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THE REACTION OF ARYL DIAZONIUM IONS WITH 5-ALKYL-4,6-PYRIMIDINEDIOLS†: A NOVEL PYRIMIDINE TO 1,2,4-TRIAZINE RING TRANSFORMATION

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SUMMARY: The reaction of diazotised arylamines with 5-methyl and 5-ethylpyrimidine-4,6-diol gives 6-alkyl-2-aryl-1,2,4-triazin-5(2H)-ones.

The usual site for electrophilic substitution in pyrimidines is the 5-position. However in a number of cases 5-pyrimidinols having other electron releasing groups at the 2- and 4-positions have been shown to undergo diazo coupling at the 6 position (ref. 1 and references therein). 5-Pyrimidinol has also been show to undergo diazo coupling at the 4-position,[2] and 4,6-dimethyl-5-pyrimidinol has been reported to undergo coupling at the 2-position.[3] However the position of attack did not seem to have been confirmed and may have occurred at the 4-methyl group, which has been observed in some other cases.[4]

We have reacted diazotised arylamines with 5-methyl[5] and 5-ethyl-4,6-pyrimidinediol(1)[6] in which such side chain attack would not occur and coupling might occur at the 2-position.

When the reaction was carried out under typical diazo coupling conditions using some p-substituted anilines yellow to orange-red solid products were obtained (40-45%) whose ^{1}Hnmr spectrum in each case showed signals for the 5-alkyl group, the p-substituted benzene ring, and a non-exchangeable low field singlet (~δ9) Mass spectrometry in each case gave a molecular weight 43 mass units less than is required for the diazo coupled product. Elemental analysis (CHN) confirmed that the products contained the unit CHNO less than expected.

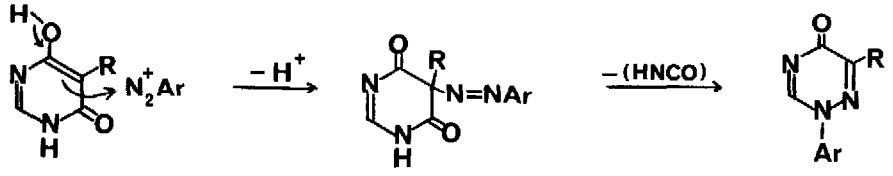
This evidence leads us to believe the products to be 6-alkyl-2-aryl-1,2,4-triazin-5(2H)-ones (2) and this is supported by the mass spectrometric fragmentation of the products, each of which showed a similar pattern to that indicated below for 6-ethyl-2-p-chlorophenyl-1,2,4-triazin-5(2H)-one (2b) (Figure 2).

The reaction seems to involve an unusual loss of the elements HNCO from the pyrimidine ring under conditions of electrophilic substitution and to provide a novel pyrimidine to triazine ring transformation with incorporation of the diazo group into the ring. The

† To simplify nomenclature, hydroxy derivatives of pyrimidine have been termed "pyrimidinols" irrespective of their true tautomeric nature.

mechanism of the reaction may involve a (4+2) addition with subsequent elimination of HNCO, or possibly attack at the 5-position with subsequent HNCO elimination (Figure 1).

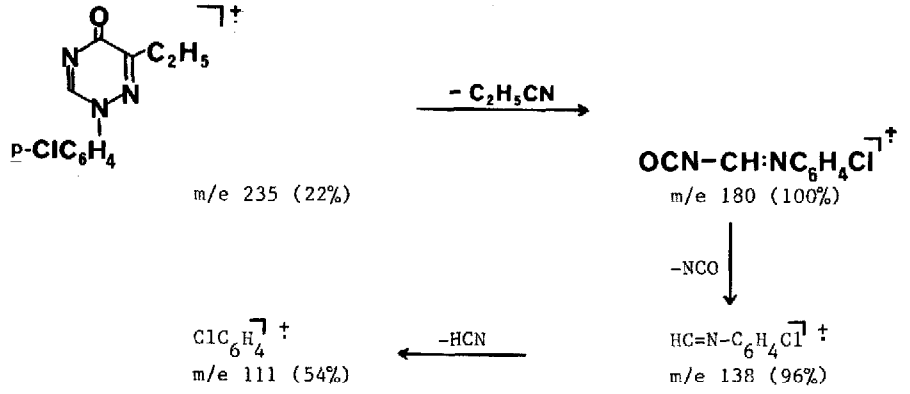
We shall investigate this reaction further and present a fuller account of the work in due course.



(1) R = Me,Et

(2) R = Me, Et
(a) Ar = p-BrC_6H_4
(b) Ar = p-ClC_6H_4
(c) Ar = p-$HO_2CC_6H_4$

Figure 1



(2b) m/e 235 (22%)

Figure 2

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