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PHOTOISOMERISATION OF β,γ -UNSATURATED OXO-STEROIDS

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In the previous paper,[1] we reported the acetone-sensitised photoepimerisation of the β,γ -unsaturated ketones (1)[2] and (2),[3] at C5. These reactions are not typical of the normal triplet excited state reactions of β,γ -unsaturated ketones,[4] and it was of interes therefore to examine possible singlet excited state reactions of compounds (1) and (2).

To this end, benzene solutions of compounds (1) and (2) were irradiated in quartz apparatus under nitrogen using a medium pressure mercury lamp. Compound (1) gave the anticipated cyclobutanone (3) (17%) ($\nu_{max.}$ 1770 cm.$^{-1}$) which is formed via a 1,3-acyl shift.[4] In addition, the cyclopropane (4) (τ 9.6-9.7, m), which is derived photolytically from the compound (3), was isolated in admixture with olefinic material. It was necessary to hydrogenate this mixture to allow the separation of compound (4), and the olefinic material remains unidentified at this time. The photolytic extrusion of CO from steroidal and other cyclobutanones is well known.[5]

Compound (6) (40%) was the major product from the dione (2). The structure (6) is supported by the following spectroscopic and other data. The molecular weight (356, mass spectrum), indicates that ketene has been lost from the parent compound (2). The ^{1}H n.m.r. and i.r. spectra clearly indicate the presence of two olefinic methylene groups [τ 3.87 and 4.95 (doublets J ca. 1.5 Hz.), 5.20 and 5.31 (narrow multiplets); $\nu_{max.}$ 3100, and 944, 920, and 912 cm.$^{-1}$]. The presence of the vinyl methyl group is supported by the ^{1}H n.m.r. spectrum (τ 8.17, broad s.), and the i.r. and u.v. data for the conjugated enone system ($\nu_{max.}$ 1735 cm.$^{-1}$, $\lambda_{max.}$ 230 nm.) are in reasonable agreement with those quoted for similar systems.[6] Two isomeric tetrahydro-derivatives were obtained on hydrogenation of the dienone (6), and reduction with sodium borohydride gave a mixture of epimeric alcohols (7) (via initial Michael addition). Oxidation of the alcohols (7) gave the dihydrocompound

(8) which on ozonolysis gave the diketone (9). The diketone (9) was readily converted by base into the aldol (10).[7] The isolation of the oxo-diacid (11) (as its dimethyl ester) from the ozonolysis of compound (6) also supported the proposed structure.

Brief irradiation of compound (2) allowed the isolation of compound (5).[1] Little of the dienone (6) was present in the early stages of the photolysis and thus compound (5) appears to be the first intermediate. This was confirmed by conversion of compound (5) to compound (6) in high yield by irradiation in benzene solution.† The conversion of compound (2) to compound (6) was observed in hexane solution, and addition of naphthalene failed to quench this reaction. Also, piperylene did not quench the conversion of compound (5) to compound (6) in benzene. These preliminary experiments suggest that the conversion of compound (2) to compound (6) either involves singlet or very rapidly reacting triplet excited states.

Two possible mechanisms for the conversion of compound (5) to compound (6) are tentatively outlined in the scheme.§ Cleavage of the 1,2-bond would give the allylic radical (a) which could lose ketene as shown to give the radical (b). Collapse of radical (b) to the dienone (c) could lead to the radical (d). A 1,2-vinyl shift in the radical (d) could give the radical (e) which on ring contraction would give compound (6). Alternatively radical (b) could rearrange to compound (6) via radical (f). The intermediacy of compound (5) in the photochemical rearrangement of compound (2) to compound (6) does not support any mechanism involving initial simple cleavage of the 5,6-bond in compound (5). β-Cleavage of γ,δ-unsaturated ketones, as is proposed for the formation of radical (a), is not without precedent.[8]

Satisfactory spectroscopic data are available for all new compounds.

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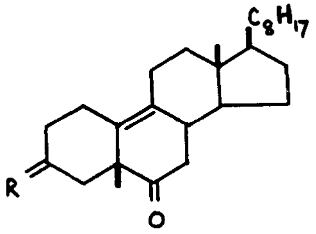
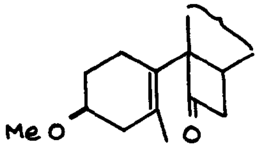
† Ketene was trapped as acetanilide by carrying out the irradiation in the presence of aniline.

§ Radical intermediates are assumed throughout for convenience.

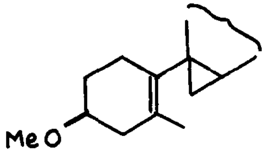


(1) R = β-MeO,H

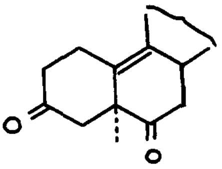
(2) R = O



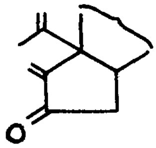
(3)



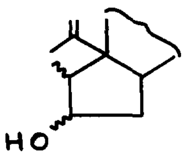
(4)



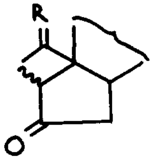
(5)



(6)

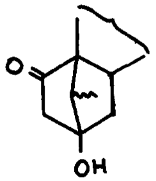


(7)



(8) R = CH_2

(9) R = O



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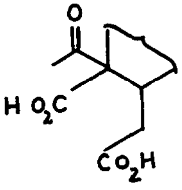

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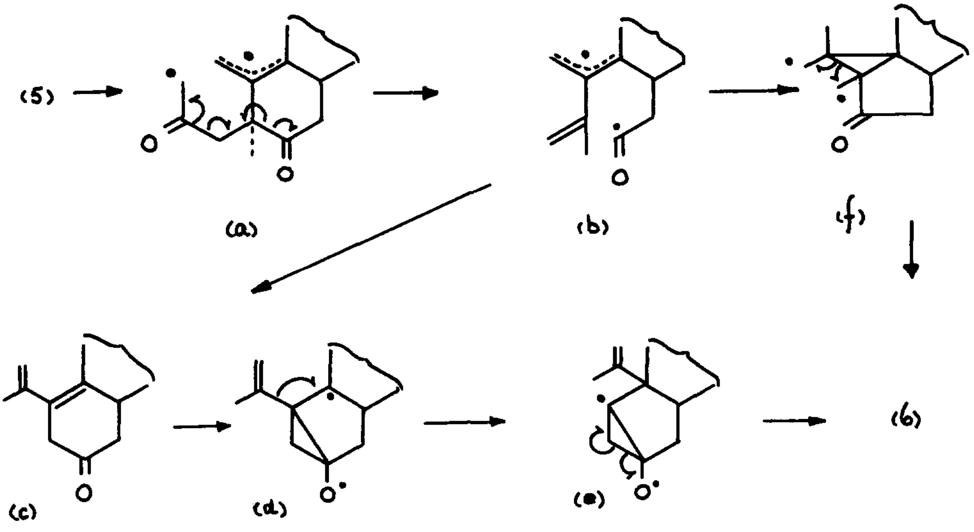

Scheme

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