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HETEROCYCLES. II.[1] PHOTOCHEMISTRY OF 4-(3',4'-DIMETHOXYPHENYL-ACETYL)-2-METHYLISOCARBOSTYRIL AND ITS ENOL ACETATES[2]

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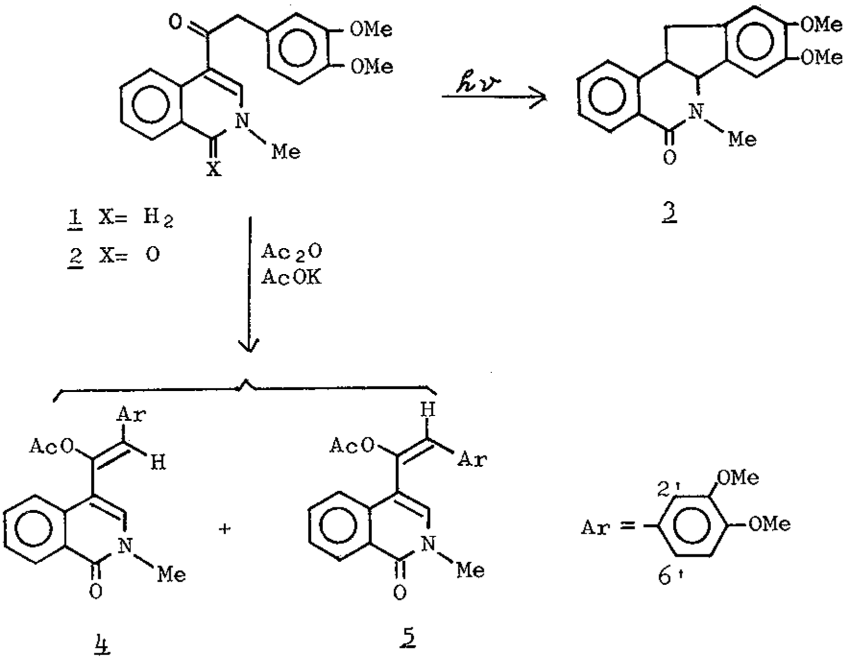
Photolyses of the isocarbostyril (2) and its enol acetates (4) and (5) are examined. The former affords the C-nor-benzo[c]phenanthridine (3). The Z-isomer (4) of the enol acetate isomerizes to the E-isomer (5) along with formation of the acetylene (6). Photolysis of the E-isomer (5) in the presence of iodine gives the 11-acetoxybenzo[c]phenanthridines (7) and (8). Structures for all photo-products are confirmed on the basis of their NMR spectra.

A synthesis of the 11-oxygenated benzo[c]phenanthridines may be achieved from the 4-phenylacetylisoquinolines. It was found, however, that the attempted cyclization of the 1,2-dihydroisoquinoline (1) was unsuccessful.[3] We now wish to report photolyses of the isocarbostyril (2) and its enol acetates (4) and (5).

It has been known that benzyl 1-cyclohexenyl ketone was smoothly photocyclized to 1,2,3,4,4a,10a-hexahydro-10-phenanthrone.[4]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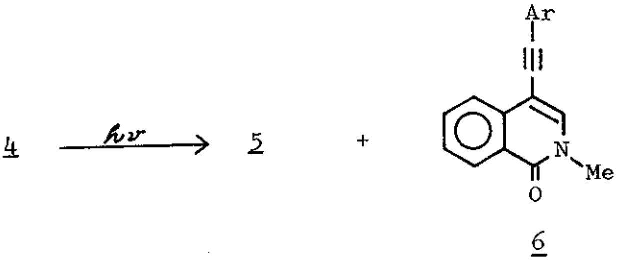
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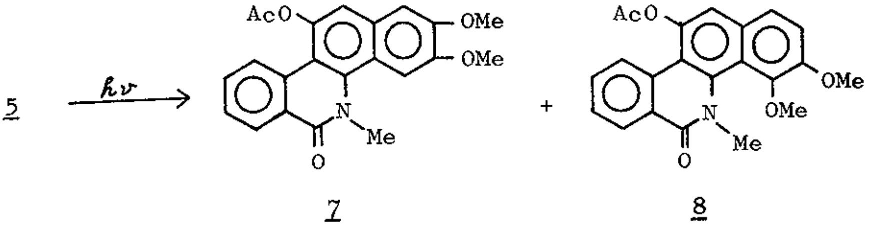
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8

Although 2 is similar to the above ketone, a quite different result was obtained. Photolysis of 2[3] in methanol with a 30 W low pressure mercury lamp gave the cyclized compound (3), mp 162-162.5°, $C_{19}H_{19}NO_3$, in 10 % yield. The only carbonyl band observed at 1649 cm^{-1} in its IR spectrum (CCl_4) corresponds to that of the lactam group. The NMR spectrum of 3 indicates the characteristic signals for the 4-H at δ 6.92 (s), the 1-H at δ 6.76 (s), the 4b-H at δ 4.88 (d, J 6 Hz), the 10b-H at δ 3.81 (m) and the 11-H_2 at δ 3.17 (d, J 6 Hz). On the basis of these data and the molecular formula, the C ring in 3 is considered to be a five-membered one, whose cis B/C ring fusion would be assigned from the coupling constant of the 4b-H.[5] The same result was obtained with a 100 W medium pressure mercury lamp.

We, next, examined photolyses of 4 and 5. On acetylation with acetic anhydride in the presence of potassium acetate, 2 afforded 4 and 5 in 70 and 15 % yield, respectively. The NMR spectrum of 4 shows the signals for the 3-H at δ 7.39 (s), the vinyl-H at δ 6.29 (s), the 2'-H at δ 7.12 (d, J 2 Hz), 6'-H at δ 7.06 (q, J 9 and 2 Hz). That of 5 exhibits the signals for the corresponding protons at δ 7.29 (s), 6.50 (s) and 6.64-6.61. On saturation of the vinyl-H in 4 the NOE enhancements of 12.2, 6.4, 5.9 and 5.9 % for the 3-, 5-, 2'- and 6'-H, respectively, are observed. Saturation of the Me (δ 2.19) of OAc group in 4 increases the signals for the 2'- and 6'-H by 14.8 %. On the other hand, saturation of the vinyl-H in 5 gives no effect on the signal intensities for the 3- and 5-H. Considering 4 and 5 to be the Z- and E-isomer, respectively, these NOE results can be understood. In the case of the E-isomer, two rings would loose coplanarity by the steric interaction. This is responsible for the upfield shifts of the 3-, 2'- and 6'-H in 5 compared to those in 4. The downfield shift of the vinyl-H in 5 is ascribed to the anisotropic effect of the OAc group.

Photolysis of 4 in benzene with a 100 W medium pressure mercury lamp gave 5 and the acetylene (6), mp 156-157°, $C_{20}H_{17}NO_3$, in 63 and 4 % yield, respectively. The NMR spectrum of 6 shows no signals for the vinyl-H and OAc group existed in that of 4. The ^{13}CNMR spectrum of 6 provides the signals for the acetylenic carbons at δ 92.83 and 82.10. These spectral data support the structure of 6. The enol acetate (5) afforded 6 in 10 % yield under the same conditions.

Photolysis of 5 in the presence of iodine under the same conditions as above afforded, expectedly, the 11-acetoxybenzo[c]phenanthridines (7), mp 208.5-210°, and (8), mp 171-171.5°, in 17 and 14 % yield, respectively.[6] Their structures are confirmed by the following spectral data: 7; NMR, δ 8.70 (q, J 8 and 2 Hz, 7-H), 8.61 (q, J 8 and 2 Hz, 10-H), 7.80-7.42 (m, 8- and 9-H), 7.49 (s, 4-H), 7.30 (s, 12-H), 7.09 (s, 1-H), 4.00 (s, 2 x OMe), 3.97 (s, N-Me), 2.49 (s, OAc). IR ($CHCl_3$), 1763 (OAc), 1640 cm^{-1} (CON). 8; NMR, δ 8.64 (q, J 7 and 2 Hz, 7-H), 8.62 (q, J 7 and 2 Hz, 10-H), 7.83-7.43 (m, 8- and 9-H), 7.56 (d, J 9 Hz, 1-H), 7.35 (d, J 9 Hz, 2-H), 7.29 (s, 12-H), 4.00 (s, 3-OMe), 3.75 (s, 4-OMe), 3.50 (s, N-Me), 2.47 (s, OAc). IR ($CHCl_3$), 1763 (OAc), 1639 cm^{-1} (CON). The upfield shifts of the 4-OMe and N-Me groups observed in 8 may be explained as being due to their spatial orientation which arises to be free from their sterically mutual interaction.

REFERENCES AND NOTES

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2 IR spectra were recorded on a JASCO IR-G. NMR and ^{13}CNMR spectra were taken on a JEOL JNM PS-100 at 100 and 25.1 MHz, respectively, for a deuterochloroform solution.

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