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# PYRIMIDINE MONO-N-OXIDE PHOTOCHEMISTRY (1,2)

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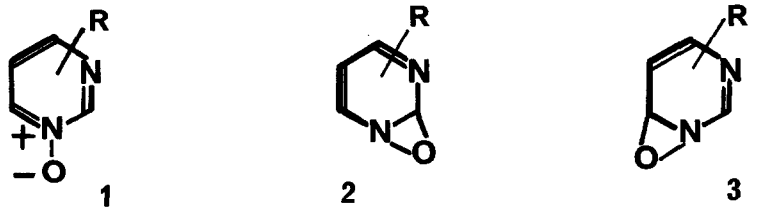
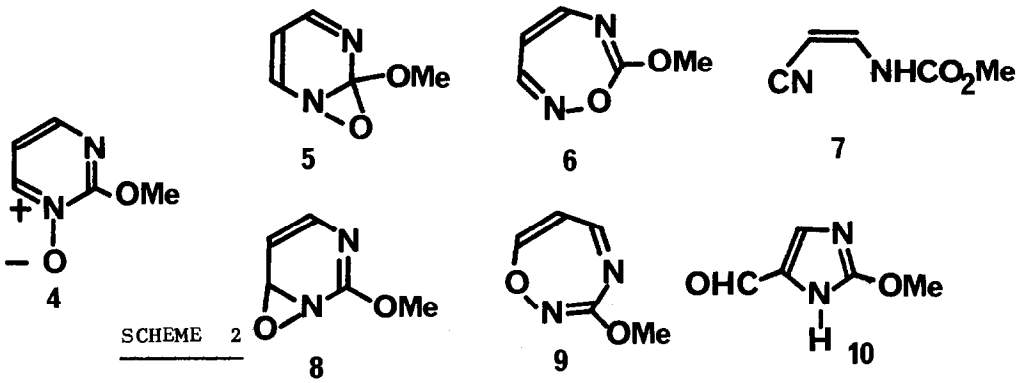
It is generally accepted that photoinduced rearrangements of heteroaromatic N-oxides proceed via oxaziridines (2,3), although, to our knowledge, no direct proof has ever been put forward in favour of such intermediates or short lived transients(4). We must therefore consider the elusive oxaziridines merely as formal first intermediates of our mechanistic hypothesis. With this statement in mind, we may assume that pyrimidine-N-oxides 1 photoisomerize either to type 2 or to type 3 oxaziridines (Scheme 1). In previous articles we described the results obtained with various pyrimidine-N-oxides and derived the formation of the isolated photoisomers from these two types of oxaziridines (2). A simple HMO model(2) as well as a PPP-SCF calculation(5) have been proposed in order to account for the electrocyclisation of pyrimidine-N-oxides 1 toward 2 or 3 type oxaziridines: both models predict that such ring closures are favoured in the first excited state but not in the ground state. Considering now the regiospecificity of pyrimidine-N-oxide photoisomerisation, our previously described experimental results fitted roughly with the predictions derived from the HMO model(2), although the balance of products was not satisfactory when compared with the amount of starting material: some "polymer" material of unknown nature is also formed. As to Kaneko's calculations, which have not been published yet(5), they allegedly predict regiospecificities of rather opposite sign; this PPP-SCF model seems to correlate with the recent findings of Van der Plas(6).




SCHEME 1

We would like to describe some additional results along these lines, which compel us to be more cautious when it comes to the application of either one of the two mentioned semi-empirical models. When an acetonitrile solution of 2-methoxypyrimidine-N-oxide 4 (7) is irradiated under argon atmosphere, in an all-PYREX glass apparatus by means of a mercury high pressure lamp, one obtains traces of 2-methoxypyrimidine and two colourless cristalline products. The less polar one, mp 97°-101° (yield:11%), proved to be the expected enaminonitrile 7 (8) [U.V.(MeOH), $\lambda_{max}$ 252 nm (ε:19.000); IR (KBr) ν(N-H) 3310, 3260 $cm^{-1}$, ν (C=O) 1760, 1745 $cm^{-1}$, ν (C=C) 1650 $cm^{-1}$; NMR ($CDCl_3$) τ 2 ppm (1H; very broad band which disappears after treatment with $D_2O$), τ 2.78 ppm (1H; d; J=9Hz), τ 5.58 ppm (1H; d; J=9Hz), τ 6.25 ppm (3H; s)]. The 9Hz coupling constant is typical for a cis enaminonitrile (1,2). The more polar compound, mp 150-151° (yield 9%), is the 2-methoxy 4(5)-formyl-imidazole 10 [UV (MeOH) $\lambda_{max}$ 273 nm (ε:21.000); IR (KBr), ν (N-H) 3340 $cm^{-1}$, ν (C-H, aldehyde) 2790, 2720 $cm^{-1}$, ν (C=O) 1685 $cm^{-1}$, ν (C=C aromatic) 1610, 1585, 1565 and 1550 $cm^{-1}$; NMR (acetone-$d_6$), τ 0 ppm (1H;very broad band which disappears after treatment with $D_2O$), τ 1.25 ppm (1H; s), τ 3.18 ppm (1H; s), τ 6.63 ppm (3H;s)].

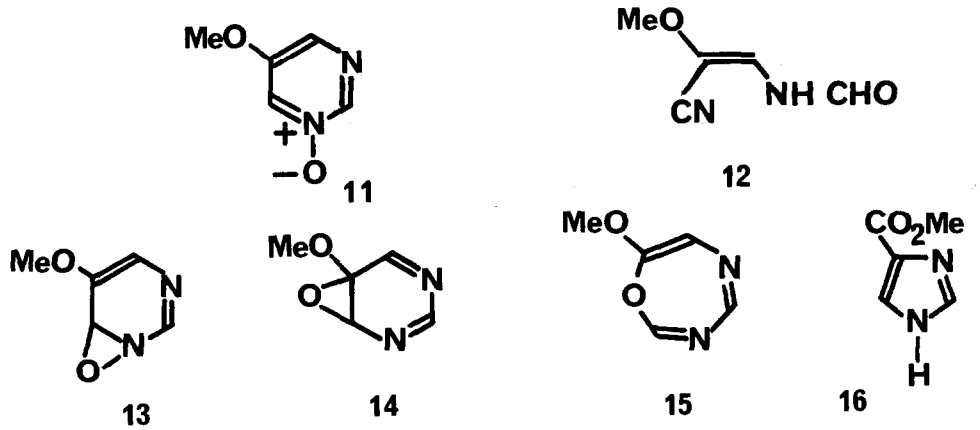



4 5 6 7 8 9 10

SCHEME 2

The formation of compound 7 is best explained by assuming the following consecutive steps: i) photoinduced electrocyclisation toward C-2 which leads to 5; ii) valence tautomerisation toward oxadiazepine 6; iii) base induced deprotonation and N-O cleavage which gives the cis enaminonitrile according to a hypothesis which we had already postulated (1,2) (Scheme 2). The simultaneous formation of imidazole 10 can be accounted for by assuming, first a photoinduced electrocyclisation toward C-6 which gives 8, and thence the seven membered ring 9; eventually ring contraction of oxadiazepine 9 may occur through an open chain nitrene intermediate (3) to yield the final product. Most of the starting product yields insoluble and intractable material (polymer?), the structure of which has not been investigated. From these results we may deduce that the predicted regiospecificity does not prevail, since we get about equal amounts of products which derive from C-2 and C-6 electrocyclisation.

According to our HMO model(2), the photochemistry of 5-methoxypyrimidine N-oxide 11 (9) was expected to yield predominantly ring closure toward C-2. We do get the corresponding enaminonitrile isomer 12, mp 83-85°, but in 11% yield only [UV (MeOH) $\lambda_{max}$ 265 nm (ε:16.500); IR ($CHCl_3$) ν (N-H) 3400 $cm^{-1}$, ν (CN) 2220 $cm^{-1}$, ν (C=O) 1770 $cm^{-1}$, ν (C=C) 1665 $cm^{-1}$; NMR ($CDCl_3$), τ 1.88 ppm (1H; large singlet), τ 2.75 ppm (1H; d; J=11Hz; a singlet results after exchange with $D_2O$), τ 1.7 (1H; very broad band which disappears after exchange with $D_2O$)]. The main product, mp 153-154° (yield: 34%), proved to be the 4(5)-methoxycarbonylimidazole 16, a known compound (10) which could easily be synthesized in a standard way from 4(5)-hydroxymethylene-imidazole(11) [identical mp's and all spectral data superimposable: IR, UV, $^1H$ and $^{13}C$ NMR and MS (12)]. In addition to products 12 and 16, 5-methoxypyrimidine is isolated in 16% yield.




SCHEME 3

The formation of the main product 16 is best explained by assuming the following steps: i) photoinduced electrocyclisation toward C-6, ii) 1,5 sigmatropic shift which leads to epoxypyrimidine 14 (3); iii) valence tautomerism to oxadiazepine 15; iiii) eventually we shall assume for the last step a ring contraction for which we do not have any straighforward explanation (Scheme 3).

These second series of results are best interpreted when using Kaneko's PPP-SCF model, which favours a photoinduced electrocyclisation toward C-6. Nevertheless more physico-chemical data are needed, in order to gain a better knowledge of the chemically active excited states, before applying semi-empirical or theoretical models.

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