Photochemical *i*-Steroid Rearrangement

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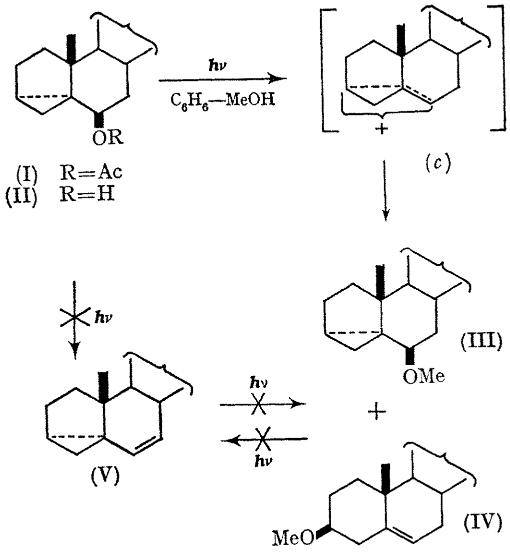
The benzene-sensitized photochemical addition of alcohol to olefins,[1] dienes,[3] and allylic and homoallylic alcohols[3] is an ionic-type photoreaction. The benzene-sensitized migration of a methyl group[4] is also a good example of this type of reaction. We report here another such reaction, related to our previous study on allylic and homoallylic alcohols.[3]

The *i*-steroid rearrangement goes *via* an homoallylic bridged ion *c*, nucleophilic attack on which, *e.g.* by methanol, gives very largely the kinetic product (III) and a little of the thermodynamic one (IV)[5] in a ratio of *ca.* 13 : 1.

We have found that the irradiation of 3α,5-cyclo-5-α-cholestan-6β-ol (1·13 g.) in benzene–methanol (3 : 1) by a high-pressure mercury lamp (Hanau Q81) gives the same two ethers (III) and (IV).

After chromatographic separation, we obtained 63% of a mixture of the two ethers (III) + (IV) plus 35% of starting material (I). Further chromatography and crystallisation of the mixture afforded 700 mg. of pure (III) and *ca.* 20 mg. of (IV). The ratio of (III) to (IV), *ca.* 35 : 1, is similar to that in the above-mentioned solvolytic reaction.



This rearrangement occurs neither with the acetate (II), nor with 3α,5-cyclo-5α-cholestan-6α-ol†. Boiling the alcohol (I) in the same mixture of benzene–methanol for 48 hr. produces no rearrangement. We were unable to detect any (V) in the product of the rearrangement. Nevertheless, it could be considered as an intermediate in this reaction, if it is assumed that the formation of (V) is the rate-determining step, and that the benzene-sensitized addition of methanol to it is the fast step. The ether (III), subjected to u.v. irradiation, undergoes no change at all, and is not in equilibrium with (V). The compound (V),[6] when irradiated under the same conditions, undergoes decomposition and gives many products, none of which is (III) or (IV). Thus (V) is definitely not an intermediate. As far as the mechanism of this *i*-steroid rearrangement is concerned: (i) a radical-type photorearrangement is not involved since it has been shown that a "nonclassical radical" analogous to carbonium ion *c* does not exist.[7] Furthermore, a radical reaction would lead to the addition of CH_2OH;[1b] (ii) an ionic-type photochemical rearrangement explains most of the experimental facts and can be rationalized by analogy with our previous work on allylic and homoallylic alcohols.[3]

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† Under solvolytic conditions, the leaving group is an ester or an halogen and both diasteroisomers, 6α and 6β, react.[5] We cannot yet explain why the photochemical reaction is so different in these instances.

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