

THIOCARBONYL PHOTOCHEMISTRY. I. HYDROXYALKYLATION OF
1, 3-DIMETHYL 4-THIOURACIL

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Among the minor nucleosides of t-RNA (1), 4-thiouridine 1 is of special interest since it can take part in specific photoreactions (2, 3). As a model for 4-thiouridine photochemistry we have recently investigated the light-induced reactions of 1, 3-dimethyl 4-thiouracil 2.

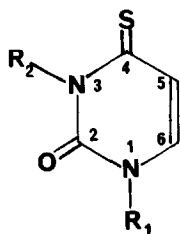
When the latter is irradiated in hydrogen-donating alcohols (ethanol or 2-propanol), the C-6 hydroxyalkylated 5, 6-dihydro derivative 3 is the major photoproduct (Scheme). It is noteworthy that 1, 3-dimethyluracil 4 yields 5, 6-dihydro 1, 3-dimethyluracil 5 under irradiation in 2-propanol (yield 50 %) (4).

In a typical experiment a 5.10^{-3} M solution of 2 in alcohol (ethanol or 2-propanol) is irradiated (5) until 70 % of the 335 nm absorption band of 2 has disappeared. Silicagel chromatography yields unreacted 2 along with 3 ($R=R'=CH_3$; m.p. 114-115°) ($R=H$, $R'=CH_3$; oil). Based on reacted 2, compound 3 is produced in 60 % yield.

Structure 3 ($R=R'=CH_3$) was ascertained in the following manner: $POCl_3$ /pyridine dehydration leads to a mixture of compounds which are isomerized upon treatment with EtOH/HCl giving 6 (oil) (NMR H_5 : 6, 6 ppm). Photolysis in the presence of oxygen (2) of a t-BuOH solution of 6 gives rise to 7 (oil) (NMR H_5 , s, 5.7 ppm). The observed diamagnetic shift for the H_5 signal is typical for the change from a thio-4 uracil (6) to a uracil derivative (7) and clearly establishes structure 3.

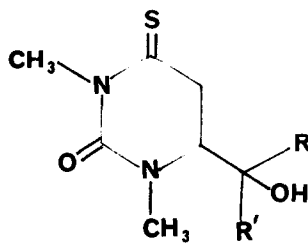
Compound 3 was also photolyzed under oxygen in t-BuOH yielding 8, m.p. 100-102°, the NMR spectrum of which (CD_3COCD_3) displays a quartet for the H_6 signal at 3.40 ppm consistent with a pseudo-axial hydroxypropyl group at C-6 (6, 7_e) ($J_{H_{5e}H_6} + J_{H_{5a}H_6} = 9$ Hz).

This C-hydroxyalkylation photoreaction is to our knowledge the first example so far reported involving an ene-thione system. In sharp contrast to the related enone system (4, 8), only minor amounts of the 5, 6-dihydro derivative 9 (9) were isolated. Further studies on the photochemistry of related compounds are currently in progress in this laboratory (10).

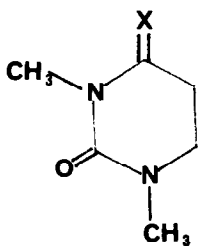


1 $R_1 = \text{Ribosyl}$ $R_2 = \text{H}$

2 $R_1 = R_2 = \text{CH}_3$

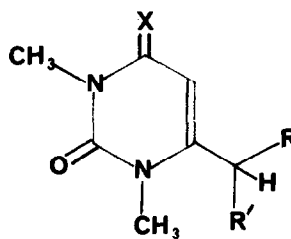


3



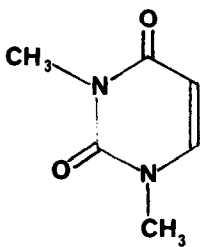
5 $X = \text{O}$

9 $X = \text{S}$

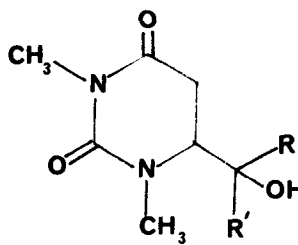


6 $X = \text{S}$

7 $X = \text{O}$



4



8

Scheme

Acknowledgement

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10. This paper is dedicated to Professor E. Lederer on his 65th birthday.