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PHOTOADDITION ON CONJUGATED DIENES AND PHOTOCHEMICAL ALLYLIC REARRANGEMENT

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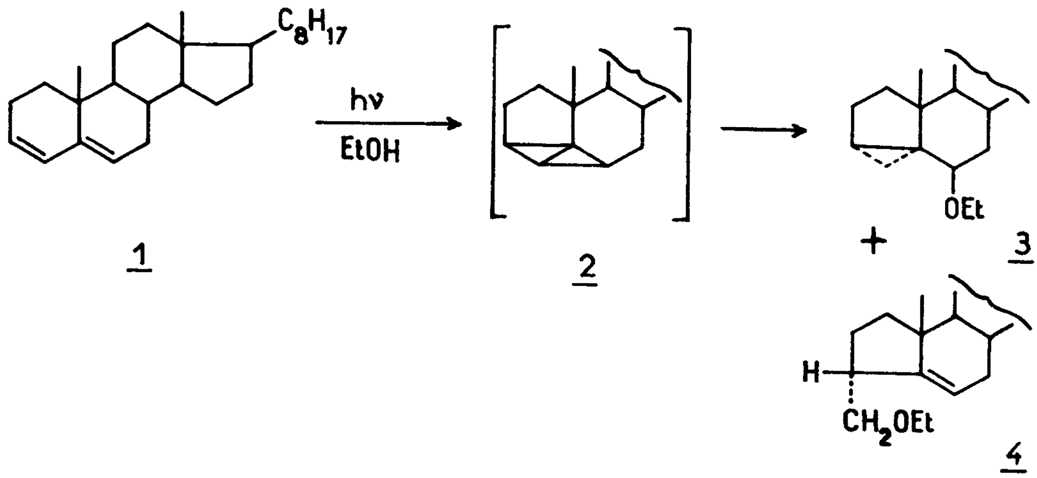
Among the conjugated dienes which have been intensively investigated (1), the transoid 3,5 cholestadiene is of particular interest for photoaddition studies.

It was shown that a 1-3 and a 1-1 addition on the bicyclobutane intermediate 2 give rise respectively to the ethers 3 and 4 (2).

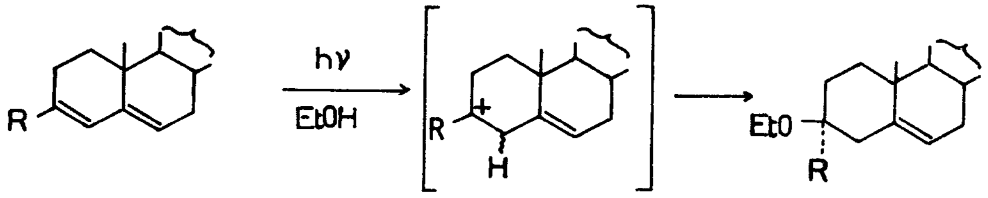
Later, the influence of various substituants on carbon atom 3 ($R=CH_3$; OCH_3 ; OCH_2CH_3) was studied and it was shown that the formation of the product 7 can be explained by a 1-2 addition proceeding through the carbonium intermediate 6 (3). We report here an example of another type of addition which to our knowledge has not yet been described.

The irradiation of 1 in a mixture of benzene methanol (1 : 4) by a high pressure mercury lamp (Hanau Q 81) during fifteen hours gives an oil. After repeated chromatographic separations on silicagel, we have obtained ca 25% of the starting material, and the three ethers 8 (10-15%), 9 (ca 5%) and 10 (ca 30%) and several fractions (ca 30%) containing very polar compounds which have not yet been investigated. The structures of the three ethers have been established by direct comparison with authentic samples prepared in our laboratory.

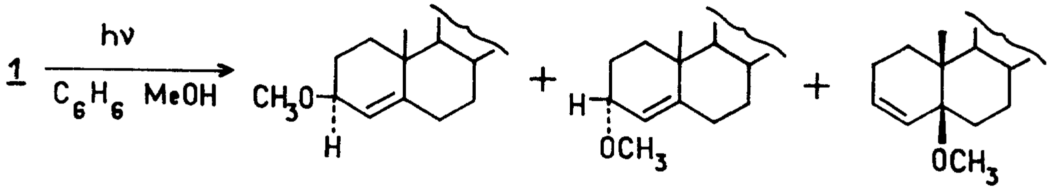
The ether 10 seems to be the primary protoproduct since, when it is irradiated under similar conditions it gives a mixture of 8 and 10 and only traces of 9 and starting material 1. The irradiation of 10 in pure benzene gives also a mixture of 8 and 10 ; however in this case, there is no more of 9 but a larger amount of the cholestadiene 1. The irradiation of 8 under similar conditions leaves this compound unchanged ; we have not found in the literature any other case of photo allylic rearrangement.



1 2 3 4



5 6 7



8 9 10

It is to be mentionned here that the photoaddition of methanol by irradiation in a mixture benzene methanol has recently been reported, and can be rationalized by a Markownikov type ionic addition on a highly energetic trans double bond in a cyclo hexene ring (4, 5). This kind of photoaddition seems to occur also in conjugated dienes since the primary product 10 proceeds by a Markownikov addition on the double bond between carbon atoms 5 and 6. While the previous authors (2, 3) have used mixtures of alkohol and saturated hydrocarbon, we have used benzene. This solvent ($\emptyset_{ST}$ = 0,24 ; E_T = 84 Kcal/mol) possibly acts like a photosensitizer, transferring its triplet energy to the diene 1 and finally giving rise to a cholestadiene triplet (E_T = 60 Kcal/mol for trans butadiene triplet (6)).

We intend to study further the addition of different ionic species on a series of dienes to generalize the photochemical addition on dienes and the subsequent photo allylic rearrangement.

References

(1) R. Srinivasan, in Advances in Photochemistry, Vol. 4, Intersciences Publishers, 1966, p. 113.

(2) W.G. Dauben, J.A. Ross, J.A.C.S., 81, 6521 (1959) ;
W.G. Dauben, F.G. Wiley, Tetrahedron Letters, 893, (1962).

(3) G. Bauslaugh, G. Just, E. Lee-Ruff, Canad. J. of Chem., 44, 2837 (1966).

(4) P.J. Kropp, J.A.C.S., 88, 4091 (1966)

(5) J.A. Marshall, R.D. Carroll, J.A.C.S., 88, 4092 (1966)

(6) R.S.H. Liu, N.J. Turro Jr., G.S. Hammond, J.A.C.S., 87, 3406 (1965).