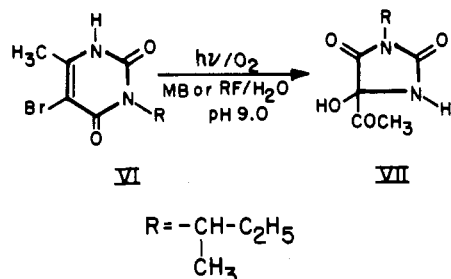


Photosensitized Decomposition of Terbacil in Aqueous Solutions

Aureliu J. Acher,* Sarina Saltzman, Nelly Brates, and Ezra Dunkelblum

The dye-sensitized photolysis of aerated aqueous solutions of terbacil (3-*tert*-5-chloro-6-methyluracil, I) exposed to solar irradiation was investigated under different reaction conditions. After 2 h of exposure to sunlight, in the presence of methylene blue (3 ppm) or riboflavin (10 ppm), the major photodegradation product in the pH range of 3.0–9.2 was 3-*tert*-butyl-5-acetyl-5-hydroxyhydantoin (II). In alkaline reaction mixtures (pH 8.0 or 9.2), this product undergoes deacylation, giving 3-*tert*-5-hydroxyhydantoin (III). In experiments carried out under neutral or acidic conditions (pH 6.8 or 3.0) with riboflavin, two additional products were isolated: a mono-*N*-dealkylated terbacil dimer (IV) and a nonidentified water-insoluble product (V). The structures of II, III, and IV were determined by using proton and carbon-13 nuclear magnetic resonance, infrared, ultraviolet, and mass spectroscopy.

Terbacil (3-*tert*-butyl-5-chloro-6-methyluracil, I), a photosynthesis inhibitor, is widely used for the selective control of many annual and some perennial weeds in fields and orchards. Its half-life under field conditions is ~5–6 months (Gardiner et al., 1969), and it may be translocated to the foliar portions of agricultural crops, where it is partially or totally metabolized (Rhodes, 1977; Jordan et al., 1975; Gardiner et al., 1969). Although the photochemistry of pyrimidine ring containing compounds has received much attention (Wang, 1976), there is little information on the photolysis of uracil derivatives used as herbicides (Kearney et al., 1969; Jordan et al., 1965; Moilanen and Crosby, 1974). Recent studies of the photodecomposition of bromacil (3-*sec*-butyl-5-bromo-6-methyluracil, VI) showed that aerated aqueous solutions



exposed to sunlight in the presence of dye sensitizers resulted in rapid and complete degradation. The major photooxidation product was identified as a mixture of diastereoisomers of 3-*sec*-butyl-5-acetyl-5-hydroxyhydantoin (VII) (Acher and Saltzman, 1980; Acher and Dunkelblum, 1979). Compound I differs from VI in the halogen substituent at C-5 as well as in the *N*-alkyl group (Cl and *tert*-butyl instead of Br and *sec*-butyl, respectively). Although less chemical reactivity of I, as compared with that of VI, could be expected, due to the halogen substituent, the presence of the *tert*-butyl group could increase its reactivity under specific conditions. The aim of the present work was to study the effect of sunlight irradiation on the stability of I in aqueous solutions under different experimental conditions and to identify the major degradation products in order to understand the fate of this compound in the environment.

EXPERIMENTAL SECTION

Materials. Terbacil (5-chloro-3-*tert*-butyl-6-methyluracil, I), provided by Agan Ltd., Israel, was purified by

recrystallization from 2-propanol; mp 172–174 °C (chromatographically pure).

The sensitizers methylene blue (MB), rose bengal (RB), riboflavin (RF), and humic acids (HA), the specifications of which were given in a previous work (Acher and Saltzman, 1980), were used as 0.1% aqueous solutions.

Instrumentation. The apparatus used for the irradiations and identification of I and its reaction products were described previously (Acher and Dunkelblum, 1979; Acher and Saltzman, 1980).

Laboratory Lamp Photodegradation Procedure. Aqueous solutions (10 mL) of I (~250 ppm) containing 3 ppm of MB or 10 ppm of one of the other sensitizers (RF; RB; HA) were exposed in Pyrex test tubes (20 mL) to laboratory lamp irradiation, under continuous aeration. The initial pH of the solutions was adjusted by adding 0.1 N NaOH or 0.1 N HCl.

The concentrations of I in the reaction mixtures were monitored by UV spectroscopy at 281 nm.

Sunlight Photodegradation Procedure. Aqueous solutions (2 L) of I (~700 ppm) containing 3 ppm of MB or 10 ppm of RF were exposed outdoors to direct solar irradiation (1950 $\mu\text{Einsteins m}^{-2} \text{s}^{-1}$) under continuous aeration in Erlenmeyer flasks. The photoreactions were carried out at ambient temperature (35–38 °C), or at 12–15 °C, by immersing the bottom of the flasks in an ice-water bath. In the experiments carried out in alkaline solutions, the pH of the reaction mixtures was maintained either at 9.2 by continuous addition of 1 N NaOH or at pH 8.0 by an initial addition of 0.5 g/L NaHCO_3 . In the experiments carried out in acid solution, the pH (3–4) of the reaction mixture was adjusted by addition of 1 N HCl. The concentrations of I in the reaction mixtures during irradiations were monitored by UV spectroscopy at 281 nm. In prolonged irradiation experiments (more than 1 h), the concentration of the sensitizer was kept constant by occasional addition of MB or RF. After exposure to solar irradiation, the reaction mixtures were concentrated by lyophilization to ~10% of the initial volumes. Ammonium sulfate (~30%) was added to the defrosted concentrates and then extracted 4 times with 30 mL (each) of ethyl acetate. The organic extract was dried over sodium sulfate, filtered, evaporated to dryness in a rotovapor, redissolved in a minimum amount of methylene chloride, and submitted to column chromatography (silica gel 60; 230–400 mesh; E Merck). The elution of I, II, III, and IV from the column was accomplished by a mixture of methylene chloride-ethyl acetate (7:3). The eluted products were further purified by recrystallization. The separation was followed by thin-layer chromatography (TLC; aluminum sheets; Merck silica gel 60, F 254 precoated; methylene chloride-ethyl acetate, 7:3). The spots were visualized by UV light

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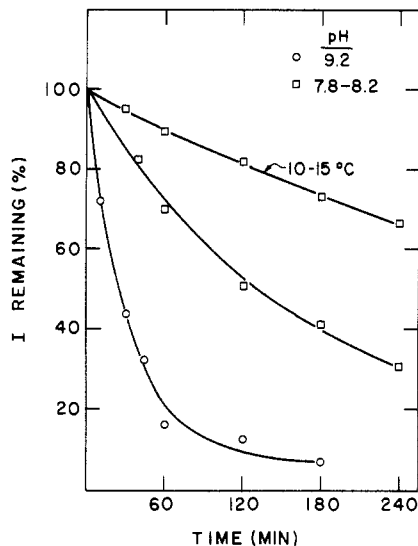


Figure 1. Photodecomposition of I in the presence of MB, as affected by pH and temperature.

(I and IV) and by iodine vapors (II-V).

RESULTS

Preliminary experiments on the stability of I in aqueous solutions (250 ppm) at different pH values (4-10), showed that its concentration remained unchanged over a month at room temperature ($\sim 25^\circ\text{C}$). The photochemical reactivity of I in aqueous solutions, checked by irradiating the solution in test tubes with a laboratory lamp, showed no changes in the concentration of I after 1 h of irradiation (at pH 4-10). Addition of dye sensitizers as MB or RB to the irradiated solutions had no effect at pH ≤ 6.6 , but above this pH the photosensitizing effect became evident and the concentration of I decreased during the irradiation. The HA tested had no significant photosensitizing effect, while RF was very effective in sensitizing the photochemical degradation of I at an initial pH range between 4 and 10.

As the best photosensitizing effects were obtained with MB and RF, the photodegradation of I in the presence of these two sensitizers was studied.

(A) Stability of I in Aqueous Irradiated Solutions.

(1) *Alkaline Solutions.* The concentration of I in alkaline solutions (pH 9.2) decreased rapidly during exposure to sunlight (Figures 1 and 2). The degradation reaction was faster during the first 60 min, decreasing the initial amount of I by a rate of 1.8 or 1.2%/min when using MB or RF, respectively. After 2 h of irradiation less than 10% of the initial amount of I remained in the reaction mixtures.

The analysis of the relative composition of the reaction mixtures after 2 h of sunlight exposure (Table I) showed that in the solutions at pH 9.2 the photosensitizing effect of MB and RF was rather similar; the same reaction products and in similar relative amounts were identified in both cases. The main degradation products present in the ethyl acetate extract of the reaction mixture concentrates were II and III. The relative composition of the reaction mixtures is time dependent. When the time of solar irradiation was increased to 8 h, the analysis of the reaction mixtures showed a complete disappearance of compounds I-III.

(2) *Slightly Alkaline Solutions.* The rate of the photodecomposition of I in slightly alkaline solutions (pH 7.8-8.0) was significantly slower as compared to that of pH 9.2 (Figures 1 and 2 and Table I). The amount of I remaining after 2 h of irradiation at pH 8.0 was 51% when using MB, and 16% when using RF as compared to 4 and

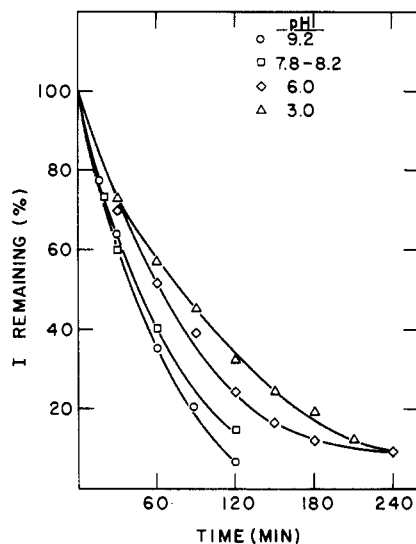


Figure 2. Photodecomposition of I in the presence of RF, as affected by pH.

Table I. Relative Composition of the Reaction Mixtures after 2 h of Solar Irradiation

product	relative composition, %				
	pH 9.2		pH 7.8-8.0		pH 3.0-6.8
	MB	RF	MB	RF	RF
I	4	8	51 (83) ^a	16	33
II	42	39	24 (17)	48	20
III	18	22	5 (0.0)	9	
IV					9
V					25
(VN) ^b	36	31	20 (0.0)	27	13

^a Numbers in parentheses are for 10-15 °C. ^b The yields of the volatile and nonextractable products which were not isolated were calculated by difference.

8%, respectively, at pH 9.2 for the same working conditions.

The composition of the ethyl acetate extracts of the reaction mixture concentrates (Table I) suggested a similar photodecomposition mechanism of I at slightly alkaline and alkaline pH in aqueous solutions. The main reaction product identified was II. However, the ratio of compounds II/III was much greater at pH 7.8-8.0 ($\sim 5:1$) than at pH 9.2 (about 2:1), due to the greater chemical stability of compound II in slightly alkaline solutions.

The temperature dependence on the photodegradation reaction rate of I at pH 7.8-8.0 is indicated by the results given in Figure 1 and Table I: after 2 h of irradiation the concentration of I at 10-15 °C was ~ 1.5 -fold higher than at 35 °C. The only reaction product present in the reaction mixture at 10-15 °C was the compound II (at this pH and temperature no deacylation reaction of II to III took place). Under these reaction conditions no volatile and nonextractable reaction products were formed, and the amount of II in the organic extract was equivalent to the amount of I which disappeared.

(3) *Acid Solutions.* The photochemical transformation of I in acid solution could be accomplished only with RF as sensitizer (Figure 2). The rate of the reaction was relatively fast (0.6-0.7%/min in the first 60 min), although slower than that at slightly alkaline pH. After 2 h the degradation of I reached $\sim 90\%$, and the pH of the reaction mixture decreased from 4.0 to 2.7. The composition of the reaction mixture is shown in Table I. In addition to compound II, which is a common degradation product under all the experimental conditions tested, two other

Table II. ^{13}C NMR Spectra of Terbacil (I) and the Photoproducts II-IV^a

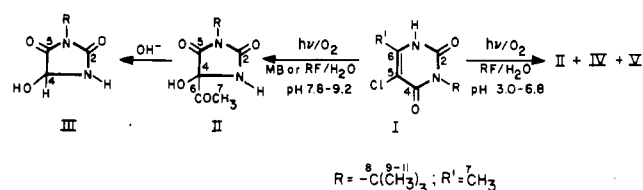
compound	I	II	III	IV	
				ring A	ring B
C-2	161.1	157.8	155.8	162.5	164.9
C-4	153.3	170.5	173.0	149.9	156.0
C-5	108.0	85.3	79.6	119.0	83.2
C-6	145.0	200.3		144.5	94.0
C-7	16.5	23.5		15.9	23.8
C-8	63.5	58.9	54.8		62.5
C-9-11	29.9	28.4	28.4		29.8

^a The chemical shifts of ^{13}C are δ from Me_4Si , and the spectra are proton decoupled.

reaction products were isolated. One product, IV, was identified as a new type of dimer of I. The second one, V, which precipitated during the photolysis, is probably an oligomer of I which had not yet been identified. Periodical checks of the reaction mixtures by TLC and visual observations (V precipitates) showed that the reaction products appeared in the order II, IV, and V. As the reaction progressed, the concentration of II decreased and that of IV and V increased. The concentration of II in acid solution (pH 3.0) stored at 35–40 °C was found to be constant over several days; therefore it was assumed that the decrease in concentration of II during irradiation was due to further photochemical transformations of this compound. Prolonged irradiations (8 h) resulted in almost complete disappearance of I, II, and IV.

(B) Kinetics. The decrease in the initial concentration of I was followed up to its almost total decomposition from the reaction mixtures. Under all the experimental conditions tested, this photodecomposition reaction seemed to obey a first-order reaction kinetics, as the results obtained fitted this reaction equation. The rate constants of the photoreactions were 2.5×10^{-2} and 4.6×10^{-3} in the presence of MB, at pH 9.2 and 8.0, respectively; with RF the values were 2.3×10^{-2} (pH 9.2), 7.6×10^{-3} (pH 8.0),

Scheme I



and 5.3×10^{-3} (pH 3.0). Actually, the photochemical kinetics of I degradation is much more complex, involving several reaction steps and chemical and photochemical reactions of the intermediate products.

(C) Photodegradation Products (Table I; Scheme I). (1) *3-tert-Butyl-5-acetyl-5-hydroxyhydantoin (II)*. This compound was the main reaction product found in the organic extracts of the concentrated reaction mixtures after the first 2 h of irradiation, in alkaline, slightly alkaline, or acidic solutions, both with MB- or RF-sensitized reactions. Aqueous solutions of II at pH 8.0 and 9.2 (35–40 °C) undergo deacylation at C-5, giving III. This deacylation process may be avoided at pH <8.0 if the solution is kept cold (≤ 15 °C). Under such reaction conditions, II was the only reaction product formed.

Pure II (white needle crystals) was obtained by recrystallization (ether-hexane, 1:5) of the crude material eluted from a silica gel column after elution of I: TLC $R_f = 0.85$ and $R_{III} = 1.5$; mp 104–106 °C. The chemical structure of II was established by comparison with VI (Acher and Dunkelblum, 1979). It had the following spectroscopic characteristics: ^1H NMR (90 MHz) (in CDCl_3 plus CD_3OD) δ 2.31 (s, 3 H, CH_3CO), 1.62 [s, 9 H, $\text{C}(\text{CH}_3)_3$] (the chemical shifts are δ from Me_4Si); ^{13}C NMR (30 MHz) see Table II; IR (KBr) 3300 (OH), 1710, 1780 cm^{-1} (C=O); high-resolution MS (70 eV) is shown in Table III. The most significant peaks are the result of the cleavage of ketene or acetyl and the loss of the *N*-alkyl group by a single and double McLafferty rearrangement (Safe and Hutzinger, 1973).

Table III. High-Resolution MS: Major Fragmentation of II-IV

compound	mass found	% abundance	composition					^{35}Cl	^{37}Cl	structure
			C	H	N	O				
II	214	7	9	14	2	4			M^+	
	197	6	9	12	2	3			$\text{M}^+ - \text{H}_2\text{O}$	
	172	5	7	12	2	3			$\text{M}^+ - \text{CH}_2\text{CO}$	
	171	7	7	11	2	3			$\text{M}^+ - \text{CH}_3\text{CO}$	
	159	5	5	7	2	4			$\text{M}^+ - \text{C}_4\text{H}_7$	
	116	16	3	4	2	3			$\text{M}^+ - \text{C}_4\text{H}_8, \text{CH}_2\text{CO}$	
	115	12	3	3	2	3			$\text{M}^+ - \text{C}_4\text{H}_8, \text{CH}_3\text{CO}$	
	57	100	4	9					$\text{C}(\text{CH}_3)_3$	
III	172	5	7	12	2	3			M^+	
	158	36	6	10	2	3			$\text{M}^+ - \text{CH}_2$	
	157	100	6	9	2	3			$\text{M}^+ - \text{CH}_3$	
	117	11	3	5	2	2			$\text{M}^+ - \text{C}_4\text{H}_7$	
	99	5	3	3	2	2			$\text{M}^+ - \text{C}_4\text{H}_7, \text{H}_2\text{O}$	
	57	100	4	9					$\text{C}(\text{CH}_3)_3$	
IV	374	3	14	16	4	4	2		M^+	
	318	5	10	8	4	4	2		$\text{M}^+ - \text{C}_4\text{H}_8$	
	286	8	10	9	4	4		1	$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}$	
	284	23	10	9	4	4	1		$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}$	
	285	7	10	8	4	4		1	$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}$	
	283	23	10	8	4	4	1		$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}$	
	282	14	10	7	4	4	1		$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}$	
	247	8	10	7	4	4			$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}_2$	
	240	8	9	7	3	3	1		$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}, \text{HNCO}$	
	241	5	9	6	3	3		1	$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}, \text{HNCO}$	
	239	19	9	6	3	3	1		$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}, \text{HNCO}$	
	214	8	8	7	3	2		1	$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}, \text{HNCO}, \text{CO}$	
	212	14	8	7	3	2	1		$\text{M}^+ - \text{C}_4\text{H}_8, \text{Cl}, \text{HNCO}, \text{CO}$	
	57	100	4	9					$\text{C}(\text{CH}_3)_3$	

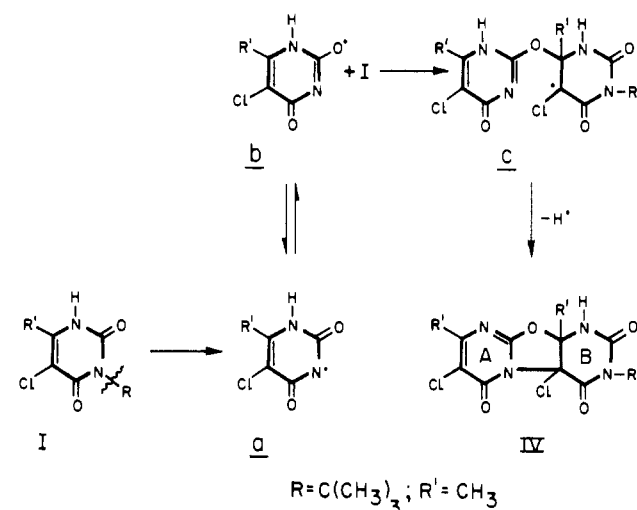
(2) *3-tert-Butyl-5-hydroxyhydantoin (III)*. This compound was obtained only in the photoreaction of I carried out at pH ≥ 7.8 and a temperature > 15 °C. Experiments showed that under such conditions this compound may also be obtained from II in the dark and without sensitizers. Therefore, it was assumed that the formation of III in the reaction mixtures was not caused by a photochemical process but was the result of a base-catalyzed deacylation at C-5. The maximum yield of III was reached ~ 4 – 5 h (pH 9.2; 33–40 °C) after the beginning of the photoreaction.

Pure III (white needle crystals) was obtained by recrystallization (ether–hexane, 1:4) of the crude material eluted from a silica gel column after the elution of II: TLC $R_I = 0.56$ and $R_{II} = 0.7$; mp 206–208 °C. The chemical structure of III was established by spectroscopic means: ^1H NMR (90 MHz) (in CDCl_3) δ 5.16 (s, 1 H, α to OH), 4.90 (br s, 2 H, OH, NH, exchanged with D_2O), 1.5 [s, 9 H, $\text{C}(\text{CH}_3)_3$]; ^{13}C NMR (20 MHz) see Table II; IR (KBr) 3240 (OH), 1710, 1760 cm^{-1} (C=O); high-resolution MS (70 eV) is shown in Table III [in addition to single and double McLafferty rearrangement (m/e 117), there was a very easy loss of a methyl (m/e 157) and the formation of the protonated fragment (m/e 158)].

(3) *5-Chloro-6-methyl-(3'-5')-5'-chloro-6'-methyl-5',6'-dihydro-6'-hydroxy-6',2-anhydro-3'-tert-butyluracilyl-uracil (IV)*. This product was obtained only when RF was used as sensitizer in neutral or acidic reaction mixtures. Pure IV was obtained by recrystallization (ether–ethyl acetate, 1:4) of the crude material eluted from a silica gel column following the elution of II: TLC $R_I = 0.50$, $R_{II} = 0.6$, $R_{III} = 0.9$; mp 258–260 °C dec. The chemical structure of IV is tentative and is based on the following spectroscopic analyses: ^1H NMR (90 MHz) (in CDCl_3) δ 2.79 (s, 3 H, C-7B), 2.00 (s, 3 H, C-7A), 1.49 [s, 9 H, $\text{C}(\text{CH}_3)_3$]; ^{13}C NMR (20 MHz) the chemical shifts of the carbons in ring A were almost identical with the corresponding carbons in I, and the different structure of ring B was reflected in C-5 and C-6 (see Scheme I and Table II); IR (KBr and Nujol) 1760 (C=O), 1630 cm^{-1} (C=N) (no OH groups present); UV (water) λ_{max} 274.5 nm ($\epsilon = 84\,000$) as compared to λ_{max} 281 nm ($\epsilon = 69\,400$) for I; high-resolution MS (70 eV) the highest mass unit (374) corresponded to the empirical formula of a dimeric cation of I with the loss of one *tert*-butyl group and one hydrogen (Table III), and this ion underwent a number of fragmentations [(1) loss of one chlorine preferentially together with other groups [$\text{M}^+ - \text{C}_4\text{H}_9$, Cl (31%); $\text{M}^+ - \text{C}_4\text{H}_8$, Cl (30%); $\text{M}^+ - \text{C}_4\text{H}_9$, Cl, HCNO (24%)], indicating the different character of each of the two chlorine atoms in IV; (2) the *tert*-butyl group fragmented as C_4H_9 , as C_4H_8 by a single McLafferty rearrangement, or as C_4H_7 by a double McLafferty rearrangement (Safe and Hutzinger, 1973); the double rearrangement proved the presence of two carbonyls on both sides of the *N-tert*-butyl group; (3) the many fragments formed by loss of HNCO proved the presence of this unit in IV]; chemical ionization MS confirmed the molecular weight of IV ($\text{M}^+\text{H} = 375$) and the different character of each of the chlorine atoms ($\text{M}^+\text{H} - \text{HCl} = 339$).

(4) *A White Amorphous Unidentified Compound (V)*. This reaction product was obtained only in the neutral or acidic (pH 3.0) reaction mixtures photosensitized with RF. The appearance of V as a white precipitate started ~ 30 min after the beginning of the photoreaction. The compound was insoluble in water or in organic solvents. It seems to be thermostable, as it remained unchanged up to a temperature of 300 °C (Fisher-Johns melting point apparatus). The mass spectrum (70 eV) showed fragments

Scheme II



higher than 450 mass units, indicating polymeric character.

(5) *Volatile Nonextractable Compounds Which Were Not Isolated (VN)*. This group of reaction products was formed in the reaction mixtures during the solar irradiation either by the photodegradation of the primary photoreaction products or by chemical decomposition. By increasing the time of solar exposure the amount of these compounds increased and eventually after 9 h none of the compounds I–IV could be detected.

DISCUSSION

Recently we demonstrated the very specific effect of sensitizers such as MB in the photolysis of VI (Acher and Dunkelblum, 1979; Acher and Saltzman, 1980). It was of interest to study the influence of a different halogen and alkyl group in the uracil moiety, and therefore the choice of I was of both chemical and practical importance. The mode of photolysis of I was sensitizer and pH dependent. At basic or slightly basic pH, both MB and RF gave similar products, although at somewhat different rates. The major product in all these experiments was II. The same reaction mechanism as described previously (Acher and Dunkelblum, 1979) was probably responsible for the photooxidation of I to II. The rate of formation of II was slower than that of VII as expected due to the stronger C–Cl bond in I than the C–Br bond in VI. The formation of III was a base-catalyzed deacylation of the primary photoproduct II and not a direct phototransformation of I. Treatment of II with aqueous base (pH 9.2) in the dark resulted in the quantitative formation of III. In addition, product III was not formed in the acidic photolysis with RF.

Under acidic conditions MB was ineffective as observed in the case of VI. The efficiency of singlet oxygen production sensitized by MB is reduced at acidic pH (Bonnea et al., 1975). Unexpectedly, RF sensitized the photolysis of I down to pH 3. The composition of the reaction mixture in acidic conditions was significantly different from that at higher pH (Table I), implying a different mode of reaction. In addition to product II which is formed by a similar reaction mechanism already described, two new products IV and V were isolated.

A plausible mechanism (Scheme II) for the formation of IV from I might be based on the homolytic cleavage, catalyzed by RF and O_2 (the necessity of RF and O_2 was proven by blank experiments) of the tertiary C–N bond. The first step was the formation of the radical a which tautomerized to b. The radical b attacked the double bond of I to produce the intermediate c. Compound IV was formed from c by hydrogen expulsion. This type of di-

merization differs from the usual dimerization reactions as observed in different halogen uracils (Feneslau and Wang, 1969; Wang, 1976). The fact that a similar compound was not obtained from VI (Acher and Dunkelblum, 1979) is due to the more facile homolytic cleavage of the *tert*-butyl group as compared to that of the *sec*-butyl group. The formation of V, which is an oligomer, although its exact structure has not yet been elucidated, implies probably a radical reaction mechanism, initiated by RF (Oster, 1954). As the main purpose of this work was to investigate the photodegradation reaction of I under different reaction conditions, the yields of the products were not optimized. The relative amounts of compounds I-V changed with sensitizer, pH, temperature, and time.

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Acid-Catalyzed Alteration of 2,3-Dihydro-2,2-dimethyl-7-benzofuranyl (Di-*n*-butylaminosulfenyl)methylcarbamate via Nitrogen-Sulfur Bond Cleavage. Formation of Polysulfide Derivatives

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A new experimental insecticide, 2,3-dihydro-2,2-dimethyl-7-benzofuranyl (di-*n*-butylaminosulfenyl)-methylcarbamate (DBSC), was unstable in acidic media, e.g., dichloromethane-acetic acid (9:1), and was converted into a number of alteration products via N-S bond cleavage. The principal products were carbofuran, dibutylamine, a mixture of polysulfide derivatives of DBSC (I), biscarbofuran *N,N'*-disulfide (III), and a mixture of biscarbofuran *N,N'*-polysulfides (IV), the structures being confirmed by MS and NMR analyses of purified products. I and IV, which were indicated to be a mixture of polysulfide derivatives, gave single spots on silica gel thin-layer plates with several different solvent systems. The rates of acid-catalyzed alteration of DBSC and formation of carbofuran, dibutylamine, I, III, and IV were determined by using [*carbonyl*-¹⁴C]- or [*dibutylamino*-¹⁴C]DBSC. The rate of DBSC decomposition was first order in DBSC.

2,3-Dihydro-2,2-dimethyl-7-benzofuranyl (di-*n*-butylaminosulfenyl)methylcarbamate (DBSC or Marshal) is a sulfenylated derivative of carbofuran which is currently undergoing development as a broad spectrum insecticide. Previous reports from this laboratory described the metabolic and environmental fate of DBSC in plants (Umetsu et al., 1979), soil (Clay et al., 1980), and the rat (Marsden, 1980). These studies indicated that significant nonenzymatic degradation of DBSC was taking place in a biological system. Another study (Umetsu et al., 1980) showed that in an acidic, aqueous environment or one containing sulfhydryl agents, DBSC was readily converted to carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) by N-S bond cleavage but was stable under

neutral and alkaline conditions. Since carbofuran was by far the major product observed, these findings pointed to the greater lability of the carbamyl N-S bond compared to the amino N-S bond. Previous studies (Chiu et al., 1975; Umetsu et al., 1979; Mallipudi and Fukuto, 1979) had revealed the ready susceptibility of N-S bonds in sulfenylated methylcarbamates to thiolytic cleavage by attack of the sulfur atom by sulfhydryl-containing agents.

During the course of a study on the behavior of DBSC under different solvent conditions, we discovered that DBSC also was unstable in a dichloromethane-acetic acid (9:1) mixture, being converted into a variety of different products in significant quantities, in addition to carbofuran. Because of the possible significance of acid-catalyzed nonenzymatic alteration on the mode of action and toxicological properties of DBSC, a further probe into the nature of the alteration products was made. Initial studies were made in an aprotic, inert solvent in order to identify all alteration products that were formed from DBSC in an acidic environment. This paper is concerned with the isolation and identification of these products, along with

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