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NOVEL PHOTOPRODUCTS OF ALLETHRIN

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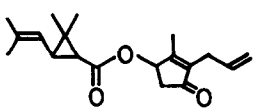
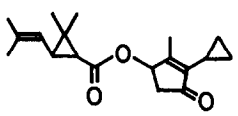
Abstract: Two polar photoproducts of allethrin, allethrolone and allethronyl glyoxylate, were isolated and identified. The formation mechanisms of these were also discussed.

Allethrin (1) is the first potent pyrethroid[1] and is widely used to exterminate vermin. Its use is limited, however, only to indoor one since it is less stable under sunlight than most other insecticidal chrysanthemates lacking an alkenylrethronyl substituent.[2] Several photochemical studies of (1) have been carried out in this connection so far : Cyclopropylrethronyl derivative (2) was produced almost quantitatively (>95% conversion) from di-π-methane rearrangement by irradiation through quartz or Pyrex in hexane[3] ; in addition to this photoreaction, isomerization, oxidation, and epoxidation of the isobutenyl group in the chrysanthemate moiety were observed in the solid phase or in solution by sunlight or UV light (λ360nm) at low conversions[4], and most of the photodegradation products were found to retain the ester linkage. At higher conversions there were found more copious products. Most of them, however, were left unidentified and unquantitated because of their instability to sepatation and purification procedures. Recently, E.C. Kimmel et al.[5] reported a novel product, 1-cyclopropyl-5-methyl-6-oxabicyclo-[3.1.0]hexan-2-on-4-yl chrysanthemate, which also retained the ester linkage. Only one ester cleavage product, trans-chrysanthemic acid, in fact was identified, but no fragments from the alcohol moiety were structurally defined. We want to report here the isolated polar photoproducts, which give us some important information for photochemical reaction of (1).



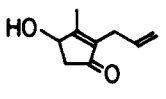
(1)



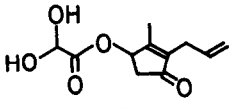
(2)

When (1) was applied on the surface of slide glass (4.0 mg/cm^2) and subjected to irradiation by a fluorescence lamp (15W) for 5 to 7 days or UV

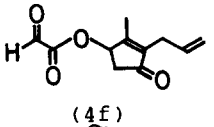
lamp for one day from a distance of 30 cm at 37 °C, many polar degradation products were formed. Two of them [(3) and (4)] were isolated and purified by silica gel thin layer chromatography (tlc) using benzene/methanol=7/1 (v/v) as a solvent system (Rf values of 0.33 and 0.46 for (3) and (4), respectively). These were fairly polar compounds judged by tlc Rf values of 0.02 and 0.04 in a solvent system of toluene/ethyl acetate=6/1 (v/v), in contrast to Rf=0.58 for (1). Purified (3) was identified as allethrolone based on ^{1}H-, ^{13}C-NMR and precise mass spectral data[6] and tlc cochromatography with the authentic sample. Product (4) was rather unstable at room temperature or even at 4 °C and converted to (3) to a considerable extent. Purified (4) was analyzed with ^{1}H-, ^{13}C-NMR and precise and field desorption mass spectrometry.[7] It was observed that (4) was retaining cyclopentenone and allyl group of allethrolone unchanged (no di-π-methane rearrangement to cyclopropane occurred) and ester linkage by ^{1}H-NMR spectrum. The molecular ion peak at m/z 208.0766 by precise mass spectrum (GC introduction) indicated that the molecular formula of (4) was $C_{11}H_{12}O_4$ with an error of +3.1 mmu. This formula, fragmentation pattern including conversion to (3) and NMR spectrum suggested (4) has the structure of $CHOCOOC_9H_{11}O$. Field desorption mass spectrum of (4) also showed molecular ion peak at m/z 208 and unidentified peak at m/z 226. However, there was one discrepancy in understanding NMR : there was a signal at δ9.44 ppm assigned as a formyl proton. The integral value, however, was too small to explain the whole existance of formyl group. In addition, ^{13}C-signal at δ87.1 ppm indicated that 2-position C of the acid moiety was mostly sp^3-C (-$\underline{C}H(OH)_2$) rather than sp^2-C (-$\underline{C}HO$) and this was agreed with the large proton signal at δ5.3 ppm ($C\underline{H}(OH)_2$) and the small one at δ9.44 ppm ($C\underline{H}O$) in ^{1}H-NMR. From these spectroscopic data including FD mass spectra (e.g. M^++18), (4) was concluded to be consisting of an equilibrium mixture of allethronyl dihydroacetate (4h, allethronyl glyoxylate monohydrate) and allethronyl glyoxylate (4f), the ratio of 4h/4f being >10 by NMR. For confirmation, (4) was synthesized with glyoxylate monohydrate and allethrolone in the presence of conc. sulfuric acid. The spectroscopic data of synthesized (4) were completely identical with purified one, exhibiting an equilibrium mixture of (4h) and (4f).



(3)



(4h)

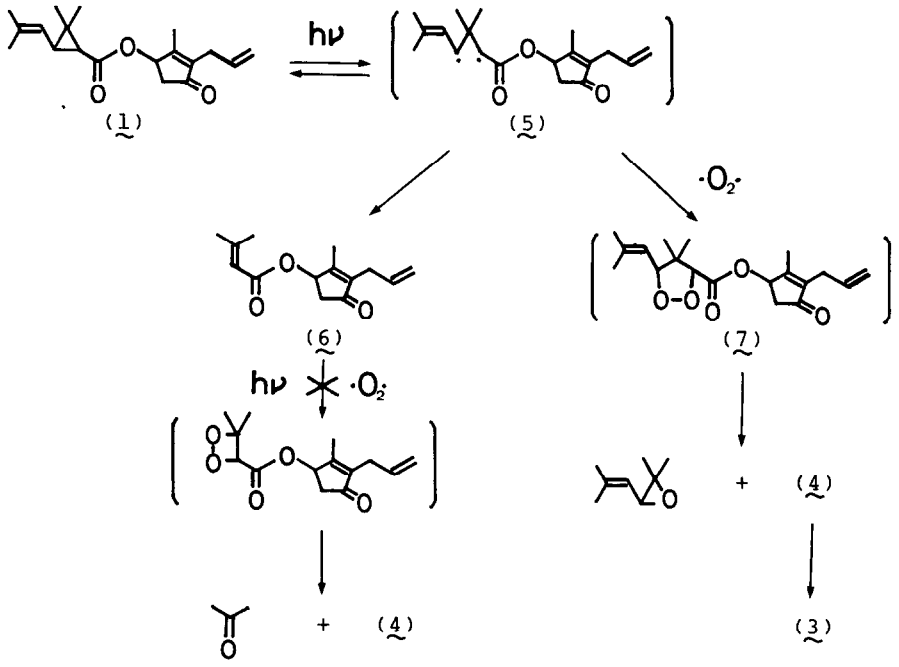


(4f)

Both light and oxygen appear to be essential for formation of (3) and (4) since if one of these factors is deficient, production of (3) and (4) are extremely restrained and practically none of them can be detected. For example, (3) and (4) were not detected when fluorescence lamp was irradiated

under nitrogen. Formation of (3) and (4) were also reduced by addition of BHT (2% wt), a well-known antioxidant and radical scavenger.[8] In these cases allethrin itself was recovered undegraded even though the biradical intermediate (5) appears to have been generated during irradiation.[9] These results imply that BHT scavenges oxygen and diminishes the reaction of oxygen with biradical (5) or unsaturated ester (6). The ester (6), which was said to be formed by sigmatropic migration from (5)[10], was detected in this experiment. However, (6) is not responsible for formation of (3) and (4) since the synthetic (6)[11] could not be converted to (3) and (4) by UV irradiation in air. Here, it is most likely as shown in scheme 1 that biradical (5) reacts with oxygen to form a hypothetical intermediate (7), which then yields product (4) and that product (3) is derived from (4) or other esters by hydrolysis.[4]

Scheme 1



References and Notes

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6) ^{1}H-NMR (100MHz,$CDCl_3$) δ2.10(s,3H), 2.28(dd,J=2.2,18.3Hz,1H), 2.81(dd,J=6.1,18.3Hz,1H), 2.96(d,J=5.9Hz,2H), 3.50(s,1H), 4.73(m,1H), 4.9-5.0(m,1H), 5.0-5.1(m,1H), 5.75(ddt,J=17.6,9.5,6.1Hz,1H) ; ^{13}C-NMR (25MHz,$CDCl_3$,COM) δ13.7(), 27.0(), 44.3(), 71.3(), 115.7(), 133.8(), 139.3(), 170.9(), 205.5(>C=O) ; precise-MS (GC introduction) m/z obs. 152.0877($C_9H_{12}O_2$,+4.1mmu,P.C.38.0), 137.0602($C_8H_9O_2$,+0.0mmu,P.C.20.5), 109.0571(C_7H_9O,-8.1mmu,P.C.100.0).

7) ^{1}H-NMR (100MHz,$CDCl_3$) δ2.04(s,3H), 2.34(dd,J=12.3,2.0Hz,1H), 2.92(dd,J=12.3,6.3Hz,1H), 3.01(d,J=5.9Hz,2H), 3.50(d,J=2.0Hz,2H), 4.91-5.00(m,1H), 5.08-5.12(m,1H), 5.3(m,1H), 5.56-5.96(m,2H), 9.44(s,slight) ; ^{13}C-NMR (25MHz,$CDCl_3$,COM) δ13.9(), 27.1(), 41.1(), 74.5(), 87.1(-CH(OH)$_2$), 116.2(), 133.2(), 142.0(), 165.5(), 170.5(), 204.0(>C=O) ; precise-MS (GC introduction) m/z obs. 208.0766($C_{11}H_{12}O_4$,+3.1mmu,P.C.15.6,M^+), 135.0856($C_9H_{11}O$,+4.7mmu, P.C.50.4,$M^+-C_2HO_3$), 134.0789($C_9H_{10}O$,+5.8mmu,P.C.43.2,$M^+-C_2H_2O_3$) ; FD-MS m/z 226(M^++H_2O,P.C.6), 208(M^+,P.C.100), 152(allethrolone$^+$,P.C.35), 135(M^+-CHOCOO,P.C.48), 29(CHO^+,P.C.50).

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11) 3-Methyl-2-butenoyl chloride (10 mmol) in benzene was added to allethrolone (10 mmol) and pyridine (10 mmol) and stirred for 1.5 hr at 50 ℃. The reaction mixtures were purified on silica gel column chromatography (toluene/ethyl acetate=9/1,v/v) to give an oil (2.21 g). The yield was 94%. ^{1}H-NMR (100MHz,$CDCl_3$) δ1.92(s,3H), 2.02(s,3H), 2.19(s,3H), 2.36 (d,J=2.0Hz,1H), 2.80(d,J=6.1Hz,1H), 2.99(d,J=6.3Hz,2H), 4.94(m,1H), 5.07 (m,1H), 5.5-6.0(m,3H) ; EI-MS (20eV,GC introduction) m/z 234(M^+,P.C.50), 134(M^+-$(CH_3)_2$C=CHCOOH,P.C.90), 83($(CH_3)_2$C=$CHCO^+$,P.C.100).

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