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PHOTOCHEMISTRY OF 1,3-DIMETHYLURACIL.
A NOVEL PHOTOCHEMICAL RING-OPENING LEADING TO AN ENAMINE

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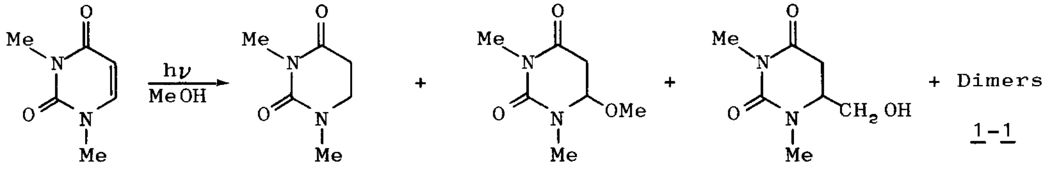
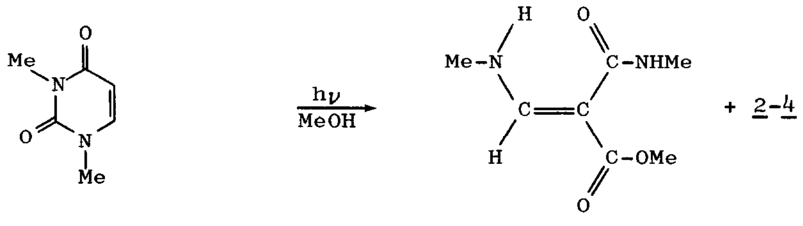
Abstract - Besides known reduction and solvent addition products, the photolysis of 1,3-dimethyluracil in methanol resulted in formation of the enamine 2-methoxycarbonyl-N-methyl-3-methylaminopropenamide (5) *via* a novel ring-opening reaction. A mechanism for the formation of 5 is suggested and its structure was confirmed by an independent synthesis.

The photochemistry of uracil derivatives has long been of great interest as model systems for the interaction of UV-light with DNA and RNA.[1] We have for some time been interested in the photochemistry of 1,3-dimethyluracil (1) in methanol. Several workers[2] have reported on various photoproducts which combined may be summarized as follows.



1 2 3 4

We have detected all of these photoproducts under various irradiation conditions and have found that the product distribution is very sensitive to the wavelength utilized.[3] In addition, however, we have found that irradiation of 1 in methanol using a Rayonet reactor at 254 nm or an unfiltered Hanovia lamp resulted in an unusual ring-opening of the uracil ring leading to 2-methoxycarbonyl-N-methyl-3-methylaminopropenamide (5) in about 10% yield.



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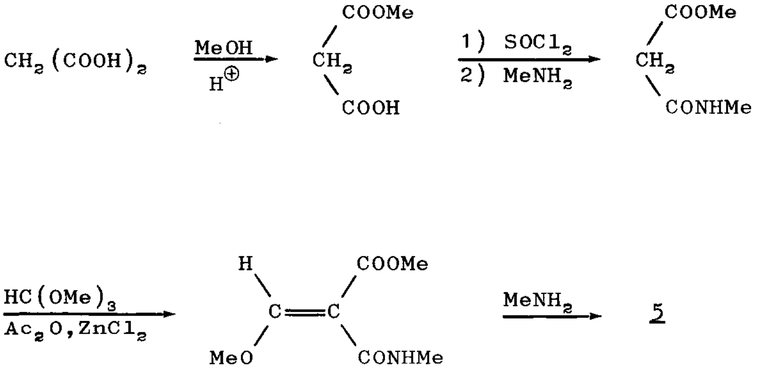
5 (E or Z)

The enamine (5) was isolated by column chromatography and identified from its spectral properties. The proton NMR spectrum[4] in $CDCl_3$ showed peaks at δ 2.85 and 3.09 (both d, 3H, J = 5 Hz, NH-Me), 3.70 (s, 3H, OMe), 7.85 (d, 1H, J = 14 Hz, H-C=C, the large coupling constant suggests the anti conformation of H-N-C-H as shown in 5), 8.50 and 10.25 (both br, 1H each, H-N). The carbon spectrum[4] in C_6D_6 showed resonances at δ 25.11 and 34.67 (both CH_3-N), 50.38 (CH_3-O), 89.78 (N-C=C), 159.45 (N-C=C), 168.75 and 175.15 (both C=O); MS (m/e): 172 (M^+), 142 (M^+-NHMe), 141 (M^+-OMe), 84, 82, 42; IR (film): 3350 (br, s), 2950 (s), 1700 (s), 1650 (s), 1550, 1360, 1320, 1270, 1100, 810 cm^{-1}; UV (λ_{max} in MeCN): 280 (ϵ = 20000), 230 (ϵ = 7800). The geometry around C=C (E or Z) could not be established.

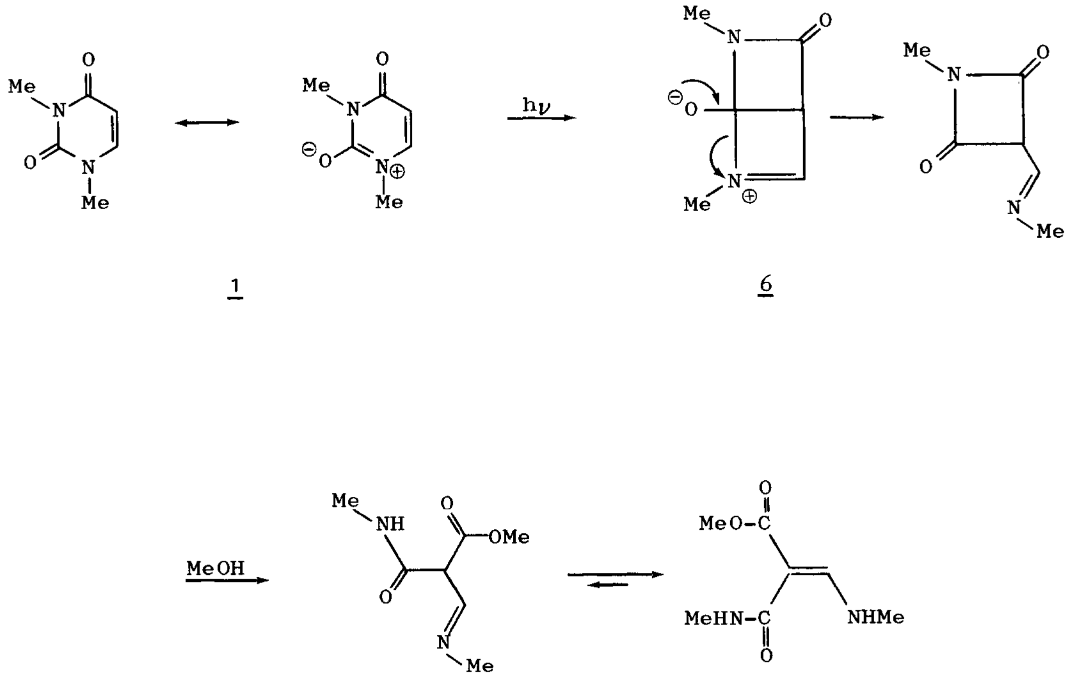
The identity of 5 was confirmed by an independent synthesis:



Both the photolytic and synthetic route to 5 led to a fluorescing compound with emission maximum in acetonitrile at 450 nm and excitation maximum at 390 nm. Upon purification of 5, the emission disappears, and we do not know as yet the identity of its origin.

The formation of 2-4 was quenched by added triplet quenchers like *trans*-1,2-dichloroethylene and oxygen suggesting a triplet excited state precursor for 2-4.[3,5] In contrast, the photochemical formation of 5 was not quenched by addition of these quenchers.[6] This result suggests that 5 may be singlet derived. The very short singlet lifetime of 1 (4 psec[7]), however, may also suggest a vibrationally excited ("hot") ground state precursor for 5.

We suggest the following mechanism for the formation of 5 involving a Woodward-Hoffmann allowed disrotatory electrocyclic ring closure[8] in the photochemical step.



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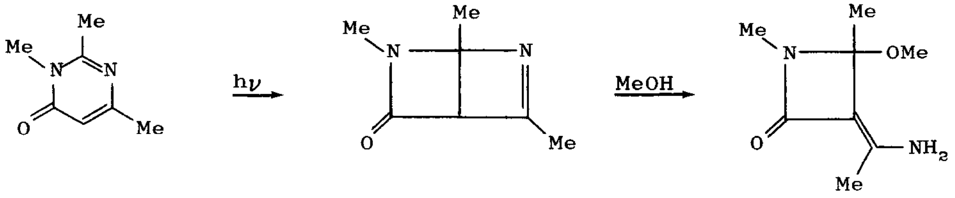
6

5

The intermediate 6 (a Dewar pyrimidion) may seem unlikely, but a similar intermediate has been observed in the photolysis of 7 in methanol.[9]



7

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4. In ppm relative to TMS at 0 ppm.
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6. In some cases an enhanced yield of 5 was noted upon addition of quencher.
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