

Ring Contraction of 1-Alkyl-1,2,4-triazinium Iodides to 1,2,4-Triazoles

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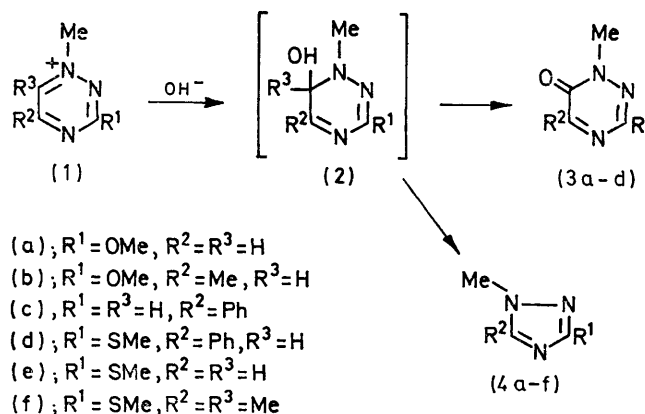
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Summary 1-Alkyl-1,2,4-triazinium iodides readily undergo ring contraction to 1,2,4-triazoles on treatment with base.

It has been shown that 1,2,4-triazines undergo the Diels-Alder reaction,^{1,2} readily form covalent hydrates across the N(4)-C(5) bond,³ and easily dimerize.⁴

If polar substituents such as a 3-oxo-group are present, a 5-alkyl substituent, with a proton on the carbon atom fused to the 1,2,4-triazine ring, readily tautomerizes to the 5-alkylidene isomer.⁵ 1,2,4-Triazin-3(2*H*)-ones, when treated with hydroxylamine-*O*-sulphonic acid in base, ring contract to imidazolin-2-ones,⁶ and to 1,2,3-triazoles when treated with chloramine.⁷

Other reported ring-contractions of 1,2,4-triazines involve the conversion of 2-amino-5-phenyl-1,2,4-triazine into 3-acetamido-5-methyl-1,2,4-triazole on treatment with acetic anhydride, the base-catalysed generation of 4-phenyl-1,2,3-triazole from 3-amino-5-phenyl-1,2,4-triazine 2-oxide, and

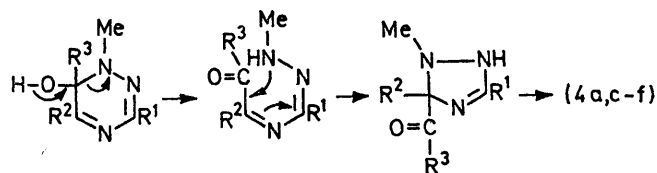


SCHEME 1

the acid-catalysed conversion of 3-acetamido-5-phenyl-1,2,4-triazine 2-oxide into 4-phenylimidazol-2(3H)-one.⁸

We now describe another unusual reaction of the 1,2,4-triazine ring system.

Hydrolysis of *N*¹-alkylated 1,2,4-triazines (**1**) under basic conditions might be expected to give the carbinolamine (**2**). In fact a minor product is the 'oxidized carbinolamine' (**3**) when C(6) is unsubstituted, but the major products (*ca.* 65%) are the ring-contracted 1,2,4-triazole (**4a-f**). Structural proof for these 1,2,4-triazoles is based upon correct molecular weights (mass spectroscopy), ¹H n.m.r. spectra, elemental analyses, and comparison with an authentic sample for compound (**4c**).⁹



SCHEME 2

This new ring contraction may occur *via* the carbinolamine (**2**) as in Scheme 2.

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