

PHOTOCHEMISTRY OF 6-AZIDO-1,3-DIMETHYLURACIL DERIVATIVES

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Photochemistry of 6-azido-1,3-dimethyluracil (1) and its 5-substituted derivatives (2 a-c) were investigated.

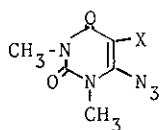
Photolysis of (1) in the presence of primary and secondary alkylamines in THF gave 6-alkylamino-5-amino-1,3-dimethyluracils (3) in which the alkylamino group arised from the amines used. On the contrary, thermal decomposition of (1) in amines at 140-150° led to no formation of (3). This implies that (3) is formed by photochemical process. The mechanism for this reaction involves a nucleophilic attack by the amines on an azirine intermediate resulted from a singlet nitrene. Furthermore, photolysis of (1) in the presence of hydrochloric acid in methanol gave 5-amino-6-chloro-1,3-dimethyluracil which is a synthetically useful intermediate.

In order to elucidate the substituent effect, photolysis of 5-substituted 6-azido-1,3-dimethyluracils(2 a-c) was examined.

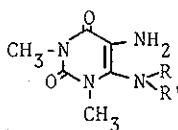
Although 6-azido-5-cyano-1,3-dimethyluracil(2a) was easily subjected to nucleophilic substitution with amines at room temperature to give 6-alkylamino-5-cyano-1,3-dimethyluracils, irradiation of (2a) in various alcohols in the absence of amines caused a ring expansion to give 1,3,5-triazepine derivatives(4), which is the first example of ring expansion of uracils and a new synthetic method for 1,3,5-triazepines.

Photolysis of 6-azido-1,3-dimethyl-5-phenyluracil (2b) in methanol gave the pyrimido[4,5-d]indole (5) via intramolecular cyclization. When (2b) was decomposed in tetralin at 150-160°, the same product (5) was obtained.

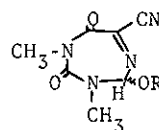
Reaction of 6-azido-1,3-dimethyl-5-formyluracil (2c) with triethylphosphine at room temperature gave triazinopyrimidine (6).



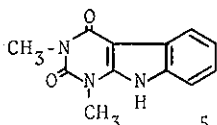
- 1 X=H  
 2 a X=CN  
 b X=Ph  
 c X=CHO



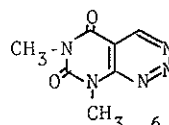
3



4



5



6