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PHOTOCHEMICAL TRANSFORMATIONS. VI.

REACTIONS OF UNSATURATED OXYGEN DERIVATIVES[1]

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Some time ago, we reported[1] that allylic chlorides and bromides undergo photosensitized rearrangements to their allylic isomers and to halocyclopropanes. We have been interested in the question of whether other heteroatoms can be induced to undergo similar 1,2 or 1,3 migrations and now wish to report our preliminary studies with certain oxygen compounds.

Neither allylic isomerization nor cyclization was observed when ca. 0.5 M solutions of trans-crotyl alcohol, its methyl ether, or its acetate, in acetone or in benzene, were irradiated (all irradiations described in this paper were conducted with a Hanovia type L 450-watt lamp). That energy transfer from the triplet sensitizer was occurring could be seen by the rapid cis-trans isomerization of the double bond. Similarly, methyl α,α-dimethylallyl ether (1) did not photoisomerize in these solvents.[2] As the triplet states of these unsaturated ethers were unproductive, we thought it might be of interest to look at the photoactivity of the singlet excited state of such compounds. When 1 was irradiated in methanol using quartz apparatus, the volatile product (16% yield) of this irradiation was not that of one of the hoped-for rearrangements, but was rather tert-amyl methyl ether,[4] the product of hydrogen addition. Reduction of carbon-carbon double bonds has been noted[5] for 1-methylcyclopentene and for norbornenes as an important process of xylene-sensitized reactions in methanol, but is stated not to occur under similar conditions with acyclic olefins. Irradiation under singlet conditions was not reported, but it seems possible that such reductions may generally be found to compete with the known[6] free-radical chain additions of alcohols to olefins. Direct irradiation in quartz of 1 in acetonitrile gave virtually no reaction in 48 hrs.

2,5-Dihydrofuran (2) was used as another example of an allylic ether. Irradiation of a degassed solution of 2 in benzene (Vycor filter) led to the gradual formation of the disproportionation products, furan (3) and tetrahydrofuran (4). No other volatile liquid products were detectable by gas chromatography although much of the starting material was consumed. The formation of 3 and 4 is similar to results described[7] on 2,3-dihydrofuran (5) in the gas phase with mercury sensitization.


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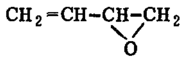
$CH_2{=}CH{-}\underset{\diagdown O \diagup}{CH{-}CH_2}$

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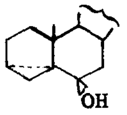
However, direct irradiation of 2 in ether, methanol, acetonitrile or cyclohexane, gave, besides 3 and 4, small amounts (*ca.* 10% of the 2 converted) of butadiene monoxide (6).[8] Our studies thus far on this rather interesting new rearrangement hardly justify mechanistic speculation, but the insensitivity to solvent suggests that polar intermediates are not involved and that a choice between a biradical intermediate and a 1,3-sigmatropic rearrangement remains. The high energy of the S_1 state would appear to permit many processes. An analogous photorearrangement of certain 2,5-dihydrothiophenes has recently been reported.[9]

Concurrent with these studies and with others in which we were unable to photosensitize homoallyl to cyclopropylcarbinyl rearrangements,[10] a paper appeared describing photochemical rearrangements of steroid derivatives involving homoallylic and cyclopropylcarbinyl intermediates or compounds.[11] We were especially interested in the report that photolysis of 3,5-cyclocholestan-6-β-ol (7) in benzene-methanol led to a mixture of cyclocholestanyl methyl ether (8) and cholesteryl methyl ether (9), and in the authors' suggestion that triplet energy transfer from benzene to the cyclopropane ring was followed by formation of the cyclopropylcarbinyl cation 10. Ion 10 was then presumably captured by methanol to give a mixture of 8 and 9, as has been shown[12] for 10 produced by solvolysis.



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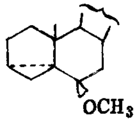

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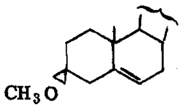

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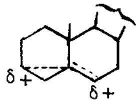

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In view of the failures described above with photosensitization of allylic alcohol and ether reactions, we decided to repeat this experiment. Authentic samples[12] of 7, 8 and 9 were separable on silica gel tlc plates with benzene development and iodine visualization. Irradiation of carefully degassed solutions of 7 in benzene-methanol gave no observable rearrangement in four different attempts. When oxygen was not excluded, 8 and 9 were formed as reported, and, in addition, irradiation of an oxygenated mixture of benzene and methanol gave a solution, which caused the formation of 8 and 9 from 7 in the dark. We conclude that the formation of 10 from 7 (and the subsequent formation of 8 and 9) is a normal acid-catalyzed reaction, similar to that described by Winstein,[12] and not a photochemical process. Rather it is induced by photochemical oxidation of methanol to give an acidic material. The unreactivity[11] of the α epimer of 7 is similarly understood.[12] Similar photochemical oxidations of methanol leading to acid-catalyzed reactions have been reported,[13] and we would caution extreme care in such matters (we have found that use of sodium carbonate[13a] will often counteract such adventitious acidic species).

Acknowledgments

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