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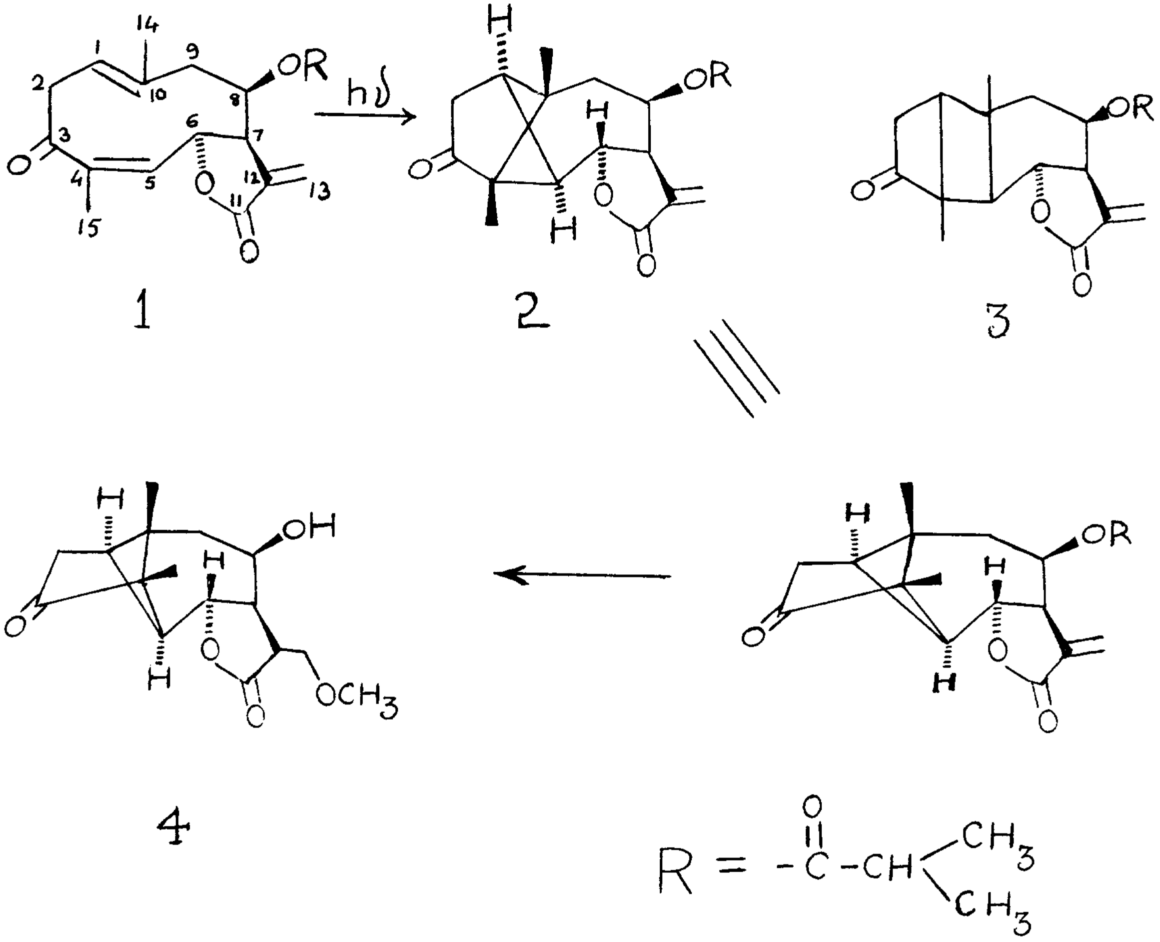
PHOTOCYCLIZATION OF A HELIANGOLIDE - A CYCLODECADIENONE

P.K. Chowdhury, R.P. Sharma* and J.N. Baruah
Division of Natural Products Chemistry
Regional Research Laboratory (C S I R)
Jorhat-785 006, Assam, INDIA

Abstract : Irradiation of the dienone 1 furnishes essentially a single tricyclic product 2 containing cyclobutane ring. The corresponding epoxide 5 furnishes tagitinin F 6 - an antileukemic compound.

Photocyclization of cyclodecenone system incorporating the isolated double bond at the γ,δ position in the cyclodecane ring have been reported to yield the major products as the tricyclic compounds containing cyclobutane ring[1,2]. However, irradiation of 0.4% absolute ethanol solution of the heliangolide 1[3] with a bare arc mercury lamp through quartz led exclusively to the formation of compound 2 mp. 140°C, which was identified as follows[4]. ^{1}H NMR spectrum ($CDCl_3$) of the photolysis product exhibited a singlet at δ 1.25 ppm integrating to six protons and thus suggesting the formation of compound 2 or 3. In the IR spectrum ($CHCl_3$) the intensity of the absorption band at 1740cm^{-1} was almost double than that at 1770cm^{-1} favouring structure 2 over 3. Methanolysis with $NaOCH_3/CH_3OH$ furnished 4 in whose IR spectrum absorption bands at 1775 and 1740cm^{-1} clearly established the identity of the photolysis product as 2. The proton under the lactone oxygen in 2 appeared as a doublet at δ 4.85 ppm with J=9.5 Hz and therefore, hydrogen at C-5 was assigned α configuration in conjunction with the molecular models. Recording the NMR spectrum of 2 in C_6D_6 shifted the methyl at C-4 to the lower field (δ 1.57 ppm) thus indicating it to be equatorial and therefore β[5]. Examination of the molecular models of 2 dictates that if C-5 hydrogen is α and C-4 methyl is β then C-10 methyl and C-1 hydrogen ought to be β and α respectively, however, this decision may be treated as tentative.

The pronounced selectivity observed in the formation of 2 reveals that the mode of photocyclization of cyclodecadienone depends upon the geometry of the conjugated double bond and the position of the isolated double bond[1,2,6]. The above studies will have implications on the synthesis of naturally occuring tricyclic sesquiterpene and sesquiterpene lactones[7,8] containing cyclobutane ring.



1

2

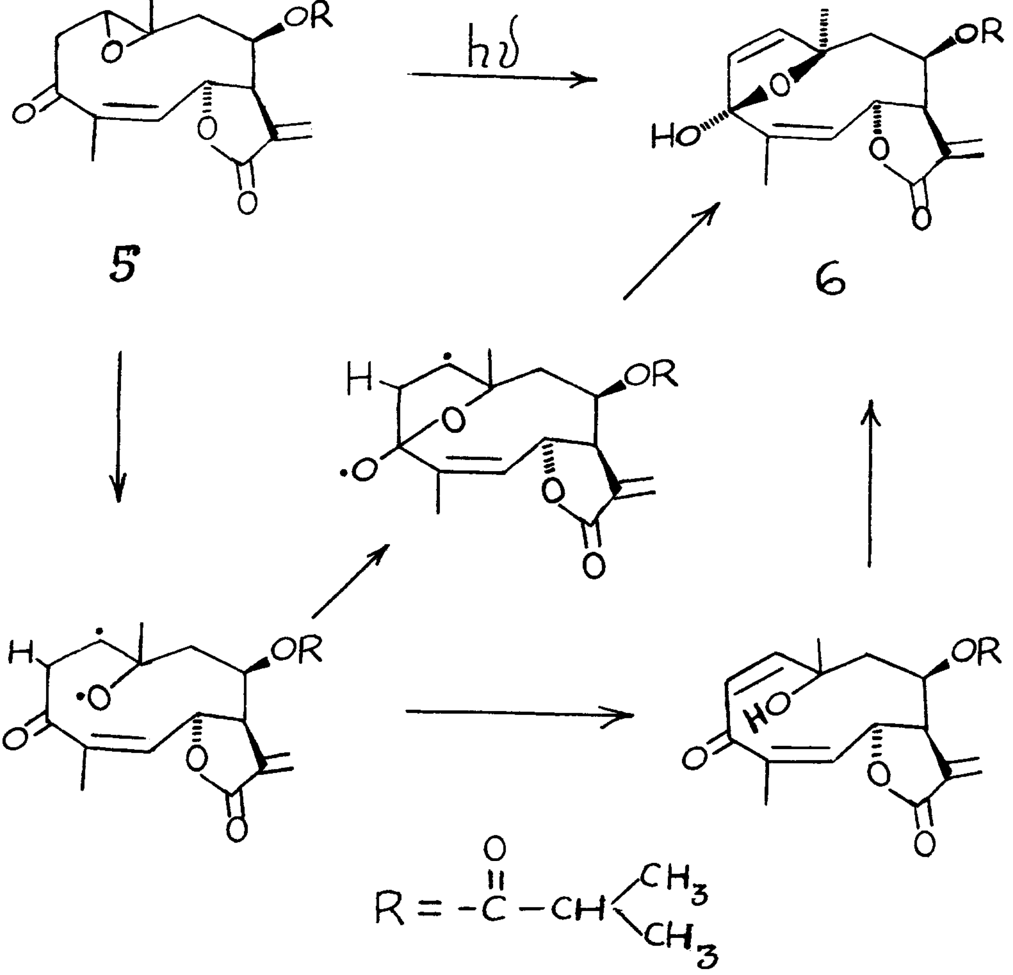
3

4

$R = -\overset{O}{\overset{\|}{C}}-CH\langle{}^{CH_3}_{CH_3}$

We also examined the photolysis of 0.4% absolute ethanol solution of the epoxide 5[3] with a bare arc mercury lamp through quartz flask, which led almost quantitatively in 6 hr to the formation of tagitinin F 6 - a highly potent antileukemic sesquiterpene lactone[9,10], 1,3 or 1,4 Hydrogen shift is suggested to be involved in the formation of tagitinin F 6 as shown in Scheme I. The possibility that tagitinin F 6 is biosynthesized in the plant through pigment sensitised photocyclization of the epoxide 5 is quite high since the corresponding C-4 alcohol of 5 known as tagitinin E is a congener of tagitinin F[9].

SCHEME - I



$R = -\overset{O}{\overset{\parallel}{C}}-CH\begin{matrix}CH_3\\ CH_3\end{matrix}$

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   Germacradienolides containing 4,5-*cis* and 10,1-*trans* double bonds are known as heliangolides.

4. The reaction was monitored on TLC. After 8 hr 50% of **2** was obtained besides recovering 40% of the starting material. Prolonged irradiation led to extensive decomposition. Compound **2** gave satisfactory analytical data.

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6. Photolysis of Germacrene D **i** gives mainly (−)-β-bourbonene **ii**, α-bourbonene and β-copaene are the minor products.

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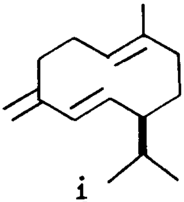
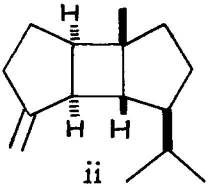


i



ii

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10. The photolysis was carried out at 20°C as higher temperature furnished small amounts of other products which were not identified. The identity of tagitinin F **6** was established by direct comparison with an authentic sample.

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