SYNTHESIS AND CHEMICAL REACTIVITY OF DIAZAPHENOTHIAZINONE

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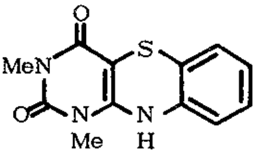
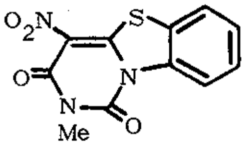
The reaction of 1,3-dimethyl-5-nitro-6-chlorouracil with 2-aminothiophenol in benzene containing an excess of triethylamine gave 1,3-dimethyl-10H-pyrimido-(5,4-b)(1,4)benzothiazine-2,4(1H,3H)-dione(I) in 90 % yield. In sharp contrast, the reaction in acetic acid resulted in the formation of 2-methyl-4-nitropyrimido-(4,3-b) benzothiazoline-1,3(2H, 10H)-dione(II) in 78 % yield. The latter reaction involves an unusual uracil-ring cleavage which can be ascribed to the unique feature of the spiro five-membered intermediate in the course of the Smiles rearrangement.

Introduction of alkoxy and amino functions into the 4a-angular position was achieved by virtue of the oxidative substitution of (I) or the Pummerer rearrangement of the corresponding sulfoxide.

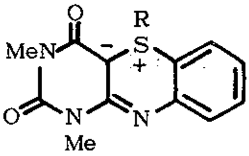
Sulfonium ylides(IIIa,b) underwent photochemical ring-exapnsion to give pyrimidobenzothiazepine derivatives in high yields. The thermal rearrangement of methyl sulfonium ylide(IIIa) gave the N-methyl derivative of (I) as well as the 4a-methyl derivative of (I). The formation of the N-methyl derivative is particularly noticeable. Pyrolysis of ethyl sulfonium ylide (IIIb), however, caused concurrently β-elimination and the Stevens rearrangement to give ethylene, (I) and the 4a-ethyl derivative.



(I)



(II)



(IIIa) R=Me

(IIIb) R=Et