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A One Step Transformation of a 7-Oxo Steroid into a 7-Oxa Steroid. A New Photo-oxidation of Cyclic Ketone[1]

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Synopsis. Irradiation of 3α,5-cyclo-5α-cholestan-7-one in methanol saturated with oxygen gives a novel cyclo-7-oxa steroid, 3α,5-cyclo-7-oxa-5α-cholestane, together with methyl 3α,5-cyclo-7,8-seco-5α-cholestan-7-oate.

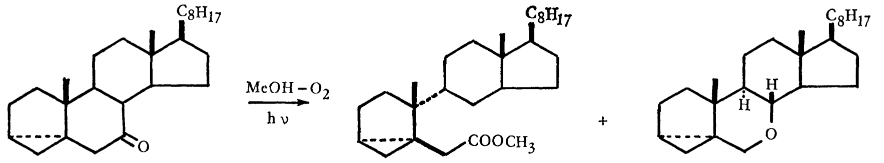
We report here a one-step transformation of 7-oxo-3α,5-cyclo-5α-cholestan-7-one (**1**)[2,3] into a novel cyclo-7-oxa steroid, 3α,5-cyclo-7-oxa-5α-cholestane (**3**), by irradiation in the presence of oxygen. The ketone **1** in methanol saturated with oxygen was irradiated with a Hanovia 450-W mercury arc through a Pyrex filter for 96 h. Preparative TLC of the reaction mixture gave two major crystalline products, **2** (12%) and **3** (18%), together with several minor products. Product **2** was identified as methyl 3α,5-cyclo-7,8-seco-5α-cholestan-7-oate,[3] which was an exclusive product when **1** in methanol was photolyzed in the absence of oxygen,[3] by a direct comparison. The less mobile compound **3** was a new compound; the structure was confirmed to be 3α,5-cyclo-7-oxa-5α-cholestane (**3**) by the analysis of the spectra. The molecular formula $C_{26}H_{44}O$ was determined by high resolution mass spectrometry. The low resolution mass spectrum showed an intense molecular ion peak at *m/e* 372 (14.4%), a M^+-CH_3 peak at *m/e* 357 (5.2%), and the base peak at *m/e* 317. The IR spectrum showed a strong band at 1087 cm^{-1} arising from C–O stretching of a cyclic ether. The NMR spectrum showed a 1H double doublet at τ 9.87 (J=8 and 6 Hz, a cyclopropyl proton) a 1H triplet at τ 9.62 (J=4.5 Hz, a cyclopropyl proton), a 3H singlet at τ 9.26 (18-H) and a 3H singlet at τ 9.01 (19-H). It also showed an AB quartet centred at τ 6.89 and 6.05 (J=12.0 Hz) and a 1H diffused triplet at τ 6.69 (J=7.5 Hz); these are assigned to the C-6 methylene protons and the 8β-H. Assuming the ring B of **3** to be in a chair conformation, the 6α-H should be shielded by the cyclopropane ring, and the doublet at τ 6.89 is thus assigned to the 6α-H.

The photochemical transformation of an oxo steroid into an oxa steroid in the presence of oxygen appears to be a new type of reaction of excited cyclic ketones. The pathway from the excited ketone (A) to cyclic ether **3** is not clear at the present stage. However, the process outlined in Scheme 2 may explain the formation of cyclic ether **3**: here a β-scission of the resulting biradical (B)[4] could lead to a peroxylactone (C) which photodecarboxylates[5] to give cyclic ether **3**.

Experimental

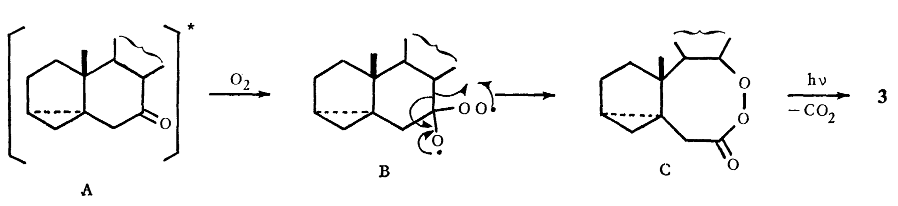
For instruments used and general procedures see Ref. 3. Mass spectra were recorded with a Hitachi JMS-D 300 spectrometer (70 eV) by Miss Yuko Chiba of the Faculty of Agriculture.

*Photo-oxidation of 3α,5-Cyclocholestan-7-one (**1**).*[2,3] Ketone **1** (200 mg) in methanol (200 ml) saturated with oxygen was irradiated with a Hanovia 450-W mercury arc through a Pyrex glass filter for 96 h. After the evaporation of the solvent, the product (213 mg) was subjected to preparative TLC (Merck, silica gel 60 F254) with a 1:1 benzene and hexane mixture to give nine fractions: A (35 mg), B (35 mg), C (17 mg), D (4 mg), E (2 mg), F (2 mg), G (2 mg), H (6 mg), and I (77 mg), in the order of decreasing mobility. The fraction (A) was recrystallized from methanol to give seco ester **2**,[3] mp 72—73 °C. The fraction B was recrystallized from methanol to yield 3α,5-cyclo-7-oxa-5α-cholestane (**3**), mp 144—145 °C. (Found: *m/e* 372.3412. Calcd for $C_{26}H_{44}O$: M^+, 372.3390); for mass, IR, and NMR spectra see text.



1 **2** **3**

Scheme 1.



Scheme 2.

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