responding substituent at the 5 position were obtained in high yield. Results are shown in Table II.

The results indicate that the method developed in this study is useful in obtaining various alkylpyrazines.

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Pyrethroid Photochemistry: *S*-Bioallethrin

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Photodecomposition of *S*-bioallethrin, the 1*R*,3*R*,4'*S* isomer of the insecticide allethrin, in the solid phase or in solution by sunlight or ultraviolet light (λ 360 nm) yields the following major products at <50% conversion: *cis*-allethrin, the di-π-methane rearrangement product at the allyl substituent, the allylic alcohol and epoxides from the isobutenyl group, and chrysanthemic acid. Triplet intermediates are involved in the cyclopropane isomerization reactions and the di-π-methane rearrangement, with the latter process predominating. The yield of epoxides formed by triplet oxygen is considerably enhanced with benzil as a mediator. Oxidation at the allylic position of the chrysanthemate moiety results from radical reactions of ground-state oxygen. Many other products obtained in low yields (<1%) presumably arise from further reactions of the primary photoproducts.

S-Bioallethrin (1 or Esbiol) is the most insecticidal isomer (1*R*,3*R*,4'*S*; 1*R*,trans,4'*S*) of allethrin, the first potent synthetic pyrethroid (Schechter et al., 1949). The uses of *S*-bioallethrin and various allethrin isomer mixtures are similar to those of pyrethrum. These compounds are less photostable as thin films than most other insecticidal chrysanthemates lacking an alkenylrethronyl substituent (Chen and Casida, 1969; Miskus and Andrews, 1972). The only identified photoproduct of 1 is the cyclopropylrethronyl derivative formed in solution (Bullivant and Pattenden, 1976). The chrysanthemate isobutenyl substituent undergoes photooxidation at the methyl group trans to the cyclopropane and at the double bond (Chen and Casida, 1969; Ueda et al., 1974). Photodecomposition of simple derivatives of the acid and alcohol components of 1 has been studied (Bullivant and Pattenden, 1971; Ueda and Matsui, 1971).

This work examines the photoisomerization and photooxidation of *S*-bioallethrin under a variety of irradiation conditions in the presence and absence of sensitizers, quenchers, and oxygen-transfer agents.

MATERIALS AND METHODS

Spectroscopy. Nuclear magnetic resonance (NMR) spectra were obtained as previously reported (Ruzo and Casida, 1980). Chemical ionization–mass spectra (CI-MS) were recorded with the Finnigan 1015D instrument equipped with a System Industries Model 150 computer using isobutane as the reagent gas at a CI source pressure of 0.3–0.5 torr at 70 eV and 60–140 °C.

Chromatography and Analyses. Gas–liquid chromatography (GLC) analysis utilized the Hewlett-Packard Model 5830A gas chromatograph with a ^{63}Ni electron-capture detector and an open tubular column (0.25 mm i.d. × 30 m) coated with SE-30 (4 μg/mL). The operating temperatures were as follows: injector, 250 °C; oven, 200 °C; detector, 350 °C. Helium was the carrier gas at a split ratio of 1:120 and argon–methane (95:5) was the makeup gas for the detector. An online computer calculated the retention time (t_R) of each peak and the normalized area as percentage of total peak area. Responses were calibrated by use of authentic standards where possible and in other cases by assuming similar electron-capture sensitivities to available standards.

Thin-layer chromatography (TLC) employed precoated 20 × 20 cm silica gel 60 F-254 chromatoplates (EM Laboratories, Inc., Elmsford, NY) with 0.25-mm gel thickness for analytical studies and 0.5 mm for preparative isolations. Three TLC solvent systems were used for one- and two-dimensional developments: hexane–ether (1:1, HE), tol-

Table I. Photoproducts of *S*-[^{14}C]Bioallethrin from Sunlight Irradiation of Thin Films

	yield, %[a]		R_f[b]		
product	1 h	3 h	TE	HE	t_R, min[b]
1	(33.0)[c]	(55.6)[c]	0.58	0.59	7.9
2	1.0	1.2	0.62	0.61	7.6
3	3.0	3.8	0.66	0.64	10.5
4	11.8	7.9	0.44	0.52	dec
5	4.2	3.2	0.35	0.45	9.9
6	5.2	6.7	0.27	0.39	9.9
7	3.6	2.9	0.40	0.48	13.0
8	3.0	3.2	0.31	0.42	13.0
9	25.2	14.7	0.38	0.52	3.3
10	0.9	1.5	0.47	0.55	7.0
11[d]	<0.1	nd	0.66	0.64	nd
unident[e]	42.0	54.9			

[a] Yields of 25 μg/cm² deposits are given as percent of [^{14}C]allethrin reacted. [b] For conditions, see the Methods section. [c] Values in parentheses are percent reaction at the indicated time. [d] Separated in CE (R_f 0.41) from 1-3 (R_f 0.35). [e] Unidentified products at R_f 0.0 in each solvent system.

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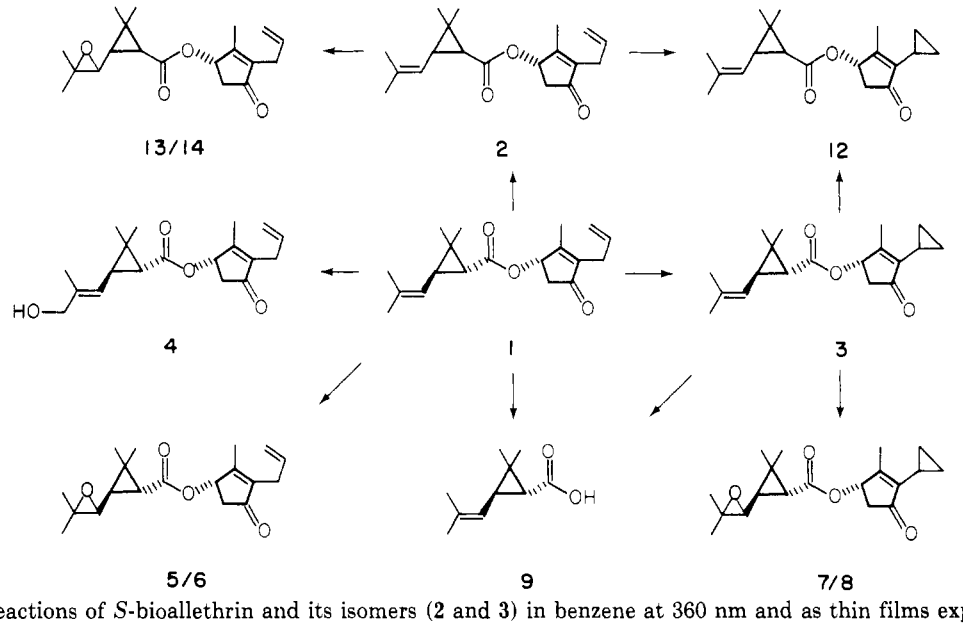

Figure 1. Photoreactions of *S*-bioallethrin and its isomers (**2** and **3**) in benzene at 360 nm and as thin films exposed to sunlight.

uene–ethyl acetate (6:1, TE), and carbon tetrachloride–ether (3:1, CE). R_f values for the HE and TE solvent systems are given in Table I. Unlabeled products were detected by their quenching of gel fluorescence at 254 nm or with 4-(*p*-nitrobenzyl)pyridine as the chromogenic reagent (Hammock et al., 1974). Radioactive products were detected on the chromatoplates by radioautography, recovered from the silica gel by extraction with ether, and quantitated by liquid scintillation counting (LSC). Quantitations of compounds **2** and **3** required combined TLC–GLC analysis.

Sources of Compounds. The compounds are designated as shown in Figure 1. *S*-Bioallethrin (**1**) and [1*R*,*trans*]chrysanthemic acid (**9**) were from Roussel-Uclaf-Procida (Paris, France) and (1*RS*,*cis*)-chrysanthemic acid and (4'*RS*)-allethrolone from Sumitomo Chemical Co. (Osaka, Japan). *S*-[^{14}C]Bioallethrin labeled in the acid moiety (1.3 mCi/mmol) was purified by TLC (TE) from material synthesized much earlier (Yamamoto and Casida, 1968) and stored at −10 °C in hexane with little decomposition. Sensitizers and quenchers were from Aldrich Chemical Co. (Milwaukee, WI).

(1*RS*,*cis*)-Allethrin (**2**) was prepared by reaction of (1*RS*,*cis*)-chrysanthemic acid (1.2 mmol) with 3 molar equiv of $SOCl_2$ at reflux in benzene (12 mL) for 2 h, followed by evaporation to dryness and treatment of the acyl chloride with allethrolone (1.4 mmol) and pyridine at 50 °C for 12 h. The product, isolated (85% yield) by TLC (TE), was characterized by NMR and CI–MS, *m/e* 303 [M + 1]$^+$. The di-π-methane rearrangement product (**3**), obtained by photolysis of **1** (1.7 mmol) in hexane (200 mL) at 260 nm for 7 h (Bullivant and Pattenden, 1976) and TLC (TE), was characterized by comparison of its NMR spectrum with that reported and by CI–MS, *m/e* 303 (M + 1)$^+$.

Epoxides **5**–**8**, **13**, and **14** were prepared by reaction of the corresponding esters with 2 molar equiv of *m*-chloroperbenzoic acid (MCPBA) in dichloromethane and characterized following TLC purification (TE) by CI–MS [*m/e* 319 (M + 1)$^+$, 301 (M − 17), and 273 (M − 45)]. The structures of **5** and **6** were further confirmed by NMR.

Photolysis Procedures. *S*-Bioallethrin was irradiated at 25–35 °C in solution (1.8–7.2 × 10^{-3} M) or as a thin film on glass (25–500 μg/cm^2) either by sunlight or with ultraviolet light in a Rayonet reactor (The Southern N. E. Ultraviolet Co., Middletown, CT) equipped with RPR 3600 or 2600 lamps. The thin films were irradiated through quartz, while solutions were contained in either quartz or Pyrex tubes transmitting light at >220 and >280 nm, respectively. Compounds **2** and **3** were irradiated at 360 nm in solution.

Singlet oxygen reactions were carried out with **1** (1.1 × 10^{-3} M) and bengal red B (1 × 10^{-2} M) in ethanol while irradiating at 360 nm and bubbling oxygen through the solution (Kearns, 1971).

Characterization of Photoproducts. *S*-Bioallethrin and its photoproducts were identified as follows: **1**, **3**, **5**, and **6** by comparison of their TLC and GLC characteristics (Table I) and their NMR and CI–MS spectra with those of authentic materials; **2** and **7**–**9** by cochromatography with standards; **4** by its NMR spectrum, no M + 1 ion in CI–MS but characteristic fragmentation to yield M − 17 (*m/e* 301, 11%) and M − 18 (*m/e* 300, 59%) ions, and an earlier finding (Chen and Casida, 1969) of trans methyl hydroxylation of the acid moiety recovered from photolyzed **1**. CI–MS data are available on two minor photoproducts, a decarboxylated derivative **10** [(M + 1)$^+$, *m/e* 259 (1 − CO_2)] and an epoxide **11** [(M + 1)$^+$, *m/e* 319]. All compounds from syntheses or photolyses designated as epoxides gave the normal purple-blue color with the 4-(*p*-nitrobenzyl)pyridine reagent (Hammock et al., 1974).

RESULTS

Photoproducts from Sunlight Irradiation of 1. *S*-[^{14}C]Bioallethrin is rapidly decomposed when exposed to sunlight as thin films on glass (Table I). The major identified products result from ester cleavage (**9**), oxidation at an isobutenyl methyl group (**4**), di-π-methane rearrangement (**3**), epoxidation (**5**–**8**), and trans–cis isomerization (**2**). Many minor photoproducts are unidentified, their number and amount being lower at <0.5 h than at 1 and 3 h (Table I) and increasing with longer irradiation times. They probably result in part from further oxidation reactions of the primary products, e.g., conversion of **4** to the corresponding allylic acid (Chen and Casida, 1969). The yield of **10** increased after 3 h, while that of **11**, a very minor component of the mixture, decreased even further, suggesting instability.

Sunlight photolysis of **1** in solution (3 h) yields most of the products observed in the solid phase. Aerated solutions give considerably greater amounts of epoxides than solu-

Table II. Effects of Oxygen, Sensitizers, and a Quencher on the Photoreactions of S-Bioallethrin in Benzene at 360 nm

compd	yield, %, with indicated additive[a]			
	none	benzophenone[b]	benzil[b]	1,3-cyclohexadiene[c]
1, % reacted	51.6 (51.6)[d]	73.3 (73.5)	66.4 (79.0)	13.1 (9.6)
3	34.9 (26.2)	18.9 (15.6)	11.4 (7.0)	<1.0
4	10.3 (9.3)	23.4 (16.3)	13.7 (10.5)	<1.0
5 + 6	21.4 (24.0)	14.7 (14.0)	35.5 (41.4)	6.2 (7.8)
7 + 8	15.3 (18.7)	17.3 (17.0)	20.1 (13.5)	<1.0
9	4.9 (4.2)	2.1 (2.0)	12.6 (10.9)	2.1 (2.2)
unident[e]	13.2 (17.6)	23.6 (35.1)	6.7 (16.7)	91.7 (90.0)

[a] 7.2×10^{-3} M ^{14}C-labeled 1, 1-h irradiation. [b] 3.0×10^{-3} M. [c] 5.5×10^{-2} M. [d] Values in parentheses refer to oxygen saturated solutions. [e] Unidentified products mostly at R_f 0.0 in each solvent system.

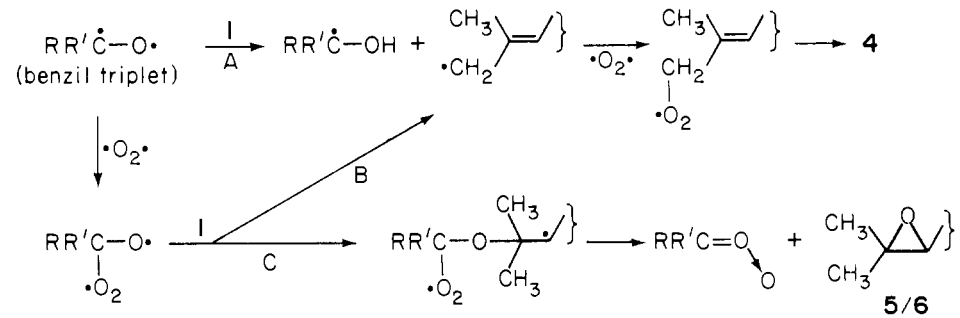

Figure 2. Photoreactions of benzophenone and the isobutenyl substituent of S-bioallethrin.

tions saturated with argon or nitrogen. Formation of **5** and **6** is greater in benzene (33%) than in hexane (12%), while their formation is not detected in methanol. Addition of benzil (0.3 M) to benzene or hexane solutions of **1** gives **5** and **6** as major photoproducts. In acetonitrile–water (4:1), **1** reacts to form **3** (70%), **2** (14%) and **5** and **6** (8%). Formation of **9** is comparable in all solvents (4–6%) but is increased in the presence of benzil.

Photoproducts from Ultraviolet Irradiation of 1. Direct photolysis of **1** in benzene at 360 nm yields **3–9** (Table II), observed previously in sunlight, plus **2**, **10–14**, and >25 other minor products. Oxygen saturation of the solvent decreases the yield of **3**, the major product, and gives a corresponding increase of epoxides **5–8**, while the yields of **4** and **9** are not affected.

The sensitizers benzophenone and benzil increase the reaction rate (Table II). At low concentration benzophenone increases the formation of **4**, and the yield of epoxides **7** plus **8** relative to **5** plus **6**. Saturation of the solvent with oxygen lowers the yields of **3** and **4** without other appreciable effects on the reaction. When benzil is used, **3** and **4** are decreased and **5** and **6** increased considerably. This effect becomes even more pronounced in oxygen saturated solutions. These trends are more evident at higher "sensitizer" concentrations, i.e., with 0.1 M benzophenone triplet products **2** and **3** are dominant while 0.1 M benzil yields predominantly **5** and **6**. With chlorobenzene as sensitizer (260 nm, hexane) and at 14% conversion, the yields are 28% for **2**, 54% for **3**, and 18% for **12**.

The quenchers 1,3-cyclohexadiene and naphthalene reduce the photolysis rate of **1**. Epoxides **5** and **6** are the only major products detected and in lower yield then in absence of quencher.

Ultraviolet irradiation of S-bioallethrin as a thin film on glass results in the same product distribution as that obtained in sunlight at low conversions.

Photochemical Formation and Fate of Isomers 2 and 3. Irradiation of **1** gives its cis isomer **2** in low yields (<1%) except, as already noted, in the presence of high benzophenone concentrations and in the presence of chlorobenzene. Compound **2** reacts in benzene at 360 nm at the same rate as **1** to give isomers **12** (54%) and **1** (9%) and the cis epoxides analogous to **7** and **8** (7%) and **13** plus **14** (5%). Under the same conditions, compound **3** reacts somewhat slower than **1**, forming **1** (74%) and **7** plus **8** (15%). With both compounds **2** and **3**, 1,3-cyclohexadiene efficiently quenches the reactions while benzil enhances epoxide formation and gives 2–4% of the corresponding chrysanthemic acids.

Singlet Oxygen Reactions of 1. Singlet oxygen reacts with **1** slowly (ca. 10% conversion in 6 h) to yield only two isomeric products which react with starch–iodide reagent (Stahl, 1960). Isolation by TLC (CE, R_f 0.16, 0.22) followed by CI–MS examination for each isomer revealed $(M + 1)^+$ at m/e 335 (2.3%), $(M - 17)^+$ (1.2%), and $(M - 33)^+$ (1.2%) with other major fragments at m/e 169 (5.4%), 167 (10%), and 135 (27%). The molecular ion indicates oxygen incorporation, possibly yielding a hydroperoxide which under CI conditions fragments by loss of water and hydrogen peroxide.

DISCUSSION

S-Bioallethrin yields many photoproducts via the excited states of the cyclopentenone, isobutenyl, and carboxylate chromophores (Figure 1). It undergoes three distinct types of photoreactions, i.e., isomerization, oxidation, and ester cleavage. Similar processes are involved in photolysis of other pyrethroids including resmethrin (Ueda et al., 1974), kadethrin (Ohsawa and Casida, 1979), permethrin (Holmstead et al., 1978), and decamethrin (Ruzo et al., 1977). Allethrin undergoes all these processes simultaneously and with relatively great efficiency. The estimated quantum yield is five–ten-fold that of the phenoxybenzyl-substituted pyrethroids, permethrin and decamethrin (Ruzo and Casida, 1980).

The present study defines the major primary photoproducts at low conversions. Most of these products retain the ester linkage. At high conversions there are more unidentified and unquantitated products, many difficult to separate and apparently unstable. Only one ester cleavage product, *trans*-chrysanthemic acid, was identified, and no fragments from the alcohol moiety were structurally defined.

The intermediacy of triplet excited states is established by the quenching effects of 1,3-cyclohexadiene (Et 50 kcal/mol) and naphthalene (Et 60 kcal/mol) and the increased yields of **2** and **3** with benzophenone (Et 69 kcal/mol) and chlorobenzene (Et 81.7 kcal/mol) at concentrations that absorb essentially all of the light. Di-π-methane rearrangement is favored over trans $\leftrightarrow$ cis isomerization because of the greater absorptivity of the cyclopentenone than of the cyclopropanecarboxylate chromophore. At lower sensitizer concentrations competitive absorption by **1** leads to product mixtures resembling those resulting from direct photolysis (Figure 1) but with enhanced yields of **4**.

The effect of benzophenone goes beyond transferring energy in its traditional role as sensitizer. It also provides a source of radicals in solution (Figure 2) which can abstract hydrogen (**A** or **B**) to yield allylic radicals leading to **4** or transfer oxygen (**C**) to form epoxides. Benzil (Et 53.4 kcal/mol) is considerably more efficient in the latter process (Shimizu and Bartlett, 1976) and gives greater yields of **5** and **6**. Epoxidation and allylic oxidation also take place in the absence of ketones probably again via radical reactions. In support of this postulate, epoxides and **4** do not form in alcohol solutions where readily abstractable hydrogen terminates radical reactions. Furthermore, oxidation processes will be less efficient in the presence of triplet quenchers since diffusion controlled quenching ($<10^{-9}$ s) would yield ground-state substrate precluding excited state reactions with oxygen (Cowan and Drisko, 1976).

Singlet oxygen is not involved in the oxidation reactions described above since the sensitizer bengal red gives a totally different product distribution.

The ester cleavage reaction producing chrysanthemic acid does not result from the triplet process, nor from nucleophilic attack by solvent as has been suggested for other pyrethroids (Ruzo et al., 1977). It may be initiated by an oxidative process since the yield of **9** increases in the presence of benzil, but the mechanism is not established.

A photoproduct mixture from allethrin was less acutely toxic than allethrin itself to mice treated intraperitoneally and houseflies treated topically (Chen and Casida, 1969), suggesting that most photoreactions of allethrin are generally detoxification processes. With the large number and variety of products now established, even in the early stages of decomposition, there is increased understanding of the major pathways followed and a sounder basis for assessing the toxicity hazards from residues of this chemical.

Supplementary Material Available: Nuclear magnetic resonance data for *S*-bioallethrin and related compounds (2 pages). Ordering information is given on any current masthead page.

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