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THE STRUCTURES OF TWO DIMERS OBTAINED UPON IRRADIATION OF CHOLEST-5-EN-7-ONE

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Irradiation of steroid 5-en-7-one systems, e. g., cholest-5-en-7-one 1, in a Pyrex flask with a 450 W high-pressure Hg lamp (>300 nm, only $n \longrightarrow \pi^*$ carbonyl excitation is induced) first affords the deconjugated enone 2 and subsequently a photostationary mixture of 2 and the bridged ketone 3.[1)]

We herewith report the results obtained upon irradiation with a low pressure Hg lamp (8 W 253.7 nm). Irradiation of 500 mg of 1 in 80 ml t-BuOH (quartz flask) for 12 hr gave 2 (20 % yield) and two dimeric compounds 4 (10 % yield) and 5 (7 % yield); separation of the two dimers was not easy and required two preparative tlc procedures. Dimer 4, mp 110 - 120°, M^+ 768, ir ($CHCl_3$) 1702 cm^{-1}, uv (dioxane) 289 nm (ε460), has an unsymmetric structure as shown by its nmr spectrum.[2)] It is stable to bases such as 10 % methanolic KOH, but is decomposed upon refluxing in dil. $HCl/CHCl_3$, a behavior which is in agreement with that of oxetanes.[3)] It is not deuterated when refluxed overnight in dioxane containing D_2O and K_2CO_3.

An oxetane containing dimeric structure for 4 could result from a combination between: (i) 1 and 1; (ii) 2 and 2; (iii) 3 and 3; (iv) 1 and 2; (v) 1 and 3; or (vi) 2 and 3. Possibilities (ii), (iii) and (vi) can be discarded as irradiation of 2 or 3 in t-BuOH only resulted in the photoequilibrium mixture 2 and 3 with no formation of dimer 4.[4)]

The 5.35 and 3.20 ppm signals in 4 are slightly coupled to each other (proven by decoupling). The oxetane structure and nmr assignments were corroborated upon similar irradiation of 6-deuteriocholest-5-en-7-one (1, 90 % D at C_6),[5)] which gave dimer 4 in which the intensity of the 3.20 ppm signal had now decreased to 1H. This finding eliminates possibility (i) because if this were the case the 5.35 ppm signal should be absent in the dimer. The bulkiness of the bridged ketone 3 does not allow its participation in the dimer formation, and hence possibility (v) is discarded; the dimer is therefore formed between the enones 1 and 2. Four modes of combinations are conceivable for a 1/2 linking leading to an oxetane, but of these only structure 4 can account for the nmr peaks (shown in 4) and the difference in intensities of the 3.20 ppm peak in 4 and its deuterated analog. Finally, dimer 4 exhibited a negative Cotton effect in its

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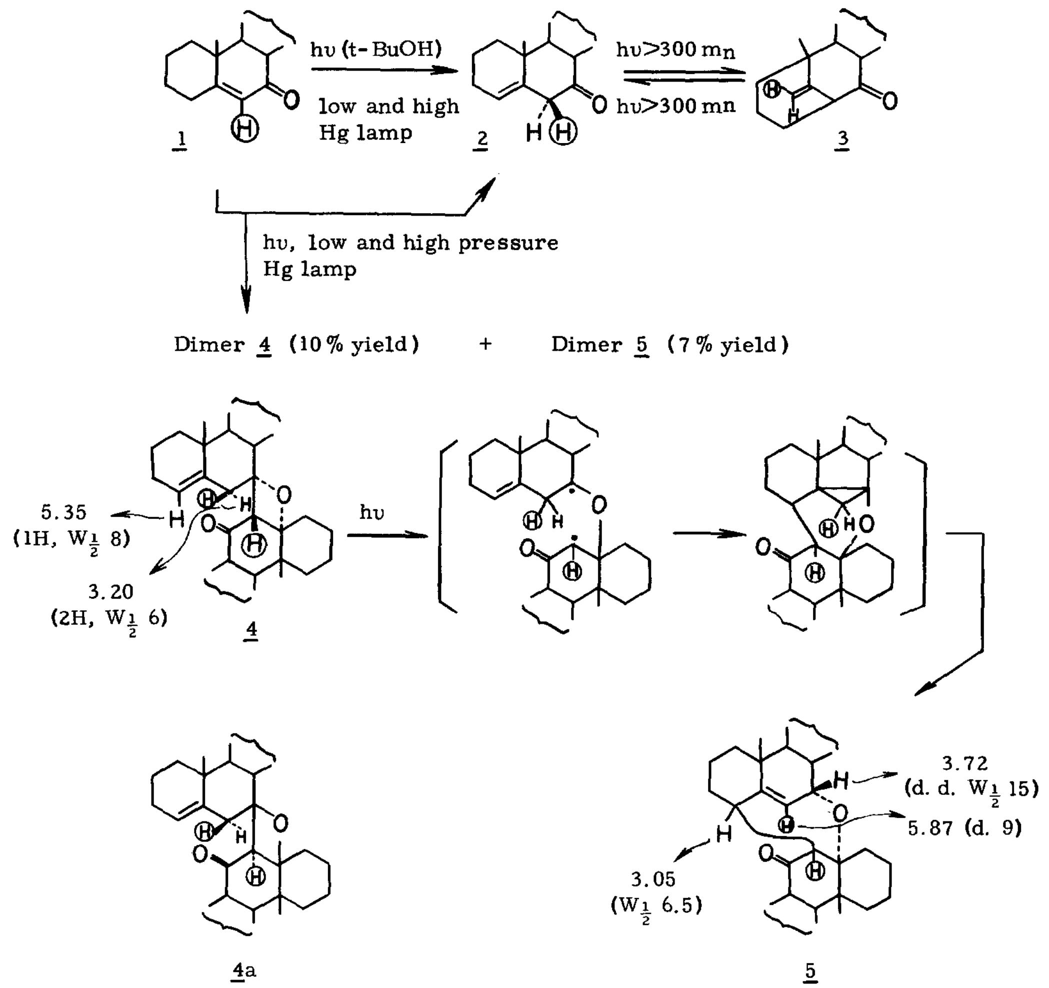

cd curve, 295 nm, Δε -3.37 (in dioxane), and this suggests an A/B trans stereochemistry 4 rather than an A/B cis structure 4a. Dimer 5, mp 179 - 181°, ir (KBr) 1715 cm^{-1}, is also an unsymmetric dimer, and moreover it is formed directly by irradiation of 4 in t-BuOH for 30 min with a low pressure Hg lamp. This observation together with the nmr peaks (couplings confirmed by decoupling) lead to only one possible structure 5. The integrated intensities of nmr peaks in deuterated 5, which were obtained upon irradiating 6-deuterio-1, were again in accord with this structure. Namely, the areas were: 3.05 (1H), 3.72 (0.6H), 5.87 (0.2 - 0.3H). We have already shown[1] that irradiation of 1 (Ⓗ = D) gives 2 in which the D atoms are distributed in 6-H$_\beta$ and 6-H$_\alpha$ in a ratio of ca 2 : 1; this ratio would be expected to be maintained at C-6 in deuterio-4, which upon conversion into 5 through the steps depicted (see Figure),[6] would lead to the measured peak intensities in deuterio-5.

It was found that prolonged (24 hr) irradiation of 1 with a high pressure 450 W Hg lamp (in Pyrex flask) also afforded small amounts of dimers 4 and 5, and hence the dimer formation is not wavelength dependent in a strict sense. The greatly enhanced yield of dimers resulting from irradiation with a low pressure lamp is due to the fact that the bridged 3 is not formed under these conditions, and therefore 2 reacts with the starting material to afford 4 and 5.

Although steroidal photo-dimerizations have been reported,7) as far as we are aware of, there appears to be no record of oxetane formation; it is to be noted that in the formation of dimer 4, the double bond of an enone system has added to a saturated ketone.8)

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