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PHOTODEALKYLATION OF N, N-1,3-DIETHYLURACIL

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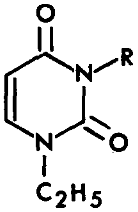
The photochemistry of the nucleic acid base uracil, and its derivatives, has received considerable study.[2] We wish to report here a new type of photoreaction of N,N-dialkyl derivatives of uracil, namely N-3 dealkylation. In particular we have studied the photodealkylation of N, N-1, 3-diethyluracil (I) to form N-1-ethyluracil (II).



I R = C_2H_5

II R = H

A 0.13 M solution of I[3] in 3:1 heptane-t-butanol was irradiated at λ = 254 nm for 120 hours in a Vycor shielded quartz tube until about 25% of the starting material had disappeared. The residue, after evaporation, was chromatographed on silica gel preparative plates using 3:1 n-butanol-heptane as a solvent. Three product bands were isolated. The first (R_f = 0.45, about 20% yield, based on reacted starting material) was identified as II by comparison of the NMR and IR spectrum with an authentic sample obtained from Cyclo Chemical Corp. (NMR: δ = 1.20 (t), 3.75 (q), 5.6 (d) 7.70 (d) in d_6-DMSO and δ = 1.20 (t), 3.83 (q) 5.84 (d), 7.68 (d) in D_2O with DSS). The second (III) (R_f = 0.9, about 75% yield) is probably a mixture of cyclobutane dimers. It had only slight UV absorption maxima above 255 nm. Spotting on a TLC plate, irradiating with 254 nm light, and then developing the plate results in appearance of the parent compound. This behavior is characteristic of cyclobutane dimers of the pyrimidine bases (2a). The compound showed complex regions of overlapping peaks in the NMR at δ = 1.17 and 3.80 and had no vinylic proton NMR resonances. The IR spectrum showed characteristic amide absorption at about 1670 and 1720 cm^{-1}. The third product (R_f = 0.3) had a yield of less than 5% and was not identified.

The result of irradiation of a 10^{-2}M solution of I at 254 nm in the same solvent was followed as a function of time by high pressure liquid chromatography on Vydac absorbant (0.5% methanol in heptane). It was found that II and III were produced concurrently, eliminating the possibility that III is the precursor of II.

The presence of hydrogens γ to the carbonyl groups on the 3-ethyl in I suggests the possibility that the observed dealkylation reaction is an example of a Norrish Type II photoelimination reaction.[4] The course of the reaction would then involve abstraction of H, from the terminal methyl on the 3-ethyl, by a carbonyl group to form a 1,4 biradical followed by elimination of ethylene to give an enolic form of II. The 4-carbonyl group would seem to be the most likely site for abstraction to occur as it is part of the light absorbing chromophore. That a γ hydrogen is required for dealkylation to occur is supported by the fact that N, N-1, 3-dimethyluracil does not photochemically dealkylate to form N-1-methyluracil.

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