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PHOTOLYSIS OF BIO-ALLETHRIN

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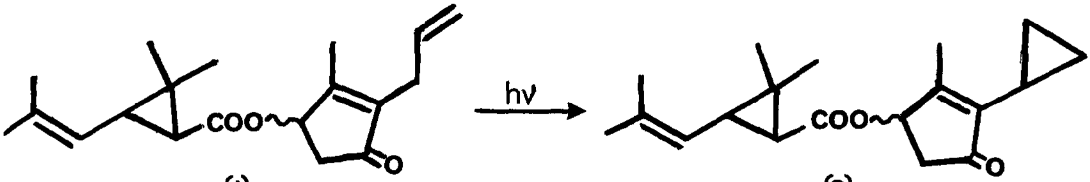
Bio-allethrin (1) is a widely employed synthetic insecticide,[2] structurally analogous to the naturally occurring 'pyrethrin' insecticides found in Chrysanthemum cinerariaefolium. The natural pyrethrins and their synthetic analogues have the desirable environmental properties of being both non-toxic to mammals and non-persistent. These features, combined with their broad spectrum of insecticidal activity, have made them commercially successful compounds, and also environmentally safe and acceptable alternatives to DDT and related insecticides. We have now examined the solution photochemistry of bio-allethrin and found that it is converted almost quantitatively to a single photoproduct corresponding to rearrangement in the prop-2'-enyl side chain of the molecule.

Irradiation of a 0.15% solution of a diastereoisomeric mixture of commercial bio-allethrin [prepared from (+)-trans acid and (±)-alcohol][3] in n-hexane, using a 100W medium pressure Hg arc and either pyrex or quartz filtered light resulted in the formation of a single photoproduct (g.l.c. and t.l.c. monitoring) which after purification by column chromatography could be isolated in up to 90% yield. Mass spectral data showed that the photoproduct was monomeric (m/e 302.1880; $C_{19}H_{26}O_3$), and furthermore, from the fragmentation pattern, indicated that the cyclopropane carboxyl moiety in (1) had been retained.[4] The n.m.r. spectrum lacked absorptions corresponding to the five hydrogens of the prop-2'-enyl side chain in (1) and instead displayed additional absorption above τ 8.9 due to cyclopropyl hydrogens; the rest of the n.m.r. spectrum of the photoproduct was closely similar to that of (1)[5]. In the infrared the photoproduct showed carbonyl maxima at 1723 (ester) and 1714 (ketone)cm.$^{-1}$ but lacked absorption bands



(1) (2)

associated with terminal vinyl C-H o.o.p. vibrations. These data were consistent with the cyclopropane formulation (2) for the photoproduct. Concomitant photochemical studies with other prop-2'-enylcyclopentenones are consistent with this conclusion.[6]

The photochemical conversion of (1) to (2) corresponds to a di-π-methane rearrangement.[7] The rearrangement to (2) was found to be completely quenched in the presence of 2,5-dimethylhexa-2,4-diene, which in conjunction with related studies[6] suggests a triplet excited state pathway from (1) to (2). Saponification of the photoproduct and separation of the acidic product, gave _trans_-cyclopropane acid only; no evidence was obtained for the accompanied formation of either _cis_- cyclopropane - and/or 3,3-dimethylacrylic esters during photolysis of (1) (_cf_. ref. 8).

In biological tests,[9] the cyclopropane photoproduct (2) showed <1% knockdown with female _Aedes aegypti_ mosquitoes and ∿10% knockdown with _Musca domestica_ in comparison with bio-allethrin (1).

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