188. A New Type of Photorearrangement of γ-Hydroxy-α,β,δ,ε-dienone

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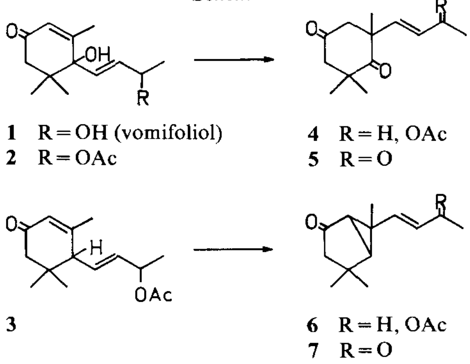
Summary

A new type of photorearrangement of the γ-hydroxy-α,β,δ,ε-dienone, vomifoliol acetate (**2**) to the diketone **4** is described, and its facile rearrangement is compared with that of desoxyvomifoliol acetate (**3**).

Photochemical rearrangement of cyclohexenones and cross-conjugated dienones have been well-studied [1]. The photorearrangement of the 4-hydroxycyclohexadienone system has also been reported [2]. Following our interest in the photochemistry of iononoid terpenes [3], we report here the photorearrangement of the γ-hydroxy-α,β,δ,ε-dienone, vomifoliol acetate (**2**) [4] as the first example of the photolysis of such a system where the δ,ε-double bond is outside the γ-hydroxy-α,β-cyclohexenone ring. The photolysis of its desoxyderivative **3** is also described.

Scheme 1



1 R=OH (vomifoliol)
2 R=OAc

4 R=H, OAc
5 R=O

3

6 R=H, OAc
7 R=O

An ice-cold solution of **2** in ether was irradiated with a 450 W high pressure mercury lamp through *Pyrex* filter. After 45 min the rearranged product **4** was isolated by column chromatography (60%). – IR. (film): 1730, 1710, 1240. – ^{1}H-NMR. (CDCl$_3$, 100 MHz): 1.14 (*s*, 3 H); 1.18 (*s*, 3 H); 1.23 (*s*, 3 H); 1.25 (*d*, $J = 7$ Hz, 3 H); 2.00 (*s*, 3 H); 2.26–2.67 (*m*, 4 H); 5.2 (*m*, 1 H); 5.5 (*m*, 2 H). – MS.: *m/z* 206 ($M^+ - 60$).

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Compound **4** was hydrolyzed to give the alcohol which was reconverted to **4** by acetylation and also oxidized to **5**, the double bond of which is (*E*) (NMR.). – UV. (EtOH): 218 (9200). – IR. (film): 1710, 1680, 1620. – ^{1}H-NMR. ($CDCl_3$, 100 MHz): 1.17 (*s*, 3 H); 1.20 (*s*, 3 H); 1.31 (*s*, 3 H); 2.20 (*s*, 3 H); 2.45–2.81 (*m*, 4 H); 5.92 (*d*, *J* = 16 Hz, 1 H); 6.71 (*d*, *J* = 16 Hz, 1 H).

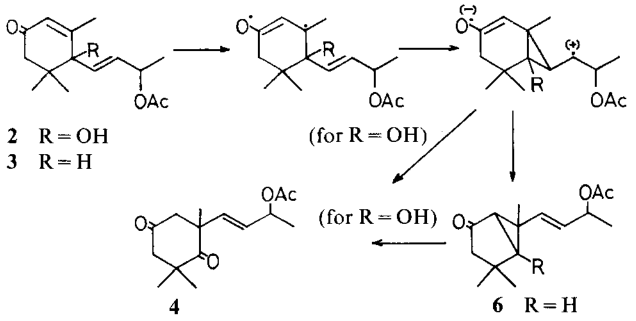
The irradiation of desoxyvomifoliol acetate (**3**) in the same manner for 4 h yielded the 1:1 mixture of the starting acetate **3** and the rearranged products **6**, which were a 1:1 mixture of diastereoisomers at the C-atom bearing the acetoxy group. Both isomers were isolated and converted to the diketone **7**. The presence of a cyclopropane ring in **6** is clear from UV. and NMR. spectra.

Data of **6**. – IR. (film): 1730, 1720, 1240. – ^{1}H-NMR. ($CDCl_3$, 100 MHz): *a)* 1.13 (*d*, *J* = 1.5 Hz, 3 H); 1.16 (*s*, 6 H); 1.27 (*d*, *J* = 7 Hz, 3 H); 2.00 (*s*, 3 H); 5.32 (*m*, 1 H); 5.52–5.74 (*m*, 1 H); 6.02 (*m*, 1 H). – *b)* 1.10 (*d*, *J* = 1.5 Hz, 3 H); 1.14 (*s*, 6 H); 1.26 (*d*, *J* = 7 Hz, 3 H); 1.98 (*s*, 3 H); 5.3 (*m*, 1 H); 5.5–5.7 (*m*, 1 H); 5.98 (*m*, 1 H). – MS.: 250 (M^+).

Data of **7**. – UV. (EtOH): 248 (9700). – IR. (film): 1720, 1680, 1615. – ^{1}H-NMR. ($CDCl_3$, 100 MHz): 1.16 (*s*, 6 H); 1.24 (*s*, 3 H); 2.19 (*s*, 3 H); 6.32 (*d*, *J* = 16 Hz, 1 H); 7.00 (*d*, *J* = 16 Hz, 1 H).

The above results show that the rearrangement from the photoequilibrium in the activated state is accelerated by the presence of the hydroxyl group at the γ-position in **2**. A plausible mechanism is shown in *Scheme 2*. This is a new example of the di-π-methane rearrangement of γ-hydroxy-$\alpha,\beta,\delta,\varepsilon$-dienones.

Scheme 2



The rearranged product, **4** could be a useful intermediate for the synthesis of terpenes.

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