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PYROLYSIS AND PHOTOLYSIS OF 6-(BENZYLIDENE-1'-METHYLHYDRAZINO)-1,3-DIMETHYLURACILS. A METHOD TO CONVERT ALDEHYDES TO NITRILES. A NEW SYNTHESIS OF PYRAZOLO[3,4-d]PYRIMIDINES

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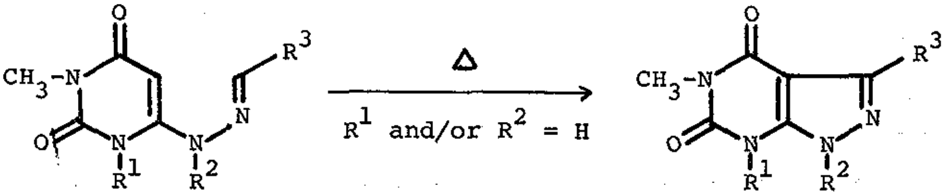
Azomethines (I) resulting from the condensation of aliphatic, aromatic or heterocyclic aldehyde with 1,3-dimethyl-6-(1'-methylhydrazino)uracil underwent decomposition by pyrolysis to yield the respective nitriles and 1,3-dimethyl-6-methylaminouracil, while the photolysis of I led to the exclusive formation of the respective pyrazolo[3,4-d]pyrimidines.

It has been shown[1] that the thermolysis of 6-benzylidenehydrazinouracils constitutes a convenient synthetic route to pyrazolo[3,4-d]pyrimidines. The reaction, however, appeared to be dependent on



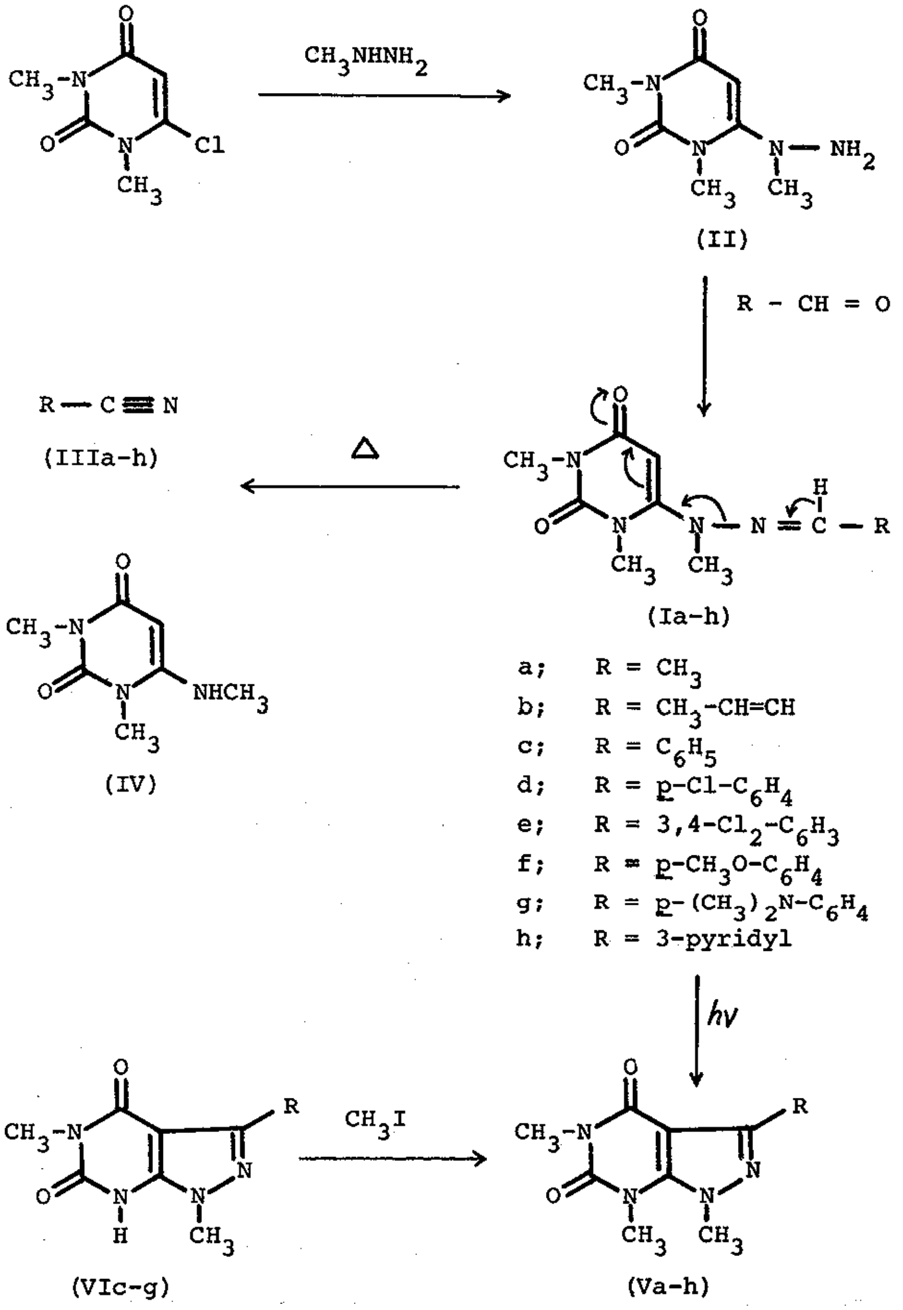
the presence of a proton at the 1-position and/or the 1'-position of 6-substituent, since under similar conditions the thermolysis of fully substituted 6-benzylidenehydrazinouracils took a completely different route and no detectable amount of pyrazolo[3,4-_d_]pyrimidines could be obtained. This communication describes the results on pyrolysis and photolysis of 6-(benzylidene-1'-methylhydrazino)-1,3-dimethyluracils (I).

The key intermediates, compound I, were prepared by treatment of 1,3-dimethyl-6-(1'-methylhydrazino)uracil (II), mp 135°, which was obtained from the condensation of 6-chloro-1,3-dimethyluracil and methylhydrazine, with aliphatic as well as aromatic or heterocyclic aldehydes in ethanol at room temperature (Table 1).

Table 1 Preparation of 6-(Benzylidene-1'-methylhydrazino)-1,3-dimethyluracils

Compound	Mp (°C)	Yield (%)
Ia	131	88
Ib	151	79
Ic	151	87
Id	231	100
Ie	225	100
If	166	81
Ig	150	87
Ih	203	95

It has been found that compounds I undergo the nitrogen-nitrogen



a; R = CH_3
b; R = CH_3-CH=CH
c; R = C_6H_5
d; R = p-Cl-C_6H_4
e; R = 3,4-Cl_2-C_6H_3
f; R = p-CH_3O-C_6H_4
g; R = p-$(CH_3)_2N$-C_6H_4
h; R = 3-pyridyl

bond cleavage accompanied with prototropic rearrangement of 6-substituent by pyrolysis to yield the respective nitriles (III) and 1,3-dimethyl-6-methylaminouracil (IV)[2] in high yields and in a state of high purity. The reaction can be performed merely by heating the starting materials at temperatures slightly higher than their melting points for about 30 minutes, followed by distillation, sublimation or extraction of the reaction mixtures with ether to give the respective nitriles. The resulting residue includes 1,3-dimethyl-6-methylaminouracil (IV)[2] exclusively. Representative examples are listed in Table 2. We consider this nitrile formation as possessing potential synthetic utility because of the good yields obtained, the high purity of products and the neutral conditions employed.

Table 2 Pyrolysis of 6-(Benzylidene-1'-methylhydrazino)-1,3-dimethyluracils

Starting material	Reaction conditions Temp (°C)	 Time (min)	Products Nitrile	 (%)	 IV (%)
Ia	160	20	IIIa	(59)	(86)
Ib	170	30	not identified		(75)
Ic	220	30	IIIc	(83)	(87)
Id	240	30	IIId	(87)	(91)
Ie	260	10	IIIe	(86)	(90)
If	220	30	IIIf	(75)	(82)
Ig	220	40	IIIg	(73)	(80)
Ih	230	30	IIIh	(69)	(75)

Next, the photolysis of compounds I was carried out. A solution of 0.5 g of compound I in 600 ml of benzene was irradiated under aerobic condition with a 100-W high pressure mercury lamp surrounded by a water-cooled Pyrex filter for 30-40 hours at room temperature. The completion of the reaction could readily be judged by tlc using silica gel G and mixtures of chloroform and methanol as developing solvents. Removal of the solvent, followed by recrystallization from ethanol or dioxane, gave the respective pyrazolo[3,4-d]pyrimidines (V) as sole products in excellent yields (Table 3). The structures of compounds V were established by microanalysis, by molecular weight determination by mass spectrometry and by comparison with authentic samples prepared by the methylation of the

Table 3 Photolysis of 6-(Benzylidene-1'-methylhydrazino)-1,3-dimethyluracils

Starting material	Product	Mp (°C)	Yield (%)
Ia	Va	251	78
Ib	Vb	215	81
Ic	Vc	192	84
Id	Vd	257	79
Ie	Ve	242	92
If	Vf	214	90
Ig	Vg	193	85
Ih	Vh	211	70

corresponding 3-substituted 1,5-dimethylpyrazolo[3,4-_d_]pyrimidine-4,6(5_H_,7_H_)-diones (VI).[1] Thus, the photolysis of compounds I has been proved to offer a new synthesis of 3-substituted 1,5,7-trimethylpyrazolo[3,4-_d_]pyrimidine-4,6(5_H_,7_H_)-diones (V).

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