

SOME NOVEL REACTIONS OF 1,3-DIALKYLURACILS

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It is well known that uracil derivatives which could be viewed as β -enamido ketones undergo interesting chemical reactions leading to products with various ring systems.

- 1) We have synthesized 6-(1,3-dialkyluracilyl)-6'-(1',3'-dialkyluracilyl)sulfide (I) from 6-chloro-1,3-dialkyluracil (II) and sodium 1,3-dialkyluracil-6-mercaptide (III).

Compound (I) was found to undergo photochemical cyclization giving rise to three isolable products with novel ring systems, namely, a 1,3,6,8-tetraalkyl-(1,4)-dithiino(2,3-d;5,6-d')dipyrimidine (IV), a 1,3,6,8-tetraalkyldipyrimidino(2,3-d;4,5-d')thiophene (V) and its dihydro derivative (VI). These compounds were fully characterized by ^1H -NMR, mass spectral and elemental analyses. A plausible mechanism for this photocyclization of I to IV, V and VI has been proposed. (Itoh et al., Tetrahedron Letters, 2595 (1977)).

- 2) We have shown that treatment of 6-chloro-1,3-dimethyluracil (II, alkyl = Me) with diazomethane in ether gave a crystalline product which was not the expected bicyclic adduct but 6-chloro-1,3;1',3'-tetramethyl-5,6'-biuracil (VII). The structure of VII was confirmed by ^1H -NMR, mass spectral and elemental analyses as well as by hydrolytic conversion of VII into 1,3;1',3'-tetramethyl-5,6'-biuracil (VIII) with Pd/C as the catalyst. We have also demonstrated that treatment of II (alkyl = Me) with a secondary amine such as pyrrolidine or piperidine afforded crystalline 6-substituted amino-1,3;1',3'-tetramethyl-5,6'-biuracil (IX). The structure of IX was established by ^1H -NMR, mass spectral and elemental analyses.
- 3) We have found a novel C-acylation of IX with dimethyl acetylenedicarboxylate (DMAD). When IX was treated with DMAD in dry tetrahydrofuran, a 1:1 adduct (X) was obtained. Mild alkaline treatment (5% KOH-MeOH) of X gave 6-methoxy-5'-(3-carboxypropynoyl)uracil (XI). Characterization of X and XI, and a plausible mechanism for this C-acylation will be discussed.