39. The Photooxygenation of $\Delta^{9(11)}$-Dehydroestrone and its 3-Methyl Ether

Photochemical Reactions XX[1])

Preliminary Communication

by **Pilar Lupón, Ferran Grau** and **Juan-Julio Bonet***

Department of Organic Chemistry, Instituto Químico de Sarriá, Barcelona-17, Spain

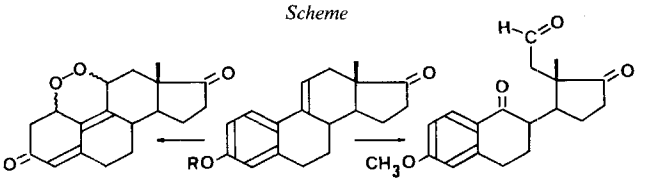
(27.IX.83)

Summary

The photosensitized oxygenation of $\Delta^{9(11)}$-dehydroestrone yields a complex mixture mainly of unstable compounds, while its 3-methyl ether gives 3-methoxy-9,17-dioxo-9,11-seco-1,3,5(10)-estratrien-11-al, in good yield.

We have recently reported that the photosensitized oxygenation of estradiol and estrone gives, in good yield, the corresponding 10 β-hydroxy-1,4-androstadienones, which can be easily transformed into 19-norsteroids [2]. Here we describe the behaviour, under the same photooxygenation conditions, of the title compounds **1** [3] and **2** [3a] (*Scheme*).

Scheme



3 **1** R=H **4**

2 R=CH_3

The photooxygenation of **1** in methanol solution, with Rose Bengal as sensitizer (*Sylvania* 500 watts tungsten-iodine lamp) yielded a complex mixture of products, from which only compound **3** could be isolated, in 3% yield. The structure of **3** is tentatively assigned on the basis of its spectral data [m.p. 162–164° (Et_2O). UV (EtOH): λ_{max} 292. IR (KBr): 1730, 1670, 1650, 1590, 1250. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.071 (*s*, H_3(18)); 2.819 (*dd*, J = 15, 6, H–C(2)); 4.9 (*m*, H–C(1), H–C(11)); 5.830 (*s*, H–C(4)). MS: 300 (M^+). No quantitative elemental analysis was performed, due to decomposition of the sample during the recrystallisation procedure].

[1]) Part XIX: [1].

The photooxygenation of **2** under identical conditions, afforded a mixture of compounds which was separated by chromatography on SiO_2. Unreacted starting material (**2**) (3% of the mixture) and 3-methoxy-9,17-dioxo-9,11-seco-1,3,5(10)-estratrien-11-al (**4**), in about 50% yield from **2**, were identified. The structure of **4** was assigned based on its analytical and spectral data [UV (EtOH): λ_{max} 205 (11,800), 224 (9,900), 274 (13,200). IR (film): 2720, 1740, 1720, 1670, 1600, 1490, 1260, 1030. ^{1}H-NMR ($CDCl_3$): 1.0 (*s*, $H_3C(18)$); 3.8 (*s*, $CH_3O-C(3)$); 7.4 (*m*, arom. H); 9.4 (*s*, H–C(11)). MS: 314 (M^+). 11,17-Bis-2,4-dinitrophenylhydrazone of **4**: m.p. 249° (CH_2Cl_2/Et_2O). IR (KBr): 3320, 3300, 1670, 1625, 1600, 1520, 1510, 1340, 1260. Anal. calc. for $C_{31}H_{30}N_8O_{10}$ (674.63): C 55.20, H 4.48, N 16.61; found: C 55.46, H 4.48, N 16.34].

The photooxygenation of styrene-type olefins may yield 1,4-endoperoxides, or allylic hydroperoxides, which can undergo a secundary *Hock*-cleavage reaction to a dicarbonyl fragment; 1,2-dioxetanes have been also isolated by low-temperature photooxygenation of indenes [4]. Work is in progress to identify the primary peroxidic product, in the formation of **4** from **2.**

One of us *(P.L.)* gratefully acknowledges the *Plan de Formación de Personal Investigador del Ministerio de Educación y Ciencia,* Madrid, for a doctoral fellowship.

REFERENCES

[1] Part XIX: *P. Lupón, J.C. Ferrer, J.F. Piniella & J.-J. Bonet,* J. Chem. Soc., Chem. Commun. *1983,* 718. For Part XVIII see [2].

[2] *P. Lupón, J. Gómez & J.-J. Bonet,* Angew. Chem. *95,* 757 (1983) and Suppl. *1983,* 1025.

[3] a) *W. Brown, J.W.A. Findlay & A.B. Turner,* J. Chem. Soc., Chem. Commun. *1968,* 10; b) *A. Bodenberger & H. Dannenberg,* Chem. Ber. *104,* 2389 (1971).

[4] For reviews see: a) *K. Gollnick,* 'Type II Photooxygenation Reactions in Solution', eds. W.A. Noyes, Jr., G.S. Hammond and J.N. Pitts, Jr., ('Advances in Photochemistry', vol. 6), Interscience Publishers, New York, 1968; b) *J. Saito & T. Matsuura,* 'The Oxidation of Electron-Rich Aromatic Compounds', eds. H.H. Wasserman and R.W. Murray, ('Singlet Oxygen'), Academic Press, New York, 1979; c) *H.H. Wasserman & J.L. Ives,* Tetrahedron *37,* 1825 (1981).