Molecular Rearrangements Yielding Δ^2-Pyrazolin-5-ones: Acyloin Rearrangement

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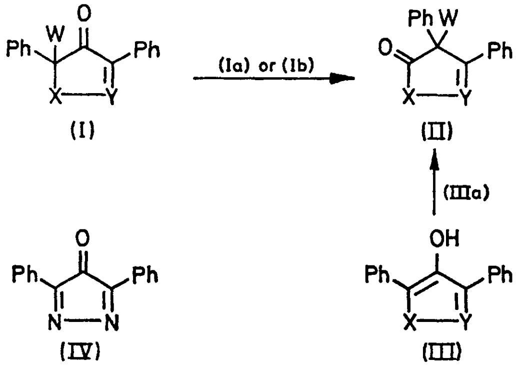
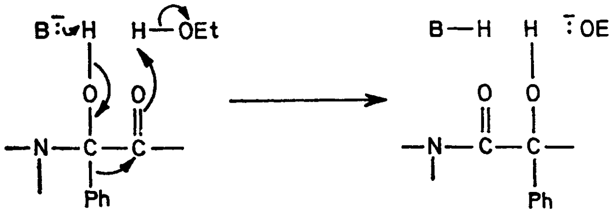
Summary 4-Hydroxy-3,4-diphenyl-Δ^2-pyrazolin-5-one may be synthesized from 5-hydroxy-3,5-diphenyl-Δ^2-pyrazolin-4-one by treatment with ethanolic sodium hydroxide or from 4-hydroxy-3,5-diphenylpyrazole by treatment with methanolic sodium carbonate in the presence of air; in both cases the reaction mechanism is thought to involve an acyloin rearrangement.

TREATMENT of 5-hydroxy-3,5-diphenyl-Δ^2-pyrazolin-4-one (Ia) or its 1-methyl derivative (Ib) with ethanolic sodium hydroxide gives 4-hydroxy-3,4-diphenyl-Δ^2-pyrazolin-5-one (IIa) or (IIb) respectively, quantitatively. This previously unknown type of conversion of a Δ^2-pyrazolin-4-one into a Δ^2-pyrazolin-5-one may be classified as an acyloin rearrangement, and probably proceeds by the mechanism given in the Scheme. The reaction also resembles the latter steps of a benzilic acid rearrangement.



	a	b	c	d	e	f	g	h
X	NH	NMe	NMe	NH	O	O	O	O
Y	N	N	N	N	CPh	CPh	N	N
W	OH	OH	H	OOH	OOH	H	OOH	H

The structures of (IIa) and (IIb) follow from their method of preparation, their spectra [(IIa) $\nu_{\max}$ (Nujol) 1704 cm^{-1}, $\lambda_{\max}$ (95% EtOH) 297 nm (ϵ 13,800); (IIb) $\nu_{\max}$ (Nujol) 1691 cm^{-1}, $\lambda_{\max}$ (95% EtOH) 310 nm (ϵ 13,000)], which resemble those of 1-methyl-3-phenyl-Δ^2-pyrazolin-5-one,[1] and from the alternative synthesis of (IIb) by oxidation of (IIc) with H_2O_2, an established[2] reagent for the hydroxylation of Δ^2-pyrazolin-5-ones.



SCHEME

We also report herein the conversion of 4-hydroxy-3,5-diphenylpyrazole (IIIa) into (IIa) (31%) by treatment with sodium carbonate in methanol in air. The probable reaction sequence involves aerial oxidation of (IIIa) to (Ia) *via* a hydroperoxide intermediate (Id) followed by acyloin-type rearrangement to (IIa). Analogies to the oxidation step exist in the work of Veibel[2] and Jucker[3] who have oxidized certain heterocyclic ketones to α-hydroxy-ketones by air, and there is a very close analogy for a hydroperoxide intermediate in that (Ie) was isolated[4] from the aerial oxidation of the furan (IIIf).† A similar hydroperoxide intermediate (Ig) involved in the decomposition of (*IIIh*) in air has also been proposed by Katritzky and his co-workers.[5]

It is of interest that the conversion of (IIIa) into (Ia) can also proceed in the opposite direction under different conditions, in which case the mechanism has been shown[6] to occur by loss of water to give (IV) which then is reduced by the solvent (ethanol) to give (IIIa).

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† This compound is thought[4] to exist as the keto isomer (If) in the solid state.

[1] A. R. Katritzky and F. W. Maine, *Tetrahedron*, 1964, **20**, 299.
[2] S. Veibel, *Bull. Soc. chim. France*, 1955, 307.
[3] E. Jucker and A. Lindenmann, *Helv. Chim. Acta.*, 1961, **44**, 1249.
[4] E. P. Kohler, F. H. Westheimer, and M. Tishler, *J. Amer. Chem. Soc.*, 1936, **58**, 1933.
[5] G. Bianchi, M. J. Cook, and A. R. Katritzky, *Tetrahedron*, in the press.
[6] M. J. Nye and W. P. Tang, *Canad. J. Chem.*, 1970, **22**, 3563.