

INSECT CHEMISTRY. APPLICATION OF THE NORRISH TYPE-I REACTION TO THE SYNTHESIS OF
PROPYLURE, THE SEXUAL PHEROMONE OF *Pectinophora gossypiella* Saunders.

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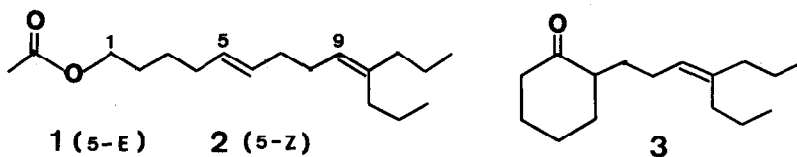
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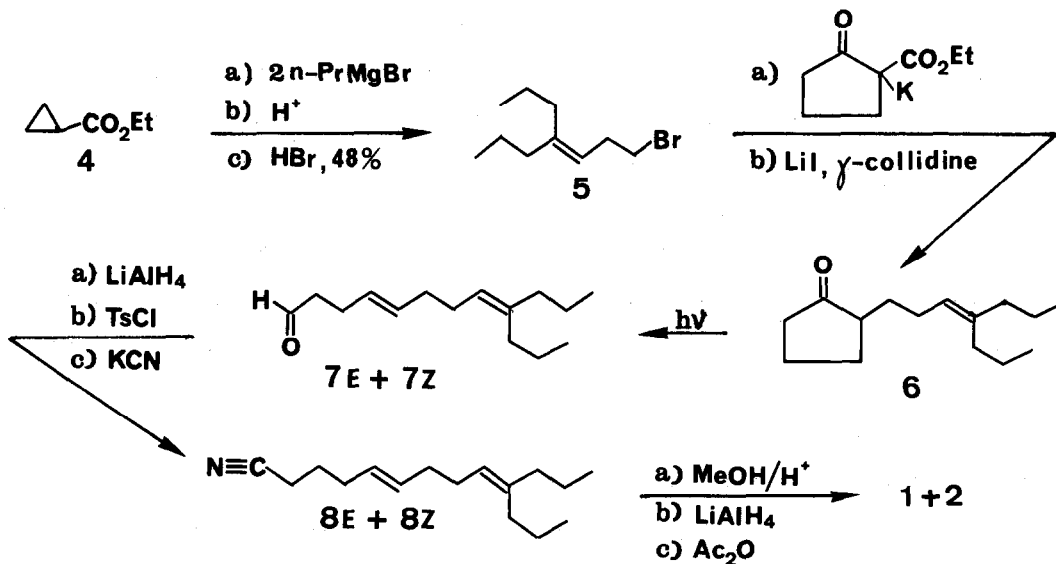
Photochemistry has been shown to be a powerful synthetic method for functionalizing molecules. The photochemical ring opening of cyclanones (Norrish type-I) into non-conjugated unsaturated aldehydes can be used, as a key reaction step, in the approach of naturally occurring unsaturated long-chain compounds. We already mentioned¹, for 2-substituted cyclohexanones, that the Norrish type-II photochemical reaction, inducing the elimination of the α -alkyl substituent, is an important side-reaction in the aldehyde formation; further work in this series indicates that a heavy non-aromatic α -substituent gives mainly ring-closure of the corresponding cyclohexanone to cyclobutanols². On the other hand, α -substituted cyclopentanones undergo only minor side-reactions and their irradiation (quartz vessel) gives, as principal photoproducts, the aldehydes resulting from the Norrish type-I reaction; furthermore, the quantum efficiency of this reaction is at least three times higher for five-membered ring ketones than for their six-membered homologues.

We describe, here, the use of the Norrish type-I photoreaction to the synthesis of propylure, the sexual pheromone secreted by the female of *Pectinophora gossypiella* Saunders (pink bollworm moth). This compound, characterized³ as 10-*n*-propyltrideca-5 (*E*), 9-dienyl acetate 1, has been synthesized by several authors ⁴ to ⁹.

Irradiation of ketone **3**, which would be a suitable starting material for preparing **1** in only three steps, gives 10-*n*-propyltrideca-5 (*E*),9-dien-al in very poor yields; the main reaction products being cyclohexanone, 4-propylhepta-1,3-diene and a mixture of isomeric 8-(2-*n*-propyl-1-pentenyl) bicyclo (4.2.0) octan-1-ols.



The substituted cyclopentanone **6**¹⁰ has been prepared, with 60% yields, by alkylation of Dieckman ester's potassium salt (DMSO solution), followed with decarboxylation in refluxing γ -collidine¹¹; the alkylating agent, 1-bromo-4-*n*-propylhept-3-ene **5**, was obtained (scheme 1) in two steps, with 80% overall yields, according to Julia's method¹² for converting α -cyclopropyl alcohols into homoallylic halides.



scheme 1

Irradiation of ketone 6 (Hanovia, 450w ; quartz; 0.1 mole in benzene) limited to 30-40% transformation, leads to the isomeric aldehydes 7E and 7Z in the 2:1 relative ratio. Aldehydes 7E and 7Z¹⁰ can be separated from 6 by preparative tlc (silicagel; benzene), and each isomer can be isolated pure by VPC¹³. A pure sample of the *trans* isomer 7E has the following spectral data: ir 2,715-1,730 and 965cm⁻¹ ; nmr (δ) 9.7 (aldehyde H), 5.4 (*m*, C-4 and C-5 olefinic H) and 5.05ppm (*t*, $J \sim 6$ Hz, C-8 olefinic H).

The usual reaction sequence, depicted on scheme 1, has been used to prepare a mixture of *cis* 9Z and *trans* 9E 10-*n*-propyltrideca-5,9-dien-1-ol¹⁰, which has been transformed into 1 + 2. Separation of the latter, carried out by column chromatography (30% AgNO₃ impregnated florisil ; elution with 9:1 ligroin-ether) gives propylure 1 with 20% overall yields from the mixture of aldehydes 7E + 7Z ; the spectral results of propylure 1 are in complete agreement with those already published^{3,4}.

Transformation of aldehydes 7E + 7Z into 9E + 9Z , using the modified Wittig's reagent, methoxymethyltriphenylphosphonium chloride¹⁴ failed in our hands, and very poor yields (<8%) of the expected enol-ether were obtained. Several experiments, using this reagent with saturated or unsaturated aldehydes, such as 2,7-dimethyloct-6-en-al, gave also very disappointing results. Similar behaviour has been reported¹⁵ for cyclopentanone.

The use of the Norrish type-I reaction as a key-step in the preparation of juvenile hormone¹⁶ and in the synthesis of other naturally-occurring unsaturated aliphatic compounds will be reported later¹⁷.

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