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PHOTOOXIDATION OF (Z,E)-9,11-TETRADECADIENYL ACETATE, THE MAIN COMPONENT OF THE SEX PHEROMONE OF THE FEMALE EGYPTIAN COTTON LEAFWORM (SPODOPTERA LITTORALIS)

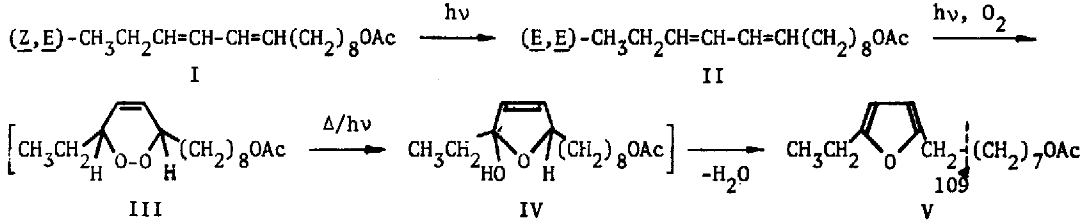
Arnon Shani* and Jacob T. Klug

Department of Chemistry and Applied Research Institute

Ben-Gurion University of the Negev, Beer Sheva, Israel

Monoolefins and conjugated dienes are known to react with singlet oxygen to form allylic hydroperoxides in the first case and endoperoxides in the second one.[1] Most of the already known insect sex pheromones are long chain aliphatic alcohols, aldehydes, ketones or esters with one or two double bonds along the chain.[2] It is thus expected that oxidation will take place when these compounds are left in sunlight. The photooxidation of (Z,E)-9,12-tetradecadienyl acetate,[3] and fatty acids,[4] are examples of this type of chemical reactivity.

The main component of the sex pheromone of the female Egyptian cotton leafworm (Spodoptera littoralis) is (Z,E)-9,11-tetradecadienyl acetate (TDDA) (I).[5] Study of its stability under field conditions (sunlight and heat, 45-55°C in summertime) revealed that it is mostly decomposed together with isomerization to form a mixture of the 4 possible 9,11-TDDA isomers.[6] While monitoring the photoisomerization by GLC, another product with longer retention time on FFAP or DEGS SCOT capillary column,[6] was detected. This compound showed a molecular ion at 266 m/e, 14 mass units higher than the starting material. A reasonable explanation for this increase is the addition of an oxygen atom and abstraction of 2 hydrogen atoms. This was proved by the inhibition of its production by an antioxidant (UOP or BHT). A very intense peak in the MS appeared at 109 m/e. The possibility of allylic oxidation to form hydroperoxide and further α,β-unsaturated ketone system was ruled out. UV and IR spectra did show an end absorption in the UV and only one carbonyl (acetate) absorption in the IR at 1735 cm^{-1}. NMR spectrum of the new product [($CDCl_3$), δ 1.10(t,3H), 1.25-1.40(m,12H), 2.03(s,3H), 2.55(t,2H), 2.64(t,2H), 4.04(t,2H), 5.83(s,2H)] showed 2 olefinic hydrogens only as a singlet at 5.83 ppm as compared to 4 olefinic protons in I.



Ring formation explains the abstraction of 2 hydrogens to produce a furan system. The proposed structure for the oxidation product is V. We assume that this product is derived from the endoperoxide III, the initial product of (E,E)-9,11-TDDA (II) with singlet oxygen. Thermal and/or photodecomposition of III, to lose H_2O, produces V.

Rose bengal as photosensitizer accelerated the conversion of I to V. Four hr of illumination yielded V, 70% of all volatile components, detected by GLC, as compared to 35% of V after 16 days without Rose bengal. Additional proof for the early isomerization of I to II is demonstrated in Fig.1. Oxidation product from illumination of I is first formed only after appreciable amount of II is accumulated.

The reaction of the conjugated (E,E)-diene system is more favourable than other possible stereoisomers in Diels-Alder reaction to form the endoperoxide. This differentiation in reactivity is applied to TCNE reaction with (E,E)-diene in order to purify other conjugated systems.[2] It was found that the sex pheromone of codling moth, (E,E)-8,10-dodecadienol, forms a similar oxidation product.[7] When the endoperoxide formed is in conjugation to a carboxylate, a lactone is isolated.[8]

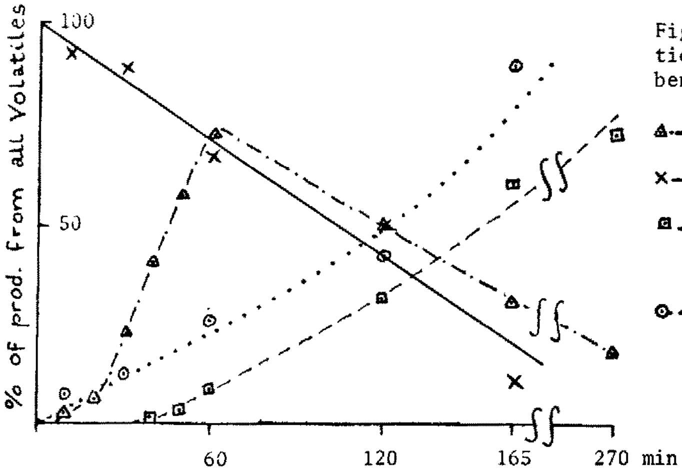


Fig.1. Photoisomerization and photooxidation of I and II in sunlight with Rose bengal a sensitizer.

This type of reaction is different from that of endoperoxides, derived from cyclic dienes, which either release singlet oxygen or decompose to diepoxides by thermal or photochemical process.[9] In previous reports[10] substituted 1,3-dienes, as a terminal system, have been studied, while in our case, internal 2,4-diene or 1,4-disubstituted butadiene is the reactive system. The relative fast reaction of the acyclic conjugated system, regardless of stereoisomeric purity, to form a furan ring, can be used, as a simple synthetic approach to the substituted heterocyclic system.

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