A Novel Synthesis of 5-Amino-2,3- or 5-Imino-2,5-dihydrofurans

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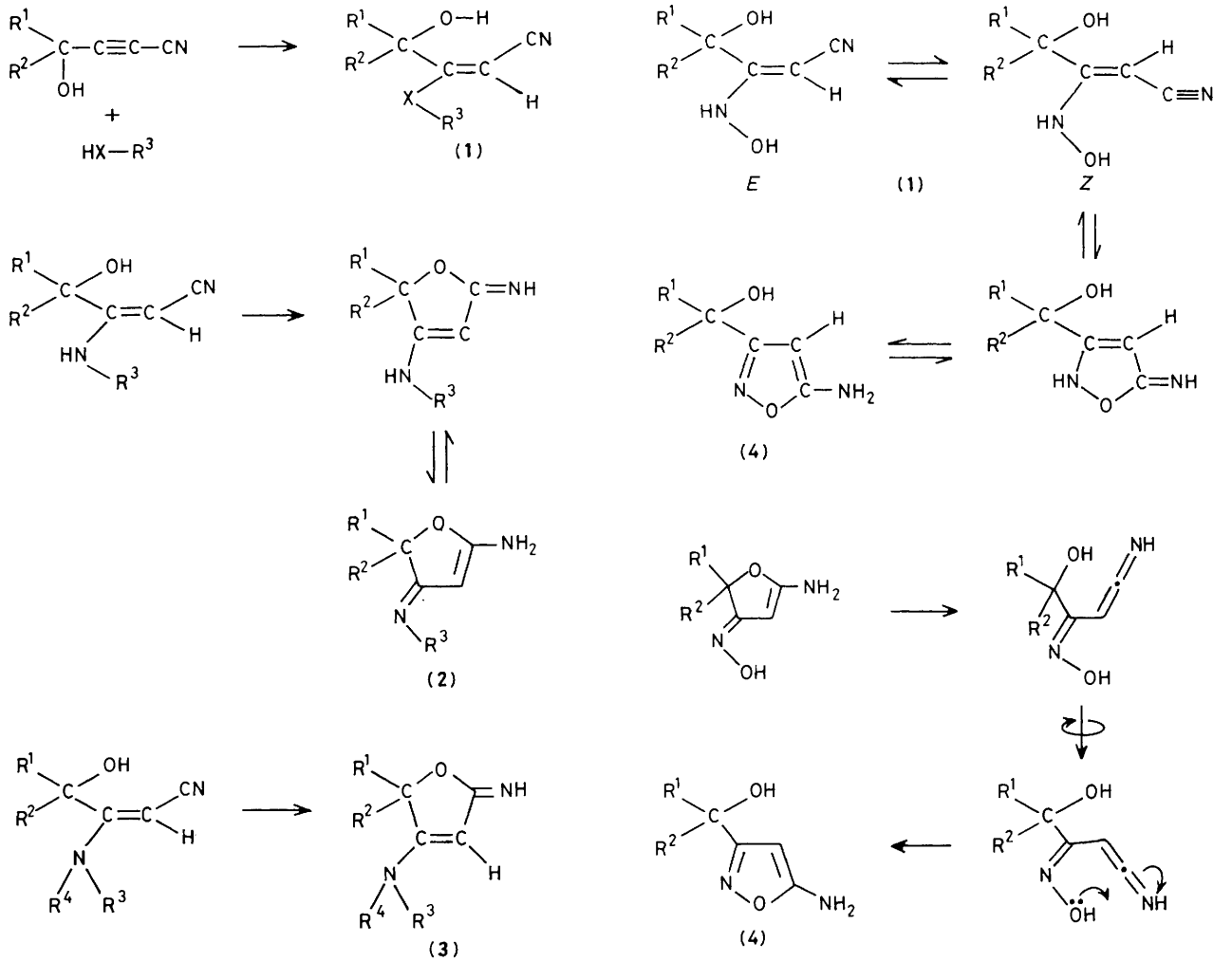
4-Hydroxy-4,4-dialkylbut-2-ynenitriles add primary amines and ring close to give 5-amino-2,2-dialkyl-3-(alkylimino)-2,3-dihydrofurans whereas secondary amines similarly yield 5-imino-2,2-dialkyl-3-(dialkylamino)-2,5-dihydrofurans.

Examples of aminofurans of any description are rare in the literature[1] and general methods of synthesis virtually unknown. We now describe a synthesis of dihydrofurans with nitrogen substituents in the 3- and 5-positions, one of which is of



For compounds (2) and (3): R^1 = Me or Et, R^2 = Et. For compound (2): R^3 = Et, $[CH_2]_2OH$, $[CH_2]_2NH_2$, $[CH_2]_3OH$, $[CH_2]_3NH_2$, $[CH_2]_4OH$, or $[CH_2]_5OH$. For compound (3): R^3 = R^4 = Et.

necessity in the imino form. 4-Hydroxybut-2-ynenitriles[2] add nucleophiles HXR^3 in the Michael position to give conjugated adducts (1) which may be isolated where X = O or S. Where X = NH, or NR^4, the adducts spontaneously cyclise at room temperature to give 5-amino-2,2-dialkyl-3-(alkylimino)-2,3-dihydrofurans (2) and 5-imino-2,2-dialkyl-3-(dialkylamino)-2,5-dihydrofurans (3) in greater than 90% yield.† The addition of the amine was carried out at 0 °C for 3 h after which the reaction mixture was allowed to warm to room temperature for 24 h.

The 5-amino-3-iminodihydrofurans (2) have u.v. absorptions in the range λ_{max} 271—274 nm (ϵ 20 000), whereas the 3-dialkylamino-5-iminodihydrofurans (3) absorb at longer wavelengths: λ_{max} 280—284 (ϵ 22 000—30 000), as expected.[3]

We have recently shown[4] that hydroxylamine, hydrazine, and phenylhydrazine add to 4-hydroxybutynenitriles, with ring closure under reflux to give isoxazoles (4) and pyrazoles but not the corresponding 5-amino-3-iminodihydrofurans. Only *E*-isomers, *e.g.* (1), can give furans whereas only *Z*-isomers can give isoxazoles and pyrazoles.

† All new compounds gave correct analytical and spectral data.

This could be rationalised in two ways as follows. (i) At low temperatures the addition of primary amines to acetylenic nitriles is known to give mainly the *E* isomers which readily ring close to give the dihydrofurans. At higher temperatures (*e.g.* under reflux in ethanol) *E*- and *Z*-forms are readily interconvertible[5] and the thermodynamically more stable isoxazole or pyrazole is formed. (ii) 5-Amino-3-iminodihydrofurans are first formed but decompose under reflux to form the ketimine which, after rotation, cyclises to the isoxazole or pyrazole.

Detailed discussions of spectroscopic data and mechanistic implications will appear elsewhere.

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References

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