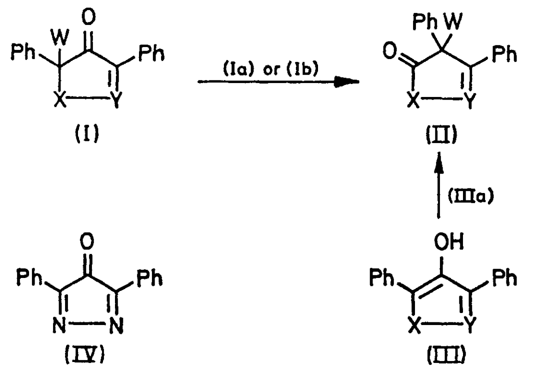
Molecular Rearrangements Yielding Δ^2-Pyrazolin-5-ones: Acyloin Rearrangement

By M. J. NYE* and W. P. TANG

(*Department of Chemistry, University of Guelph, Guelph, Ontario, Canada*)

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.

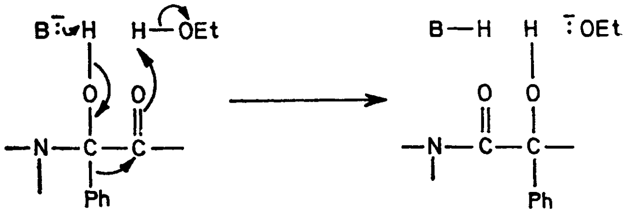


(I) (II) (IV) (III)

	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

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.

The structures of (IIa) and (IIb) follow from their method of preparation, their spectra [(IIa) ν_{max} (Nujol) 1704 cm^{-1}, λ_{max} (95% EtOH) 297 nm (ϵ 13,800); (IIb) ν_{max} (Nujol) 1691 cm^{-1}, λ_{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).

Financial support of the National Research Council of Canada is gratefully acknowledged.

(*Received, August* 19*th*, 1971; *Com.* 1465.)

---

† 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.