Photoisomerization of Protonated 5-Deuterio-5-methylhex-3-en-2-one. Evidence for a Photochemical 1,2 Hydride Shift

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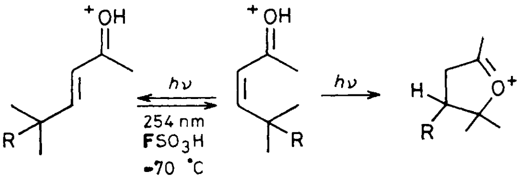
The photoisomerization of protonated 5-deuterio-5-methylhex-3-en-2-one to a protonated dihydrofuran is shown to occur with a specific 1,2 deuterium shift from C-5 to C-4.

Recently we have shown that protonated *trans*-5-methylhex-3-en-2-one (**1**) is photochemically converted into the corresponding *cis*-isomer (**2**) and that this subsequently undergoes a photochemically induced cyclization to give (**3**), equation (1).[1] Similar reactions were found with the corresponding protonated acids. It was proposed that this unprecedented photocyclization proceeded *via* a photochemical 1,2 hydride shift, equation (2), rather than a 1,5 hydrogen shift, or photoenolization, as occurs with the neutral ketone.[2] In order to establish that the photochemical conversion of (**2**) into (**3**) involves a 1,2 hydride shift, we have now studied the photoreactions of the 5-deuterio-cation (**1D**).

The 5-deuterio-5-methylhex-3-en-2-one was prepared by allowing 2-deuterioisobutyraldehyde[3] to react with ethyl diethylphosphonoacetate, this being followed by hydrolysis of the ester to give the acid, and reaction of the latter with methyllithium.[4] The ^{1}H n.m.r. spectra of the resulting ketone and its conjugate acid, (**1D**), obtained by dissolution of the ketone in FSO_3H, were fully consistent with the specific incorporation of deuterium at C-5.

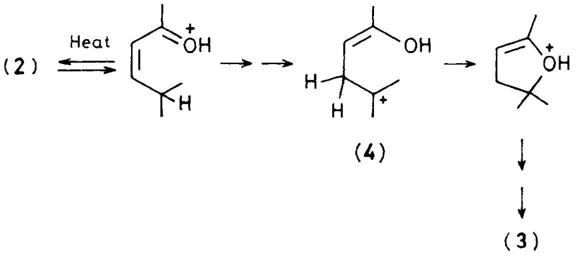
Irradiation at 254 nm of an FSO_3H solution of (**1D**) (λ_{max} 278 nm) at −70 °C caused isomerization to take place to give initially the *cis*-isomer and subsequently the cyclic product. The reactions were followed by low-temperature ^{1}H n.m.r. spectroscopy directly on the acid solutions. The deuterium was cleanly retained at C-5 in (**2D**). This was shown by the resonance attributable to the isopropyl methyl groups remaining as a singlet and the two vinyl proton resonances forming an AB quartet (*J* 15 Hz). As the reaction progressed it was apparent that (**3D**) was being produced with the deuterium specifically located at C-4. This was shown by the ^{1}H n.m.r. spectrum of (**3D**) in which the resonances of the two methylene groups appeared as a broadened triplet, area = 1 at δ 2.42 (4-H) and a doublet of area = 2 at δ 3.82 (3-H). Thermal controls were run and these showed that the observed reactions were photochemical. For example, in FSO_3H (**1**) slowly isomerizes to (**3**) only when the solutions are heated to 34 °C.[5]



(1)

(1) R = H (2) R = H (3) R = H
(1D) R = D (2D) R = D (3D) R = D

This specific photochemical conversion of (**2D**) into (**3D**) clearly indicates that a 1,2 deuterium migration has occurred during the reaction. A photoenolization mechanism (1,5 shift) would lead to deuterium loss from the substrate. The origin of this 1,2 shift can be viewed as resulting from a charge polarization accompanying an excited state twisting about the C-3–C-4 bond which leads to the localization of the positive



(2)

charge at C-4. A hydride (or deuteride) shift from C-5 to C-4 would then lead to a more thermodynamically stable tertiary ion, (**4**). This can subsequently undergo cyclization and proton shifts to give the final observed product. Such a charge polarization has been suggested to occur in the closely related protonated unsaturated imines involved in the chemistry of vision.[6] Indeed our results strongly support such a model for the charge distribution in the twisted excited state of the visual pigments.

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