New Photochemical Synthesis of 6-Alkylamino-5-amino-1,3-dimethyluracils from 6-Azido-1,3-dimethyluracil and Amines

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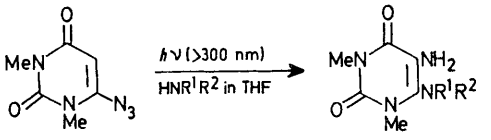
Summary Irradiation of 6-azido-1,3-dimethyluracil (**1**) in the presence of primary and secondary alkylamines gave 6-alkylamino-5-amino-1,3-dimethyluracils (**2a**—**g**) in which the alkylamino group arises from the amines used.

ALTHOUGH the photochemical transformation of aryl azides in primary and secondary amines to afford 2-amino-3*H*-azepines[1] is well known, less attention has been paid to the photochemistry of cyclic vinyl azides, which in methanol generally gives aminoketones.[2] Irradiation of a methanolic solution of 6-azidouracil, a cyclic analogue of vinyl azides, gave pyrimidopteridine.[3] We now describe the irradiation of 6-azido-1,3-dimethyluracil (**1**) in the presence of primary and secondary alkylamines to give 6-alkylamino-5-amino-1,3-dimethyluracils (**2**) which are convenient intermediates

for biologically interesting fused pyrimidines, *e.g.* xanthines and pteridines.[4]



(1) (2)

As a typical example, a solution of (**1**) (0·011 M) and dimethylamine (0·033 M) in tetrahydrofuran (THF) was irradiated with a 100 W high-pressure mercury lamp through a Pyrex filter under nitrogen for 3 h, during which time nitrogen was evolved. After evaporation, trituration of the residue with ether gave the uracil (**2a**), m.p. 142—143 °C in 59% yield. Compound (**2a**) was identical with an authentic sample prepared by the reaction of 6-chloro-1,3-dimethyl-5-nitrouracil[5] with dimethylamine followed by catalytic reduction.

Similar irradiation of (**1**) (0·011 M) and various alkylamines† (0·033 M) in THF gave the corresponding 6-alkylaminouracils (**2b**—**g**) in which the amines employed were introduced regiospecifically to the 6-position (Table).‡

To the best of our knowledge, this is the first example of the formation of *ortho*-diamines by irradiation of a monocyclic vinyl azide in the presence of amines, although the formation of *ortho*-diamines by the irradiation of polycyclic aromatic azides in secondary alkylamines has recently been reported.[6] It is noteworthy that in our preliminary studies (**2**) was formed even when primary alkylamines were used.

TABLE. Photochemical formation of 6-alkylamino-5-amino-1,3-dimethyluracils (**2**)

	R^1	R^2	M.p./°C	Yield (%)
a	Me	Me	142—143	59
b	Et	Et	164—165 (picrate)	60
c	$-[CH_2]_5-$		128—130	64
d	$-[CH_2]_2-O-[CH_2]_2-$		220—221	83
e	H	Me	189—190 (picrate)	42
f	H	Et	245—246 (picrate)	30
g	H	Pr^i	121—122·5	27

The mechanism of the present reaction is still under study, but we think it involves a nucleophilic attack by the amines on an azirine intermediate as discussed previously.[6] Thermal decomposition of (**1**) in amines at 140—150 °C did not give (**2**), implying that (**2**) is formed by a photochemical process.

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† With arylamines, the corresponding 6-arylaminouracils were not formed but undetermined products were obtained.
‡ All new compounds gave satisfactory elemental analyses and spectral properties consistent with the assigned structures.

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[3] W. Pfleiderer, K. Schündehütte, and H. Ferch, *Annalen*, 1958, **615**, 57.
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[6] B. Iddon, H. Suschitzky, and D. S. Taylor, *J.C.S. Chem. Comm.*, 1972, 879; *J.C.S. Perkin I*, 1974, 579; B. Iddon, M. W. Pickering, H. Suschitzky, and D. S. Taylor, *ibid.*, 1975, 1868; B. Iddon, M. W. Pickering, and H. Suschitzky, *J.C.S. Chem. Comm.*, 1974, 759; S. E. Hilton, E. F. V. Scriven, and H. Suschitzky, *ibid.*, p. 853; S. E. Carroll, B. Nay, E. F. V. Scriven, and H. Suschitzky, *Synthesis*, 1975, 710; J. Rigaudy, C. Igier, and J. Barcelo, *Tetrahedron Letters*, 1975, 3845.