Environmental Degradation of the Insect Growth Regulator Methoprene (Isopropyl (2E,4E)-11-Methoxy-3,7,11-trimethyl-2,4-dodecadienoate). III. Photodecomposition

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Photodecomposition products were characterized after irradiation of methoprene as a thin film on glass or silica gel, as an aqueous emulsion, and as a methanolic solution with added photosensitizer. The most abundant photoproduct of methoprene after illumination of a thin film or aqueous emulsion was 7-methoxycitronellal (9–14%). Methoprene was quite stable in methanolic solution although a slow reaction with singlet oxygen occurred. Isomerization of the 2-ene double bond to a mixture of cis–trans isomers was facile.

The utility of insect growth regulators (IGR's) as insect control agents is dependent partially on their photochemical stability. Photoinitiated decomposition probably contributes more to the environmental instability of IGR's than any other degradative mechanism. Methoprene (1, Altosid IGR, isopropyl (2E,4E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate) is a potent representative of a group of IGR's with juvenile hormone activity (Henrick et al., 1973). Methoprene is effective in controlling dipterous larvae (Schaefer and Wilder, 1973; Harris et al., 1973), but it is rapidly degraded under natural field conditions (Schaefer and Dupras, 1973).

This report represents part of a comprehensive study of the environmental fate of methoprene (for part II, see Schooley et al., 1975). We report the products and reactions resulting from perhaps the most important mechanism of environmental lability—photodecomposition.

EXPERIMENTAL SECTION

The methoprene used in these studies had the following purity: (2E,4E)-[5-^{14}C]methoprene [97.9% 2E, 1.5% 2Z, 5.0 mCi/mmol]. The [5-^{14}C]methoprene (Quistad et al., 1974) was diluted to various specific activities with nonradioactive methoprene [98.5% chemical purity; 99.4:0.6, 2E:2Z ratio; λ_{max} 259 nm (ϵ 26,000), hexane]. Radioactivity was quantified as discussed previously (Quistad et al., 1974). Mass spectra were determined at 20 eV by coupled gas–liquid chromatography (glc)–mass spectroscopy (ms) (Quistad et al., 1974). Nuclear magnetic resonance (nmr) spectra were determined on a Varian T-60 instrument. Infrared (ir) spectra were measured on a Beckman AccuLab 4. Ultraviolet (uv) spectra were determined on a Hitachi-Perkin-Elmer double beam spectrophotometer (Coleman 124).

Aqueous Solution Photodecomposition. Rate of Reaction. In order to assess the rate of aqueous photolysis, two 6-l. erlenmeyer flasks were filled with 4 l. of autoclaved phosphate buffer (0.05 M, pH 7). The sterilized water was aerated for 10 min by bubbling air from a stainless steel fritted filter (2 μ) through the solution. One flask was dosed with an acetone solution (4 ml) of (2E)-[5-^{14}C]methoprene at 0.01 ppm and the other flask at 0.50 ppm (5.0 mCi/mmol for 0.01 ppm; 0.88 mCi/mmol for 0.50 ppm). The flasks were fitted with a series of traps for the collection of ^{14}CO$_2$. Air passing into the flasks was first passed through soda lime (to remove atmospheric CO$_2$) and then rehydrated (5% potassium hydroxide). The air entered the flask and then exited into two traps containing KOH (5%, 200 ml). The flasks were exposed to direct sunlight (through ca. 2 mm Pyrex) for 3 weeks (July 11–Aug 2, 1973). The temperature of aqueous photolysate was monitored with a Tempscribe temperature recorder (Bacharach Instrument Co.). Average high temperatures are given in Table I. The weather was sunny with minimal smog. Aliquots (1 ml) from the KOH traps were counted in Insta-Gel (Packard) periodically to measure evolution of ^{14}CO$_2$. Aliquots (100 ml) of the aqueous photolysate were extracted with chloroform (3 × 75 ml) to follow the rate of methoprene photodecomposition (Table I). After 3 weeks the aqueous solutions of photoproducts were still aseptic as determined by culturing an aliquot (0.5 ml) on nutrient agar for 3 days.

The radioactivity collected in KOH traps was verified as ^{14}CO$_2$ by precipitation as Ba^{14}CO$_3$. A solution (60 ml) of BaCl$_2$ (0.4 N) and NH$_4$Cl (0.5 N) was added to the KOH solution (100 ml). The mixture was cooled in ice for 1 hr and then filtered through pre-weighed glass fiber paper; the white precipitate was washed with acetone. After drying and weighing, the precipitate was suspended in Insta-Gel (10 ml) and water (4 ml) for quantitation of radioactivity. An aliquot (1 ml) of the filtrate was also counted to determine the amount of unprecipitated radioactivity. This procedure gave a 71% yield of Ba^{14}CO$_3$. Another sample of KOH (100 ml) was acidified with HCl and purged of ^{14}CO$_2$ by adding Dry Ice while stirring. An aliquot (1 ml) was then counted to authenticate the removal of ^{14}CO$_2$. Ninety-three per cent of the radioactivity was removed from the KOH solution by this process, thus confirming the identity of ^{14}CO$_2$.

Aqueous Emulsion Photolysis. Isolation of Photoproducts. An aqueous emulsion of methoprene was irradiated in a 6-l. erlenmeyer flask (sunshine, April 4–11, 1974) to isolate photoproducts. A hard-water emulsion of methoprene was prepared with the following composition: methoprene (2 × 10^7 dpm, 400 mg), CaCl$_2$ (1.2 g), MgCl$_2$·6H$_2$O (0.56 g), Atlox 3404F (200 mg, ICI America), Atlox 847 (200 mg), and autoclaved water (4 l.). After irradiation for 1 week (sunlight through Pyrex), the entire photolysate was poured onto a column of Amberlite XAD-2 (Eastman, 4 × 11 cm). The effluent water contained little radioactivity (9%). Methanol (500 ml) eluted 83% of radioactivity and acetone (300 ml) eluted 4% of the radioactive photoproducts. Thus, 96% of the applied radioactivity was accountable. The methanol and acetone eluates were resolved into component photoproducts by tlc (silica gel GF, Merck, four 0.2 × 1 m plates; developed in benzene–ethyl acetate–acetic acid, 100:30:3). Because of the plethora of products further purification by tlc was also necessary. Photoproducts were characterized by nmr, ir, and glc–ms and showed spectral coincidence with reference standards.

The most abundant product (R_f 0.56, 9%) was 7-methoxycitronellal (2) which was isolated as its dimethyl acetal. Authentic dimethyl acetal (3) was prepared in

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quantitative yield by stirring citronellal (58 mg) in methanol (2 ml) containing p-toluenesulfonic acid (47 mg): nmr (CDCl$_3$) δ 0.91 (d, 3, J = 6 Hz, C-3 CH$_3$), 1.15 (s, 6, geminal CH$_3$), 1.33 (br s, 9), 3.19 (s, 3, OCH$_3$), 3.33 (s, 6, acetal OCH$_3$), 4.48 (t, 1, J = 6 Hz, CH(OCH$_3$)$_2$); ir (CDCl$_3$) no C=O; mass spectrum m/e (rel intensity), no molecular ion, 185 (2), 169 (5), 153 (2), 137 (13), 95 (11), 85 (14), 81 (22), 75 (90), 73 (100).

Methoxycitronellic acid (4, R_f 0.39) was isolated in 7% yield. It has been characterized from metabolic studies of methoprene (Schooley et al., 1975).

Isopropyl (2E)-4,5-epoxy-11-methoxy-3,7,11-trimethyl-2-dodecenoate (5, R_f 0.72) was recovered in 4% yield. An authentic standard was prepared in 49% yield by stirring methoprene (104 mg) with m-chloroperbenzoic acid (90 mg) in methylene chloride for 18 hr at room temperature: nmr (CDCl$_3$) δ 0.97 (d, 3, J = 6 Hz, C-7 CH$_3$), 1.16 (s, 6, geminal CH$_3$), 1.28 (d, 6, J = 7 Hz, CH(CH$_3$)$_2$), 1.37 (m, 9), 2.09 (d, 3, J = 2 Hz, C-3 CH$_3$), 2.85 (t, 1, J = 7 Hz, H-5), 3.11 (br s, 1, H-4), 3.20 (s, 3, OCH$_3$), 5.08 (m, 1, J = 7 Hz, OCH(CH$_3$)$_2$), 5.93 (s, 1, H-2); ir (CDCl$_3$) 1700 cm^{-1} (C=O); mass spectrum, m/e (rel intensity), no molecular ion, 207 (2), 98 (52), 95 (11), 81 (8), 73 (100).

8-Methoxy-4,8-dimethyl-2-nonanone (6, R_f 0.63) was isolated in 4% yield. An authentic sample was prepared in quantitative yield by treating methoxycitronellal with excess methylmagnesium bromide and oxidizing the resultant alcohol with acidic chromium trioxide in acetone: nmr (CDCl$_3$) δ 0.92 (d, 3, J = 6 Hz, C-4 CH$_3$), 1.17 (s, 6, geminal CH$_3$), 1.35 (m, 7), 2.15 (s, 3, COCH$_3$), 2.32 (m, 2, COCH$_2$) 3.20 (s, 3, OCH$_3$); ir (CDCl$_3$) 1705 cm^{-1} (C=O); mass spectrum, m/e (rel intensity), no molecular ion, 185 (2), 153 (3), 111 (5), 109 (6), 95 (10), 73 (100).

After 1 week of exposure to sunshine no methoprene was detectable from the aqueous emulsion. There were at least 46 other photoproducts but none was present in greater than 2% yield. A control showed no significant thermal decomposition at 40° in the dark.

Thin Film Photodecomposition on Glass. In order to measure the rate of photodecomposition on Pyrex glass, methoprene (3.1 mg, 0.15 mCi/mmol) was dissolved in acetone (20 ml) and uniformly coated on the walls (300 cm^2) of a 500-ml round-bottomed flask by solvent removal on a rotary evaporator. The application rate corresponds to 11 μg/cm^2 (1 lb/acre) and a film thickness of 0.1 μ. Other flasks of methoprene films were prepared in the same manner. The flasks were exposed to sunshine (Oct 5-7, 1973) with periodic removal for product assay. After addition of methanol, photoproducts were analyzed for total radioactivity and amount of methoprene (Table II).

Volatilized methoprene and photoproducts were collected in a gas trap (250 ml) containing a glass wool plug and immersed in a Dry Ice-acetone bath. Radioactive carbon dioxide was collected in two 5% potassium hydroxide traps (200 ml) connected to the outlet of the Dry Ice trap. After 6 days the methoprene (0.2%) and methoxycitronellal (4.0%) collected in the cold trap were characterized by tlc and glc. The contents of the KOH traps were verified as $^{14}CO_2$ as described above. Acidification of the trapped radioactivity in KOH followed by purging of $^{14}CO_2$ with Dry Ice liberated 83% of the ^{14}C label. Only a 14% loss of radioactivity accompanied the acidification-purging process for products collected in the cold trap; thus, little $^{14}CO_2$ was collected in the Dry Ice-acetone trap.

Thin film photoproducts were isolated after irradiation on glass. Methoprene (75 mg, 0.025 mCi/mmol) was dissolved in acetone (20 ml) and uniformly dispersed on the inner walls (1060 cm^2) of two 2-l. round-bottomed flasks. This application rate corresponds to 35 μg/cm^2 (3 lb/acre, 0.4-μ film thickness). The flasks were stoppered with glass wool plugs and exposed to direct sunlight (though ca. 2 mm Pyrex) for 4 days (Nov 1-4, 1973) during warm, clear weather. After 4 days, photoproducts in the flasks (94% of applied dose) were removed with methanol. The photolysate was preparatively fractionated by tlc on silica gel (hexane-ethyl acetate, 2:1) into six radioactive regions. The most nonpolar radioactive region (R_f 0.70) was identified as methoprene (7% of applied dose). Also isolated were methoxycitronellic acid (4, R_f 0.28, 4% yield), the epoxide 5 (R_f 0.64, 6%), and the methyl ketone 6 (R_f 0.42, 3%). There were at least 50 other photoproducts but none accounted for more than 4% yield.

Sensitized Thin Film Photodecomposition on Silica Gel. Anthraquinone (20 μg) and Rose Bengal (20 μg) were added to separate tlc plates (silica gel GF, Analtech, 5 $\times$ 20 cm, 250 μ). Methoprene (4 μg, 5.0 mCi/mmol) was dissolved in benzene and spotted on the sensitizers. Duplicates of each plate and controls with methoprene (but without sensitizer) were exposed to direct sunlight. After 1, 6, and 7 hr photoproducts were characterized by tlc (hexane-ethyl acetate, 100:15) and the distribution of photoproducts is summarized in Table IV. Radioactivity was recovered quantitatively and structures confirmed by glc.

Sensitized Methanolic Photolysis. Methoprene (290 mg, 0.94 mmol, 7.2 μCi/mmol), Rose Bengal (30 mg), and methanol (1 l.) were added to a Pyrex immersion cell. Oxygen was bubbled through the solution while stirring magnetically. The dilute solution was irradiated with a tungsten-halogen lamp (500 W, 120 V, Sylvania) for 4 days. Solvent was evaporated and the products isolated by tlc on silica gel (four 20 $\times$ 20 cm plates). The majority of the photolysate was unreacted (2E,4E)-methoprene (47%) and the 2Z,4E isomer 12 (30%).

A single major photoproduct was characterized as isopropyl 2,5-epoxy-2-hydroxy-11-methoxy-3,7,11-trimethyl-3-dodecenoate (7) which was isolated in 12% yield and characterized as follows: nmr (CDCl$_3$) δ 0.93 (d, 3, J = 6 Hz, CH$_3$), 1.15 (s, 6, geminal CH$_3$) 1.30 (d, 6, J = 7 Hz, OCH(CH$_3$)$_2$), 1.70 (t, 3, J = 1 Hz, =CCH$_3$), 3.20 (s, 3, OCH$_3$), 5.18 (m, 2, OCH(CH$_3$)$_2$ and H-5), 5.87 (s, 1, H-4); ir (CDCl$_3$) 3490 (OH), 1720 cm^{-1} (C=O); mass spectrum, m/e (rel intensity) after silylation with Regisil (Regis Co.), no molecular ion, 294 (20), 250 (11), 235 (19), 207 (10), 167 (18), 166 (26), 140 (14), 139 (14), 73 (100); uv λ_{max} 202 nm (ϵ 3900, cyclohexane). A structural isomer of 7 with the hydroxyl group at the 5 position in the dihydrofuran was excluded because the nmr spectrum lacked a methine singlet.

When 7 was treated with methanolic sodium hydroxide (0.1 M) it was converted in 45% yield into 6-(6-methoxy-2,6-dimethylheptyl)-3-hydroxy-4-methyl-2-pyrone (8): nmr (CDCl$_3$) δ 0.90 (d, 3, J = 6 Hz, CH$_3$), 1.16 (s, 6, geminal CH$_3$), 2.11 (s, 3, C-4 CH$_3$), 3.10 (s, 3, OCH$_3$), 5.86 (s, 1, H-5); ir (CDCl$_3$) cm^{-1} 3470 (OH), 1670 (C=O), 1660, 1580 (C=C); mass spectrum, m/e (rel intensity), 282 (1), 267 (13), 251 (12), 206 (9), 166 (13), 140 (12), 139 (8), 100 (12), 73 (100); uv λ_{max} 296 (ϵ 6900, cyclohexane).

Methoprene was stable under the same photolysis conditions without Rose Bengal or when oxygenated in methanol (<2% decomposition after 2 days). When a 0.3 M methanolic solution of methoprene was exposed to sunlight through 2-mm Pyrex glass for 25 days, only 10% of 1 had decomposed.

RESULTS AND DISCUSSION

Aqueous Photodecomposition. Before attempting to isolate and characterize the aqueous photooxidation products of methoprene (1), it was necessary to assess the magnitude of photolability. Therefore, an aqueous solution of 1 was exposed to sunlight through Pyrex glass, and the rate of decomposition was measured. Methoprene was rapidly decomposed in aqueous solutions of 0.5 ppm (Table I) and 0.01 ppm. The half-life of 1 at both concen-

Table I. Rate of Methoprene Photodecomposition in Aqueous Solution (0.5 ppm)

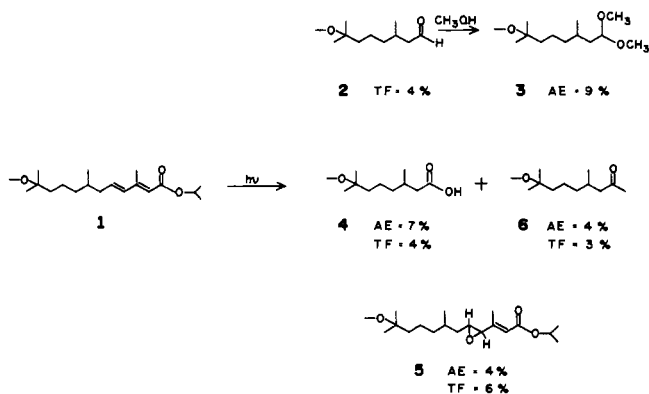| Day | % ^{14}C in water | % methoprene recovd | Extraction with $CHCl_3$ | | $^{14}CO_2/\%$ ^{14}C in KOH trap | Temp (av daily high), °C | Total ^{14}C recovd |
			% ^{14}C in $CHCl_3$	% ^{14}C in aq phase			
0	100	96	100	0	0.0	39	100
1	96	23	87	13	0.0	39	96
3	97	17	82	18	0.2	37	97
7	92	12	81	19	0.9	36	93
14	93	1	75	25	2.2	40	95
21	91	0	70	30	3.4		94

Figure 1. Photoproducts of methoprene from irradiation of an aqueous emulsion (AE) and thin film (TF) on glass.
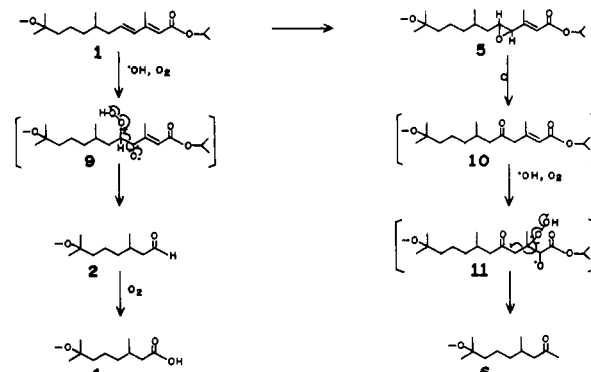

Figure 2. Possible mechanism for formation of photoproducts (cf. Swern, 1970).

trations was apparently less than 1 day although in related studies (Schooley et al., 1975) a half-life of 4–5 days was found. While the initial decomposition of 1 was extremely facile in this experiment, after 1 week 12 and 5% of the applied methoprene remained in the 0.5- and 0.01-ppm solutions, respectively. After 2 weeks there was no detectable methoprene. The rate of aqueous photodecomposition of 1 in this experiment was similar for 0.5- and 0.01-ppm solutions although somewhat faster at the more dilute concentration as expected. Total radioactivity in the aqueous photolysate was 91% of the applied dose after 3 weeks (Table I). An additional 3% was characterized as radioactive carbon dioxide which represented extensive decomposition in order to liberate C-5 in methoprene as $^{14}CO_2$. However, with 94% of the total radioactivity recovered, loss of photoproducts by volatility was minor for the aqueous photodecomposition.

Since methoprene has limited water solubility (1.4 mg/l.), it was difficult to amass enough of each photoproduct for detailed spectral analysis (i.e., nmr). Attempts were made to identify milligram quantities of five photoproducts produced in aqueous solution. These were characterized as oxygenation products, presumably involving the dienoate moiety. Four of the products (11, 13, 7.5, and 13% of the applied dose) could be acylated while the major product (25%) could not be acylated, methylated, or reduced (NaBH₄), but each of these products contained the ester and ether moieties present in the parent compound. However, no positive identifications of these substances were made. Several of these aqueous solution photoproducts appeared to be either impure or isomeric mixtures from nmr, and the mass spectra were singularly uninformative. Fragmentations of the tertiary methyl ether moiety of methoprene and its derivatives (i.e., photoproducts and metabolites) so dominate the mass spectra that relatively little information can be derived regarding modifications to the dienoate moiety (Dunham et al., 1973).

Indications of thermal instability of several photoproducts were found on glc–ms analysis.

The laborious isolation of minute amounts of products from copious quantities of water was circumvented by irradiation of an aqueous emulsion of methoprene (see Experimental Section). By photooxidizing a larger mass of emulsified methoprene (400 mg) it was considerably easier to purify enough material for spectral characterization. However, the distribution of photoproducts in the aqueous emulsion of methoprene was not identical with the profile of aqueous solution products.

After an aqueous emulsion of methoprene was irradiated for 1 week by sunlight through Pyrex glass followed by methanol chromatographic work-up, four photoproducts (24% yield overall) were characterized (Figure 1) as methoxycitronellal dimethyl acetal (3, 9%), methoxycitronellic acid (4, 7%), an epoxide of methoprene (5, 4%), and a methyl ketone (6, 4%). Unreacted methoprene was not detectable and there were at least 46 other photoproducts but none represented more than 2% yield.

The most predominant photolytic pathway involved formation of methoxycitronellal (2) and its subsequent oxidation to the corresponding acid 4. Methoxycitronellal (2) was isolated as its dimethyl acetal (3), which was undoubtedly an artifact of the isolation procedure.

Mechanistically, the formation of the aldehyde 2 (Figure 2) may involve initial peroxidation of the 4-ene double bond to give 9 (cf. Swern, 1970) which may undergo cleavage to give 2. Cleavage of similar peroxides to aldehydes has been reported (Gollnick, 1968). Air oxidation of the aldehyde 2 to the acid 4 occurs readily by autoxidation. A total of at least 16% of the methoprene was photolyzed by this or a similar pathway.

The epoxide 5 and methyl ketone 6 were produced by the operation of different mechanisms. Epoxidation of olefins is a well-known reaction even for otherwise unreactive olefinic pesticides (Crosby, 1973) although the mechanism

Table II. Rate of Methoprene Photodecomposition as Thin Film on Glass

Exposure to sun, hr	Methoprene recovd, % applied dose	Total radioact. recovd, % applied dose
0	97	100
3	79	100
6	50	100
12	29	95
27	3	72

**Table III. Collection of Volatile Photoproducts from Methoprene Photolyzed as Thin Film on Glass**

Day	2, % yield	1, % yield	% radioact. in cold trap[a]	% radioact. in KOH trap,[a] $^{14}CO_2$
1			0.4	
4	3.6	0.2	5.0	
5			6.7	
6	4.0	0.2	7.6	5.6

[a] Expressed as per cent applied dose.

is poorly understood. Formation of the 4,5-epoxide (5) follows from the greater reactivity of the 4-ene double bond than the 2-ene bond toward electrophilic peracids. Epoxidation of the 2-ene double bond is considerably slower, but can be accomplished with peracids under more drastic conditions (e.g., higher temperature). Hydration of the epoxide 5 to the diol was not detectable in contrast to a report on the photooxidation of another IGR (Gill et al., 1974). Formation of the methyl ketone 6 necessarily involved several steps. Rearrangement of the epoxide 5 would give the keto ester 10 (Figure 2). Subsequent peroxidation of 10 to 11 followed by scission of 11 would yield the methyl ketone 6. The postulated intermediates (i.e., 9, 10, and 11) could not be isolated from the crude photolysate.

Thin Film Photodecomposition. Methoprene was rapidly degraded when a thin film (0.1 µ) on glass was exposed to sunlight through glass (Table II). The half-life for photochemical breakdown under these conditions was 6 hr. After exposure to sunlight for 27 hr, only 3% of the applied dose remained as methoprene and it was isomerized to a 50:50 mixture of (2E,4E)- and (2Z,4E)-methoprene. The recovery of only 72% of the applied radioactivity after 27 hr suggested photolysis of methoprene to volatile products which were lost by vaporization. Collection of vapors above the photolysate resulted in recovery of 13% of the applied radioactivity (Table III). The volatile constituents were resolved into methoxycitronellal (2, 4%), methoprene (1, 0.2%), and $^{14}CO_2$ (6%). Since only a trace of methoprene (0.2%) was isolable from condensed vapors, volatility of methoprene was not a major route for loss of radioactivity.

Resolution of the crude photolysate after exposure of methoprene to sunshine for 4 days gave methoxycitronellic acid (4, 4%), the epoxide 5 (6%), the methyl ketone 6 (3%), and methoprene (7%, equal mixture of 2E and 2Z). There were also at least 50 other photoproducts, but none represented more than 4% yield. The production of photoproducts is summarized in Figure 1.
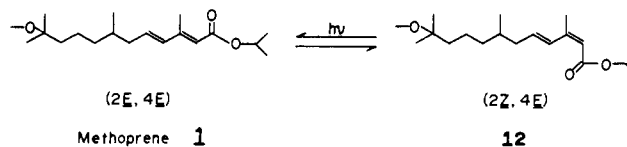
Figure 3. Photoisomerization of methoprene.

Table IV. Photoproducts from Photosensitized Decomposition of Methoprene on Silica Gel

	Time, hr	% methoprene (1) remaining	% Methoxycitronellal (2)	% origin	% other products
Control	1	91	2	4	3
(no sensitizer)	6	76	14	9	<1
Rose Bengal	1	85		11	4
sensitized	6	44	3	31	22
Anthraquinone	1	71		12	17
sensitized	6	14	6	73	7

The 2,4-dienoate chromophore of methoprene was quite susceptible to photoisomerization of the 2-ene double bond (Figure 3). (2E,4E)-Methoprene was readily isomerized to the 2Z,4E isomer 12 under most conditions (i.e., as thin film or in solution) after exposure to light (cf. Henrick et al., 1975b). Biological 2,4-dienoic metabolites (Quistad et al., 1974) and all field samples of aqueous methoprene (Schaefer and Dupras, 1973) contained substantial amounts of 2Z isomers. Photoisomerization of the 2-ene double bond drastically reduces the biological potency of methoprene, since the 2Z isomer 12 is 1000× less active on Aedes mosquito larvae (Henrick et al., 1975a). The 4-ene double bond is photochemically stable. Similar photoisomerization (50%) of the 2-ene double bond and stability of the 4-ene double bond has been observed for the 2Z,4E-dienoic chromophore in abscisic acid (Bonnafous et al., 1973).

Photosensitized Decomposition. Organic photosensitizers often accelerate photochemical reactions. The abundance of natural sensitizers (e.g., chlorophyll) justifies the inclusion of photosensitizers in a study of the environmental photodecomposition of methoprene. Two photosensitizers with different triplet energies (E_T) were selected to examine breakdown of methoprene on silica gel. Anthraquinone (E_T = 62 kcal/mol) was chosen because it was most effective in sensitizing decomposition of many pesticides (Ivie and Casida, 1971) and Rose Bengal (E_T = 42 kcal/mol) because it sensitizes the efficient production of singlet oxygen (at least in solution).

The effect of photosensitizers was observed for methoprene photodecomposition on silica gel plates. Both Rose Bengal and anthraquinone increased the rate of photocatalyzed breakdown of methoprene. The profile of products was similar to the thin film photodecomposition of methoprene on glass in exhibiting a multitude of components. Anthraquinone was more effective than Rose Bengal in this experiment (86% vs. 56% decomposition of methoprene in 6 hr) in sensitizing photodegradation (Table IV). The most prevalent product (10–14%) was methoxycitronellal (2) for the unsensitized photodecomposition on silica gel from the control (no added sensitizer). The formation of 2 was predominately photocatalyzed and not thermal since methoprene on silica gel in the dark at 40° gave only a 1–2% yield of 2. The sensitizers diverted the photo-
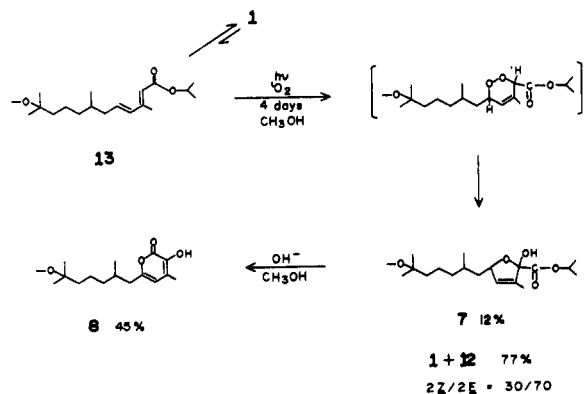
Figure 4. Methanolic photooxidation of methoprene, reaction with singlet oxygen.

chemical breakdown of methoprene from 2 to other pathways and also complicated the product distribution (Table IV). The rate of 2-ene isomerization was considerably slower on silica gel than in solution. After 7 hr exposure to sunlight on silica gel, methoprene was 36% isomerized [Z:E, 36:64] at the 2-ene bond whereas in aqueous solution the same amount of isomerization occurred in 2 hr.

Methoprene was very stable to photodecomposition in methanol. Without added sensitizer a solution of methoprene showed only 10% decomposition after 25 days in *methanol*. A dilute methanolic solution of methoprene with Rose Bengal sensitizer was also quite stable. After 4 days of photosensitized oxygenation 47% of the original (2E,4E)-methoprene was unreacted and 30% of the 2Z isomer 12 was formed (cf. Henrick et al., 1975b). A single major photoproduct (12%) was characterized as the dihydrofuranol 7. An isomer of 7 with the hydroxyl group in the 5 position was also structurally consistent with the spectral data except for multiple coupling of the methine proton in the nmr spectrum. The 2-hydroxydihydrofuran 7 should also be favored mechanistically by preferential removal of the methine proton adjacent to the carbonyl in the intermediate cyclic peroxide (Figure 4). Analogous hemiketals have been reported from the addition of singlet oxygen to other dienes (Mousseron-Canet et al., 1967). The addition of singlet oxygen to methoprene was slow and appeared to follow the mechanism given in Figure 4. A 1,4-cycloaddition of singlet oxygen to the s-cis-diene conformation of methoprene (13) could give the un-

stable cyclic peroxide which could collapse to the dihydrofuranol 7. Treatment of this hemiketal with base gave a 45% yield of the hydroxypyrone 8. The addition of singlet oxygen to the related 2,4-dienoate hydroprene has previously been shown to give the analogous hydroxypyrone although the dihydrofuranol was identified spectrally as an intermediate (Henrick et al., 1975b). Neither the dihydrofuranol 7 nor hydroxypyrone 8 could be identified as aqueous or thin film photoproducts of methoprene.

Methoprene is very susceptible to photolytic decomposition under environmental conditions. It is degraded to a plethora of photoproducts which are present in relatively low yield (<10%). The rapid degradation of methoprene and multiplicity of photolytic products are indicative of extensive photodegradability in the natural environment.

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