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INSECT CHEMISTRY III⁺. USE OF THE PHOTOCHEMICAL NORRISH TYPE I REACTION TO THE SYNTHESIS OF THE DIHYDROTERPENEDIOL SECRETED BY THE AFRICAN MONARCH BUTTERFLY

Jean Pierre MORIZUR, Gérard BIDAN and Jean KOSSANYI
(Laboratoire de Chimie Structurale et Photochimie, associé au CNRS, Université Pierre et Marie Curie, Bât.F, 4 place Jussieu, 75230 Paris Cedex 05, France)

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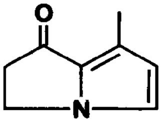
The success of the photochemical α-cleavage of cyclopentanones to give access to γ,δ-unsaturated aldehydes, intermediates in the synthesis of natural compounds (1-3), prompted us to extend this reaction to α-functionalized cyclopentanones.

Out of the already known natural compounds, the E isomer of dihydroterpenediol 1 was choosen as model for testing new applications of the NORRISH type I reaction. This compound has been characterized (4), together with the heterocyclic ketone 2, as one of the two major components of the hairpencil (brushlike glandular organs) of the *Danaus Chrysippus* (African Monarch), an old world member of the subfamily Danainae.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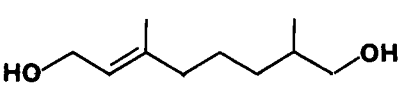
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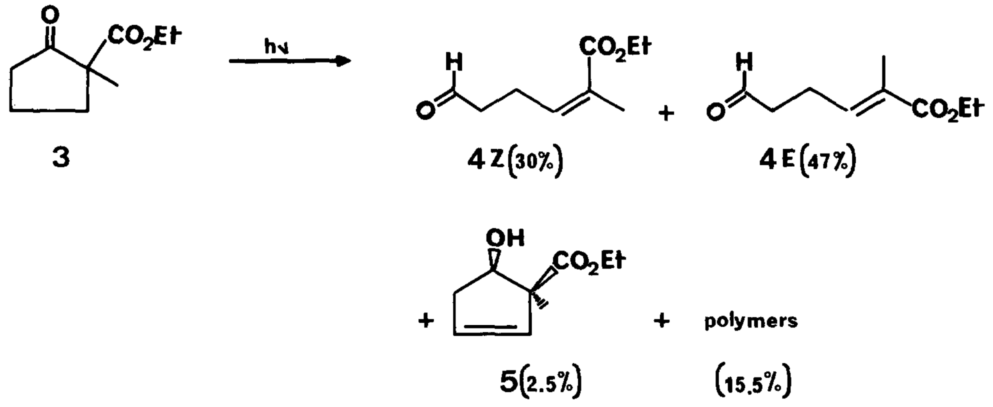
An easy access to diol 1 implies a bifunctional and unsymmetrical intermediate which could be obtained by irradiation of the α-methyl Dieckmann ester 3. The photochemical behaviour of 2-cyanocyclohexanone and 2-cyanocycloheptanone has been reported recently (5); although the corresponding aldehydes resulting from α-cleavage are formed, the reaction gives also cyclisation products in substantial yields. In the present case, irradiation (6) of ketoester 3 (prepared according to (7)) up to 95% conversion, gives aldehydes 4 (8), as a mixture of E + Z isomers, together with a small amount of hydroxyester 5 (scheme 1). 4E and 4Z can be obtained in the pure form by carefull distillation. Aldehydo-ester 4Z has been characterized from its IR (2700, 1720 and 1650cm^{-1}), NMR ($\delta(CCl_4)$: 9.80 (1H,t, $J \sim$ 1Hz), 5.95 (1H,t, J 6Hz), 4.18 (2H,q, J 7Hz), 2.80-2.45 (4H,m), 1.88 (3H,s), 1.28 (3H,t, J 7Hz)) and UV spectra ($\lambda_{max}^{cyclohexane}$ (ε): 217(9,000), 290(33)). Isomer 4E displays the following spectral results:

+ Part II, see reference 3

IR (2730-1720-1650cm^{-1}), NMR (δ(CCl$_4$) : 9.82 (1H,t, J∿ 1Hz), 6.63 (1H,t, J 6Hz), 4.15 (2H,q, J 7Hz), 2.56 (4H,m), 1.83 (3H,s) and 1.28 (3H,t, J 7Hz)), UV($\lambda_{max}^{cyclohexane}$ (ε) : 217(11,500), 290(38)).

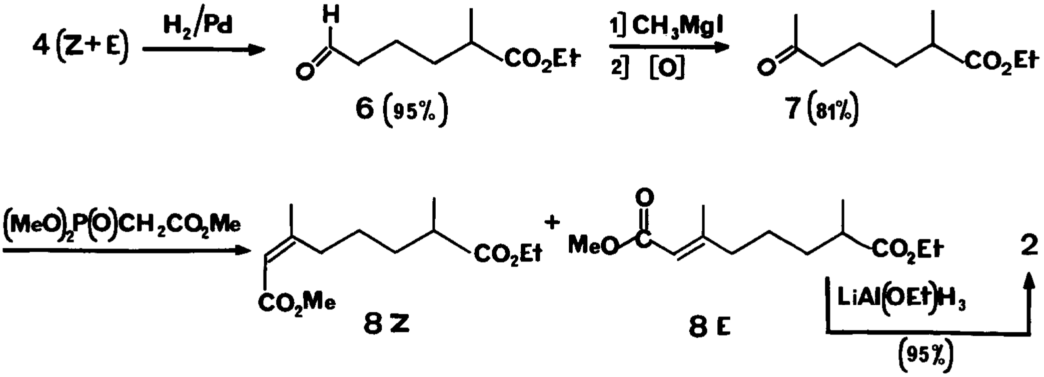


Scheme 1

The quantum yield of aldehyde formation at 3130Å is 0.19 for the E isomer and 0.03 for the Z isomer (6% conversion); the build up of the Z isomer is time-dependent and 4Z becomes the main photoproduct after irradiation for several hours. The evolution of the E/Z ratio comes from direct irradiation (quartz vessel) of the double bond of the unsaturated ester function as well as from intramolecular energy transfer of the excited aldehyde triplet to the double bond but the first process is the most efficient : irradiation of the pure E and Z isomers at 3130Å, in degazed cyclohexane solution, gives the following results for intramolecular energy transfer: $\phi_{Z\to E}$= 0.006 and $\phi_{E\to Z}$= 0.02 . The E:Z photostationary state for direct irradiation of the double bond is 8:5.

Structure of compound 5 has been verified by catalytical reduction (Pd/C) of the double bond and comparison of the reduced product with the two isomers obtained by sodium borohydride reduction of keto-ester 3 and nuclear Overhauser effect on the obtained two isomers.

The good yields obtained for preparing the aldehydo-esters 4 and the possibility for monitoring the E:Z ratio make very attractive the substituted Dieckmann esters as starting materials for the synthesis of natural products. Thus, reduction of the double bond forms compound 6 which, in turn, reacts with methylmagnesium iodide at a temperature lower than -30°, at only the aldehyde function. Jones oxidation of the obtained alcohol yields ethyl 6-keto-2-methylheptanoate 7 (scheme 2). Homologation of 7, using Wittig and Horner reagent, $(MeO)_2P(O)CH_2COOMe$ in the presence of sodium methylate and in anhydrous dimethyl formamide solution, affords with 95% yields the Z and E isomers of the unsaturated diester 8 in a 35:65 relative ratio. Separation of the two isomers is easily achieved by VPC (180° : SE30 over chromosorb w). The E isomer is characterized by the following spectral results: IR (1725,1680cm^{-1}), UV (217nm; ε= 14,500) and NMR (5.46 (1H, broad signal), 3.95 (2H,q, J 7Hz), 3.51 (3H,s), 2.4-1.9 (3H,m), 2.01 (3H,s), 1.5-1.3 (4H, broad), 1.05 (3H,t, J 7Hz), 0.98 (3H, d, J 7Hz). The 8Z isomer differs only by the intensity of the UV absorption (ε= 11,700) and by the position of the NMR signal of the methyl and methylene groups attached to the double bond : 1.73 and 2.7-2.3ppm respectively.



Scheme 2

Reduction of isomer 8Z, using an excess of lithium monoethoxyaluminium hydride(9) affords dihydroterpenediol 2 with an overall yield of 34% starting from α-methyl Dieckmann ester.

The NMR spectra of the final compound is in complete agreement with that published (4) for the natural substance.

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