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PHOTOCHEMISTRY OF β,γ-UNSATURATED 5,10-SECO-STEROIDAL KETONES

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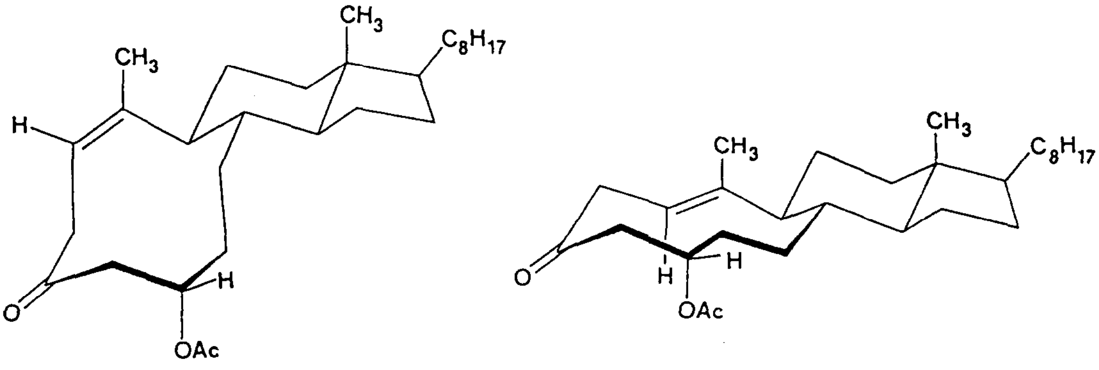
Abstract: *UV irradiation of the β,γ-unsaturated 5,10-seco-steroidal ketones* **1** *and* **2** *in dioxane or isopropanol resulted in Z/E isomerization, while similar irradiation in acetone effected, besides, epoxidation (in the presence of air) and addition of solvent to the olefinic double bond.*

The photochemistry of β,γ-unsaturated ketones has been extensively investigated.[1] Depending on the structure and the way of excitation, these compounds undergo, in addition to transformations characteristic of the homoconjugated enones, i.e. 1,3-acyl shift (usually from the excited singlet state) and 1,2-shift or oxa-di-π-methane rearrangement (from the excited triplet state), practically all of the known photochemical reactions of isolated ketones (such as α-cleavage, decarbonylation and type *II* reaction) or alkenes (for example [2+2] cycloaddition, reduction and *Z/E* isomerization).

The present study is concerned with a novel photochemical behaviour of the β,γ-enone grouping incorporated in the ten-membered ring of the (*Z*)- and (*E*)-5α-acetoxy-5,10-seco-cholest-1(10)-en-3-ones (**1** and **2** , Scheme 1),[2] induced by UV light in acetone solution.

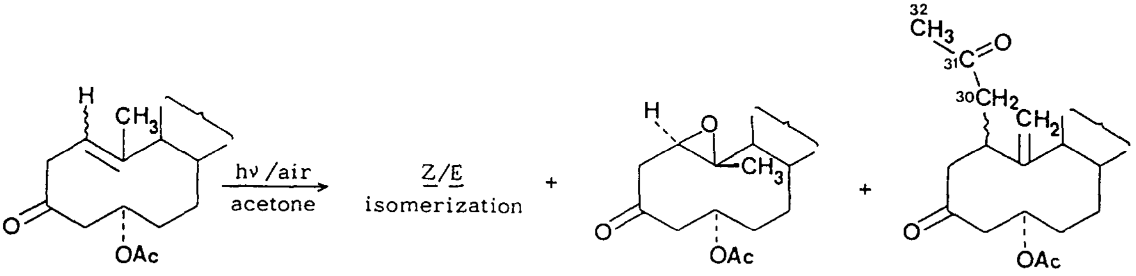


1 (Z-isomer) **2** (E-isomer)

Scheme 1

When these (*Z*)- and (*E*)-seco-ketones (**1** and **2**) were irradiated in dioxane or isopropanol solution (~2x10^{-3} M) with a high pressure mercury lamp (TQ 150 Z2), the only observable photoprocess was Z/E isomerization. In both cases, after 4 h of irradiation, a photostationary mixture of stereoisomers was obtained (with an E/Z ratio of about 1:1.1 and 1:1.6, respectively).

However, when similar irradiation of the (*Z*)- and (*E*)-seco-ketones **1** and **2** was performed in acetone solution (from which air, as above, had not been expelled), besides Z/E isomerization, two additional photochemical transformations took place as well, namely (i) epoxidation of the olefinic $\Delta^{1(10)}$-double bond, which, irrespective of the geometry of the starting seco-ketone, gave only the *trans*-1β,10α-epoxide **3** (Scheme 2) (in about 20% yield); and (ii) oxidative addition of the solvent molecule to the olefinic double bond, affording the acetonyl derivative **4** as a single (1α or 1β) isomeric form (Scheme 2) (in less than 10% yield).[3]



1(Z) or **2**(E) **3** **4**

Scheme 2

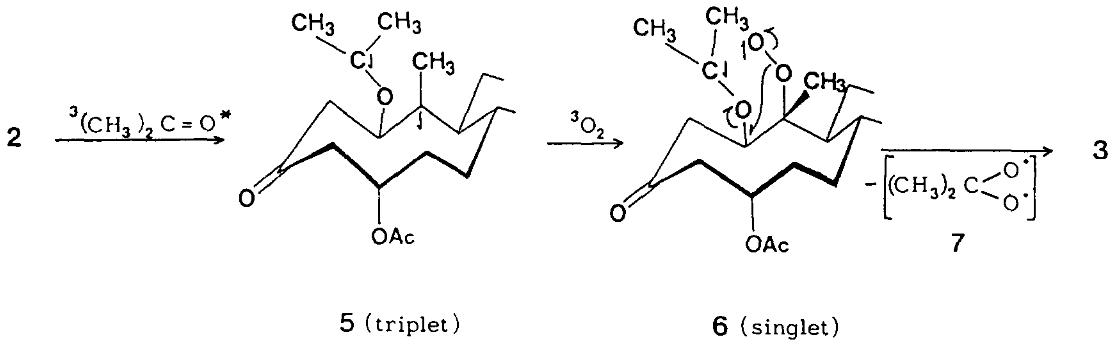
A similar result with the (*E*)-seco-ketone **2** was obtained when during irradiation oxygen was bubbled through the solution, while experiments carried out under nitrogen gave no epoxidation. However, in the latter case the yield of the acetonyl derivative **4** was considerably increased (to about 34%). The results are summarized in Table 1.

Table 1. Irradiation of **1** and **2** in acetone solution (~2x10^{-3} M) with TQ 150 Z2 lamp for 4 h

Substrate		Yields (%)			
		1	**2**	**3**	**4**
Z-isomer **1**	$\xrightarrow{h\nu/air}$	34	8	17	8
E-isomer **2**	$\xrightarrow{h\nu/air}$	32	8	20	9
E-isomer **2**	$\xrightarrow{h\nu/O_2}$	31	7	14	10
E-isomer **2**	$\xrightarrow{h\nu/N_2}$	48	11	–	34

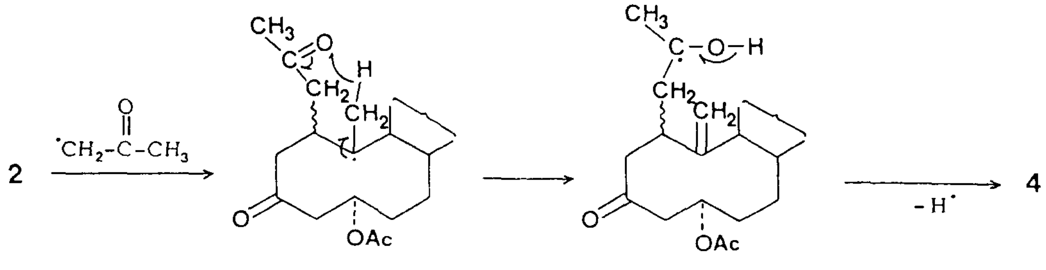
In order to get more information regarding the mechanism of epoxidation, an oxygen saturated benzene-methanol (9:1) solution of the (*E*)-seco-ketone **2** was irradiated in the presence of Methylene blue or Eosine, dyes wich are known to be sensitizers for singlet oxygen. However, they proved to be inefficient in inducing epoxidation, indicating that the reaction does not proceed by the intermediacy of singlet oxygen. Rather, all the results obtained suggest that acetone used as solvent plays an active role in the photoepoxidation.

A plausible mechanism for this reaction would consist in the initial formation of the biradical intermediate **5** (Scheme 3), arising from attack of acetone triplet at C(1) of the $\Delta^{1(10)}$-double bond, followed by the attachment of oxygen to the other, i.e. C(10), radical site of this bond.[4] The peroxy biradical thus formed (**6**, Scheme 3) closely resembles the species which Shimizu and Bartlett[5] considered as possible intermediates in the photoepoxidation of alkenes sensitized by α-diketones and benzophenone. According to the proposed mechanism, **6** could fragment into epoxide **3** and a biradical species **7** possesing a methylene dioxide structure.[6]



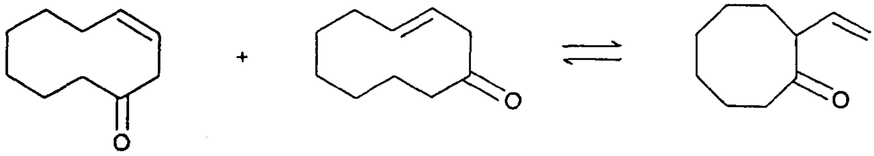
Scheme 3

On the other hand, the oxidative addition of acetone to the 1(10)-double bond of seco-ketone **1** and/or **2**, with formation of a new C—C bond, can be rationalized as a free-radical process which possibly could take place as shown in Scheme 4.



Scheme 4

Finally, it seems important to point out the difference in reactivity between the (*Z*)- and (*E*)-5α-acetoxy-5,10-seco-cholest-1(10)-en-3-ones (1 and 2), on the one hand, in which the olefinic double bond behaves as an isolated chromophore (undergoing upon UV irradiation *Z/E* isomerization, and, in acetone, also epoxidation (in the presence of air) and addition of solvent to the 1(10)-double bond), and the unsubstituted (*Z*)- and (*E*)-3-cyclodecenones (8 and 9), on the other, which upon direct irradiation undergo a photoreversible 1,3-acyl shift[7].



8 (Z) 9 (E)

Acknowledgement. The authors are grateful to the Serbian Academy of Sciences and Arts and to the Serbian Republic Research Fund for financial support.

References and Notes

1. For a review article see K.H. Houk, Chem. Rev., 76, 1 (1976).
2. Compounds 1 and 2 were prepared from the isomeric (*Z*)- and(*E*)-3β-acetoxy-5,10-seco-cholest-1(10)-en-5-ones (M. Lj. Mihailović et al., Tetrahedron, 22, 2345 (1966)). To be published.
3. Satisfactory elemental analysis and spectral data (IR, ^{1}H-NMR, ^{13}C-NMR, MS), were obtained for 3 and 4 . The structure 3 was confirmed by epoxidation of 2 with *m*-chloroperbenzoic acid. *Compound* 4 ($C_{32}H_{52}O_4$), m.p. 144-145°: MS - m/z 500 (M^+); ^{1}H-NMR (CD_3OD, 360 MHz), selected data: δ (ppm) 2.00 (s, AcO-5), 2.14 (s, H_3C-31), 2.40-3.20 (multiplets for 2 allylic and 6α to carbonyl protons), 4.94 (m, H-5), 5.02 and 5.04 (2 exocyclic vinyl H); ^{13}C-NMR ($CDCl_3$, 20.1 MHz), selected data: δ(ppm) 207.0 (C-3), 71.5 (C-5), 155.0 (C-10), 110.8 (C-19), 50.2 (C-30), 208.5 (C-31), 30.6 (C-32).
4. Biradicals of type 5 are usually intermediates in the Paterno-Büchi reaction. However, in the present case oxygen addition at C(10) is preferred to intramolecular coupling, probably because strong steric repulsion between the acetone methyl groups and hydrogens at C(11) prevents ring closure to oxetane.
5. N. Shimizu and P.D. Bartlett, J. Am. Chem. Soc., 98, 4193 (1976).
6. Eventually 7 could dimerize to a cyclic peroxide, which might fragment photochemically to acetone and molecular oxygen.
7. R.G. Carlson and J.H. Bateman, Tetrahedron Letters, 4151 (1967).

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