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REARRANGEMENTS OF 2-ALKYLDIHYDRO-1,3,5-TRIAZINES TO PYRIMIDINES AND OF A METHYLDIHYDROPYRIMIDINE TO A PYRIDINE

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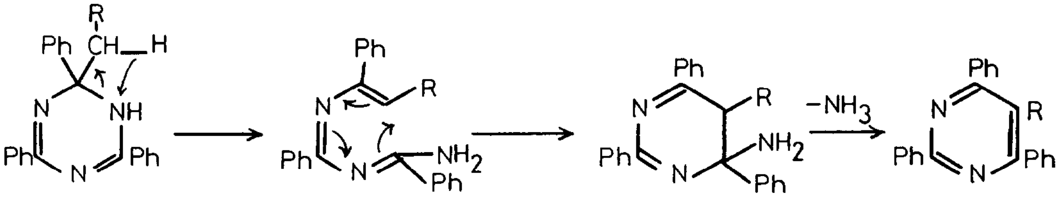
Russian workers have recently reported an interesting base-induced rearrangement of 2-alkylpyrimidinium salts to 2-aminopyridines[1] We wish to point out the resemblance of these rearrangements to a triazine to pyrimidine rearrangement reported earlier,[2] and to report an analogous pyrimidine to pyridine rearrangement, occurring without quaternisation or the presence of added base

In 1941 Anker and Cook reported that thermolysis of certain alkyldihydrotriazines (1) at 200-300°C gave pyrimidines (2) with loss of ammonia.[2] The yields were not stated, and no mechanism for the rearrangement could be proposed. This report has since been almost completely overlooked.[3] We have repeated the thermolyses of compounds (1a,1b) and obtained the products (2a, 2b) in ca 90% yields Anker and Cook reported that on pyrolysis the n-butyl compound (1d) lost butane to give s-triphenyltriazine (3) rather than rearranged, although its hydrochloride did rearrange. In our hands compound (1d) gave triphenyltriazine (3) (21%) and 2,4,6-triphenyl-5-propylpyrimidine (2d) (42%)

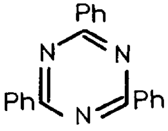
A feasible mechanism for the rearrangement, involving ring-opening accompanied by a 1,3-hydrogen shift, followed by electrocyclic ring-closure and elimination of ammonia, is shown in the Scheme



(1a) R = H
(1b) R = Me
(1c) R = Et
(1d) R = Pr^n

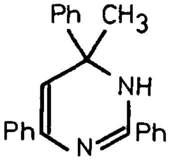
Scheme

(2a) R = H
(2b) R = Me
(2c) R = Et
(2d) R = Pr^n

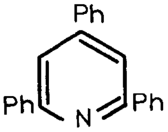


(3)

Addition of methyl-lithium to 2,4,6-triphenylpyrimidine, followed by hydrolysis, gave the dihydropyrimidine (4).[6] When compound (4) was heated at 210°C during 30 min, ammonia was evolved. The residue comprised starting material (40%) and material whose m p. indicated it to be 2,4,6-triphenylpyridine (5) (53%) Careful examination of the latter (i r., h.p l.c) showed it to contain ca 10% of 2,4,6-triphenylpyrimidine, indicating that some elimination of methane from (4) had occurred (cf compound (1d), above).



(4)



(5)

Attempts to obtain a benzene derivative by rearrangement of an alkyldihydropyridine have so far been unsuccessful

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References and Notes

1 R.S.Sagitullin, A N.Kost, and G.G.Danagulyan, Tetrahedron Letters, 4135 (1978).

2. R.M Anker and A.H Cook, J.Chem.Soc , 323 (1941).

3. It is not mentioned in an otherwise comprehensive review.[4] One citation implies that the rearrangement may occur at much lower temperatures[5] but we have not been able to substantiate this

4 H.C van der Plas, "Ring Transformations of Heterocycles", Academic Press, New York (1973)

5. A.A.Scala, N.M.Bikales, and E.I.Becker, J.Org Chem , 30, 303 (1965)

6 The structure shown is most likely, but isomeric structures cannot be ruled out, see G B Bennett, J Heterocyclic Chem., 15, 671 (1978) and R E van der Stoel and H C.van der Plas, Rec Trav.chim , 97, 116 (1978)

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