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# ON THE PHOTOCHEMISTRY OF HALODIAZA AROMATICS[1]

by

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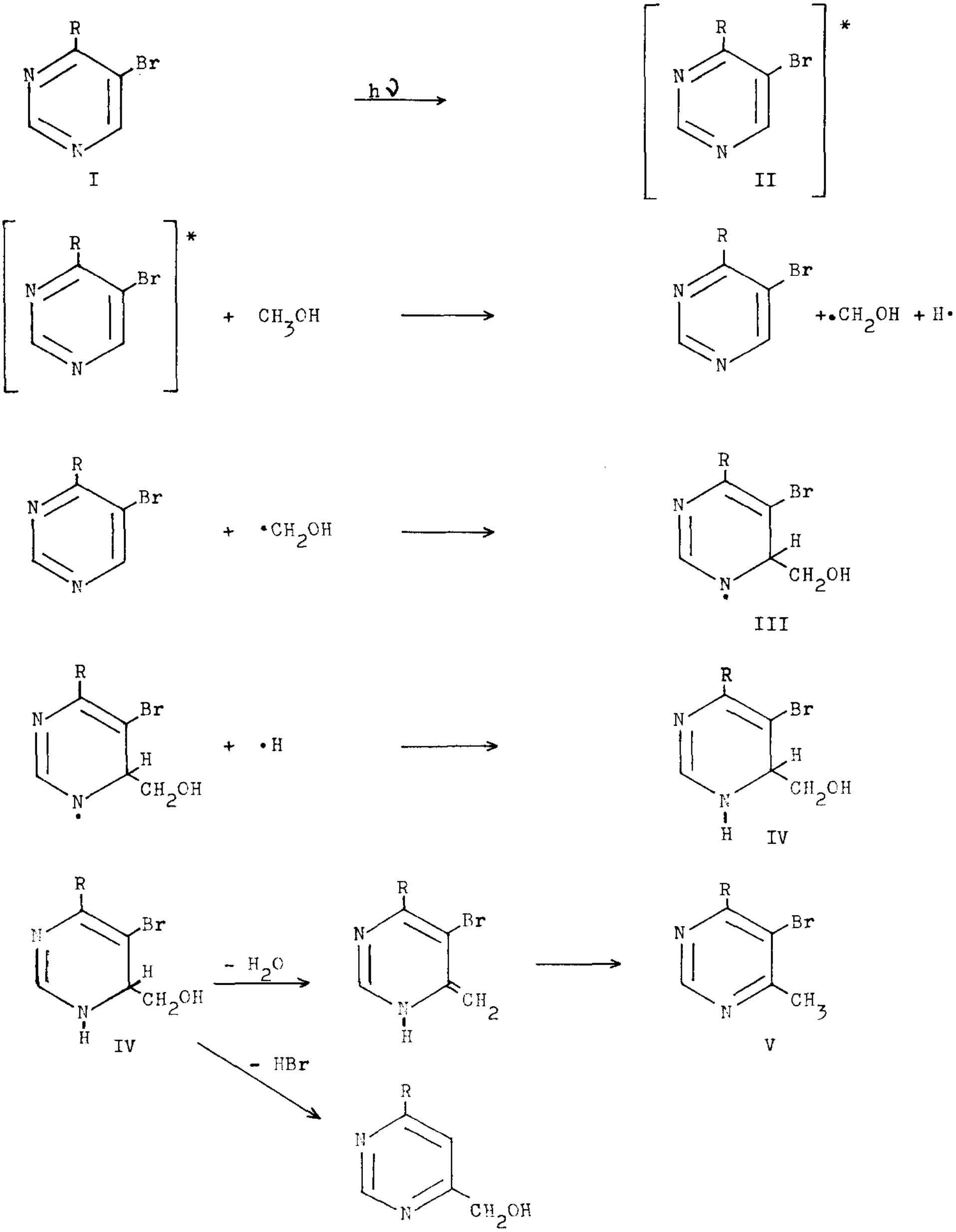
There is continuing interest in the chemical behaviour of aza aromatics on UV-irradiation in alcohol; addition of the alcohol to the azomethine bond has been observed, yielding α-hydroxyalkyl derivatives, which in some cases dehydrate into an alkylated heterocycle[2-8].

The photochemistry of bromo- and chloro derivatives of pyrimidine has hardly been studied yet[8]. In the present paper we wish to report some of our results, obtained when pyrimidine derivatives bearing a halogen substituent on positions 2,5 and 6 are irradiated in methanol.

By irradiation of 5-bromopyrimidine (I, R = H) in methanol with a Philips HPK 125 W lamp in a Pyrex glass apparatus - $N_2$gas bubbled through the solution during the irradiation procedure - a reaction mixture is obtained from which we were able to isolate a compound to which - based on IR, NMR and Mass spectral data - the structure of 4-hydroxymethylpyrimidine was assigned (yield 25-30%). This structure was confirmed by comparison of the spectral data with those of an authentic specimen. This process of hydroxymethylation combined with a simultaneous removal of the bromine from the 5-position is unknown till now. A previous reduction of 5-bromopyrimidine (I, R = H) into pyrimidine, followed by hydroxymethylation of the pyrimidine formed is not very likely: when pyrimidine is subjected to irradiation in methanol under the same conditions mentioned above we did not find 4-hydroxymethylpyrimidine. Irradiation of 2-chloropyrimidine in methanol under conditions identical to those given above afforded a product which was proved by NMR, IR and Mass spectral data to be 2-chloro-4-hydroxymethylpyrimidine. Thus in contrast to 5-bromopyrimidine the hydroxymethylation occurs without instant loss of the halogen atom.
By irradiation of 5-bromo-4-t-butylpyrimidine (I, R = t-$C_4H_9$) in methanol no indication for the formation of 4-t-butyl-6-hydroxymethylpyrimidine was found, instead 5-bromo-4-t-butyl-6-methylpyrimidine (V, R= t-$C_4H_9$)was obtained as the main product (yield 10-15%).

A possible mechanism for the latter reaction, analogous to that given by Ochiai et al[6] for the photo-induced methylation of pyrimidines and condensed pyrimidines, involves the formation of a hydroxymethyl radical by an excited pyrimidine (II, R = t - $C_4H_9$) which after addition to the 6-position yields III (R = t - $C_4H_9$) which in the last steps of the reaction via IV (R = t - $C_4H_9$) dehydrates into V (R = t - $C_4H_9$).



It is very attractive to postulate that the conversion of I (R = H) into 4-hydroxymethylpyrimidine also involves formation of the intermediate step IV (R = H) which instead of dehydration favours the dehydrobromination reaction.

Irradiation of 5-bromo-4-methoxy-2-phenylpyrimidine yielded a reaction mixture from which we were able to isolate 5,6-dimethyl-4-methoxy-2-phenylpyrimidine (yield 2-5%). Whereas the photo-alkylation in a position adjacent to the nitrogen of an aza aromatic is a rather general process, alkylation on the 5-position of pyrimidine has not been observed till now and is an interesting new aspect in photo - reactions of 5-bromopyrimidines. Until more data are available we refrain from proposing a mechanism for the photo-alkylation on position 5.

Irradiation of 6-chloro-2,4-diphenylpyrimidine in methanol (Rayonet RPR 208, 350 mμ lamps, $N_2$-gas bubbled through the solution during the irradiation procedure) gave besides alkylation on position 6 - 2,4-diphenyl-6-methylpyrimidine is formed (yield 8-10%) - a methoxyl-dechlorination reaction, 2,4-diphenyl-6-methoxypyrimidine being obtained (yield 15-20%). That the last mentioned product is a true photo product was proved by the fact that prolonged heating of 6-chloro-2,4-diphenylpyrimidine in methanol did not show any solvolysis. Furthermore also methylation on position 5 was observed as indicated by the formation of 2,4-diphenyl-6-methoxy-5-methylpyrimidine (yield 5-8%).

The scope and the mechanisms of the hydroxymethylation with or without loss of a halogen atom, of the alkylation on positions5 and 6 and of the methoxyl-dechlorination reactions is subject of further studies in this field.

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