largely on product formation. It is apparent from the nature of the C-2 substitution reaction that the mechanism of the photolysis of the 2-chloro and 2-methylthio analogs are distinctly different. Photolysis of I in water, methanol, ethanol, and *n*-butanol to yield the respective 2-hydroxy, 2-methoxy, 2-ethoxy, and 2-*n*-butoxy analogs suggests the generality of this photochemical solvolysis. Photolysis of the 2-methylthio analogs does not suggest solvent participation—but rather the possibility of a concerted rearrangement involving an intramolecular hydrogen shift.

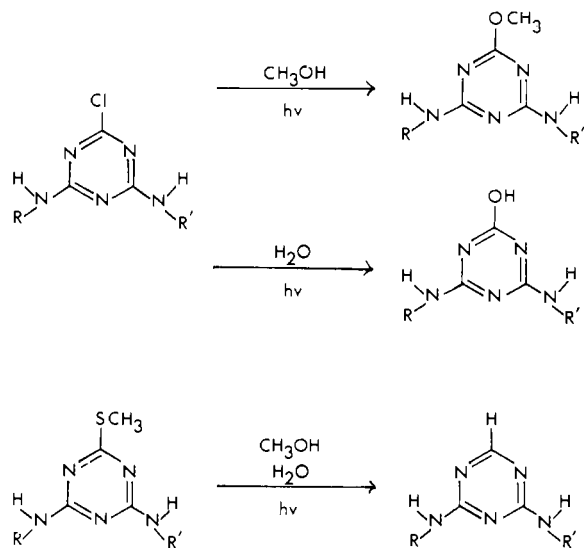
The facts that the photolysis of I, II, and III did not result in the evolution of HCl, and that the C — 2 alkoxy products were found without rearrangement of the alcoholic moiety suggest that a free radical mechanism is not operative. A carbonium ion intermediate is an attractive alternative. A positive charge on the C — 2 of the triazine ring would be greatly stabilized by its aromatic chemistry and the non-bonded electrons of the ring nitrogens and C — 4 and C — 6 electron-donating substituents. A heterolytic cleavage of the carbon–chlorine bond to yield the carbonium ion and free chloride ion is consistent with the product formation. Further mechanistic studies are being continued.

## CONCLUSIONS

Photolysis of I, II, and III in methanol and in water at 253.7 nm. yielded their respective 2-methoxy (IV, V, and VI) and 2-hydroxy (VII, VIII, and IX) analogs as the major photoproducts. Photolysis of I in ethyl alcohol and in *n*-butanol resulted in the formation of the 2-ethoxy and 2-*n*-butoxy-*s*-triazine analogs, respectively. The 2-methoxy and 2-hydroxy substituted triazines (IV, V, VI, and VII, VIII, IX) did not undergo a photochemical reaction in methanol or in ethanol.

Irradiation of X, XI, and XII in methanol, ethanol, *n*-butanol, benzene, and in water yielded the 2-H analogs [4-ethylamino-6-isopropylamino-*s*-triazine, 4,6-bis(isopropylamino)-*s*-triazine, and 4,6-bis(ethylamino)-*s*-triazine, respectively].

Photolysis occurred, in all cases, at wavelengths greater than 210 nm., an indication that the reaction was not initiated by a primary photochemical process involving the solvent (Calvert and Pitts, 1966). The rate studied at different wave-



lengths indicated that the 260-nm. absorbance was responsible for the photoreaction. No photochemical reactions were observed under laboratory conditions at wavelengths greater than 300 nm.

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