The Synthesis and Reactivity of the 1,2,3-Triazolo[3,4-*a*]pyrimidine Ring System. A New Route to 2-Substituted Pyrimidines

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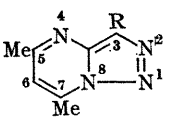
Summary Derivatives of the 1,2,3-triazolo[3,4-*a*]pyrimidine ring system are formed by condensing 5-amino-1*H*-1,2,3-triazoles with acetylacetone or ethyl acetoacetate in the presence of piperidine.

THE triazole ring in certain fused triazoles is readily cleaved by acidic reagents providing convenient synthetic routes to a variety of heterocycles.[1,2] We now report the synthesis and acid-catalysed triazole scission of 1,2,3-triazolo-[3,4-*a*]pyrimidines. These reactions constitute a convenient new route to 2-substituted pyrimidines [*e.g.* (IIIa)].

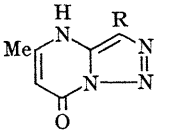
Heating 5-amino-4-phenyl-1*H*-1,2,3-triazole (obtained by

debenzylating[3] the 1-benzyl derivative[4]) with acetylacetone in the presence of piperidine afforded the triazolopyrimidine derivative (Ia). This compound was converted by hot glacial acetic acid into the acetoxypyrimidine (IIIa) whose structure follows from its smooth hydrogenolysis[1] to the known[5] pyrimidine derivative (IIIb). The acetoxy-compound (IIIa) was also formed by heating a mixture of 5-amino-4-phenyl-1*H*-1,2,3-triazole and acetylacetone in glacial acetic acid, the triazolopyrimidine (Ia) being a probable intermediate. Similar findings were obtained for the triazolopyrimidines (Ib), (IIa), and (IIb).

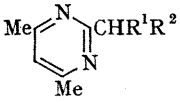
The reactivity of the triazole ring in fused triazoles towards acidic reagents can be explained[1,2] by the formation of a diazonium cation [*e.g.* (IIIc)] and reaction of the derived carbonium ion with the solvent. Conversion of the triazolopyrimidine (Ia) in acidic media into ring-opened species is indicated by ^{1}H n.m.r. measurements. Thus, the methyl absorption of the compound (Ia) changes from a pair of singlets at τ 7·21 and 7·44 in deuteriochloroform due to the nonequivalent C-5 and C-7 methyl-groups, to a single absorption at τ 7·15 in trifluoroacetic acid, indicating the formation of a structure in which the methyl groups become equivalent. Similar changes in methyl absorption in the ^{1}H n.m.r. spectra of tetrazolopyrimidines are attributed[6] to ring-opening to the azide form. Formation of the diazonium cation may occur[7] by ring-opening of the protonated triazole or by protonation of a diazoalkyl tautomer present in an initially established equilibrium. Equilibria of this type are probably involved in the Dimroth rearrangement of aminotriazoles[4,8] and find analogy in the azido-azomethine–tetrazole equilibria observed[9,10] in tetrazolopyrimidines and other fused tetrazoles.[11] The existence



(I) a; R=Ph
b; R=CONH$_2$



(II) a; R=Ph
b; R=CONH$_2$



(III) a; R^1=Ph, R^2=OAc
b; R^1=Ph, R^2=H
c; R^1=Ph, R^2=$\overset{+}{N}$≡N

of diazoalkylazomethine–triazole equilibria in triazolopyrimidines and related[1,2] fused triazoles is being investigated both chemically and by a detailed study of their i.r. and ^{1}H n.m.r. spectra.

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