

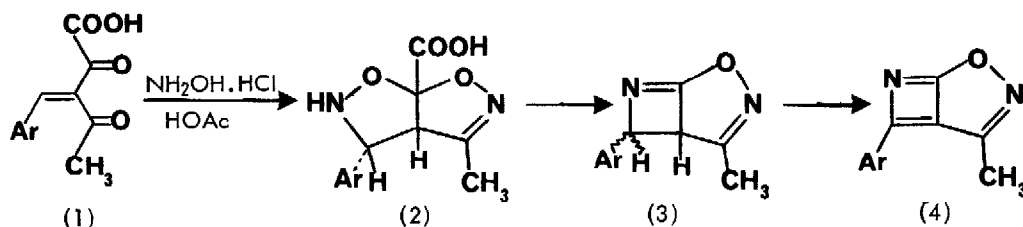
STRUCTURE OF A SUPPOSED AZETO [3,2-d]ISOXAZOLINE :  
A CORRECTION.

C.W. Rees, R.C. Storr and P.J. Whittle

The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147,  
Liverpool L69 3BX.

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Kurihara and Mori<sup>1</sup> have recently reported the reaction of the diketo acid (1) with hydroxylamine hydrochloride in refluxing acetic acid to give the azeto[3,2-d]isoxazoline (4) (Scheme 1).



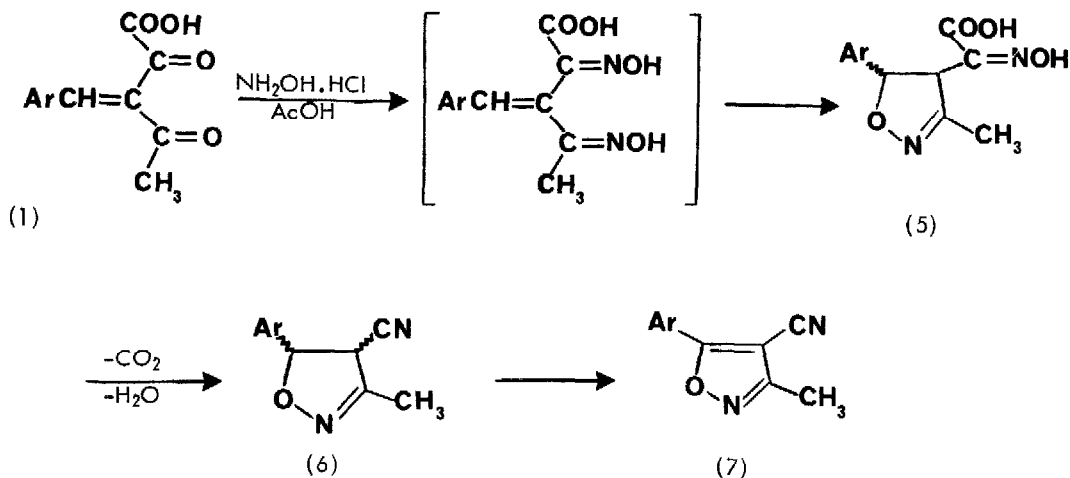
Scheme 1

Ar = *o*-chlorophenyl

This transformation is remarkable for the unprecedented mechanism proposed,<sup>1</sup> for the apparent ease with which the rare azete ring is formed, and particularly for the stability of the product. This stability and the compound's lack of colour are in striking contrast with the very reactive deep red benzazetes,<sup>2</sup> the only other fused azetes known.

We have repeated this reaction and isolated a compound m.p. 70-71<sup>o</sup>, identical with that claimed by Kurihara and Mori to be the azetisoxazoline (4). However this structure and therefore presumably those assigned to the intermediates (2) and (3) involved in its formation are incorrect and we propose the sequence of standard reactions shown in Scheme 2 to explain their observations.

Reaction of the diketoacid (1) with two moles of hydroxylamine would be expected to lead via the dioxime to the isoxazoline (5). This structure accommodates the spectral data reported by the Japanese workers for the initial intermediate in their sequence of reactions to which they assigned structure (2). Moreover the  $\alpha$ -oximinocarboxylic acid function in (5) should be readily transformed into a cyanide group by decarboxylation and dehydration and indeed the later intermediates which were given the *cis* and *trans* isomeric structures (3) by Kurihara and Mori<sup>1</sup> have reported infrared absorptions at 2270 and 2290 cm<sup>-1</sup>. We therefore reassign these compounds as the cyanoisoxazolines (6). The

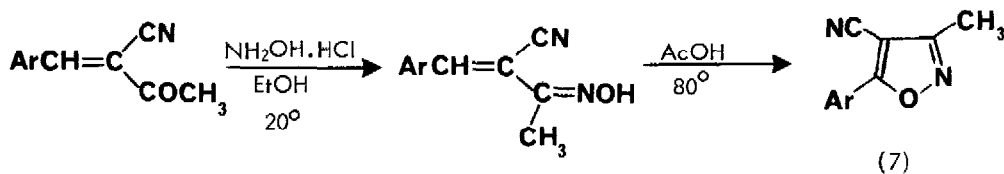


Scheme 2

Ar = *o*-chlorophenyl

coupling constants of 6 and 12 Hz reported for these compounds correspond closely to values reported for similar *trans* and *cis* isoxazolines respectively.<sup>3</sup>

The actual structure of the "azetisoxazoline (4)" is therefore 5-(*o*-chlorophenyl)-4-cyano-3-methylisoxazole (7). This structure accounts for its stability and lack of colour and also for the infrared absorption at  $2250\text{ cm}^{-1}$ , noted but not discussed by the Japanese workers.<sup>1</sup> Its formation by dehydrogenation of the isoxazolines (6) in boiling acetic acid is also entirely reasonable. Finally we have synthesised the isoxazole (7) independently as shown in Scheme 3 and confirmed this structure assignment.



Scheme 3

Ar = *o*-chlorophenyl

## References

1. T. Kurihara and M. Mori, *Tetrahedron Letters*, 1976, 1825.
2. B.M. Adger, C.W. Rees, and R.C. Storr, *J.Chem.Soc.Perkin I*, 1975, 45.
3. R. Sustmann, R. Huisgen and H. Huber, *Chem.Ber.*, 1967, 100, 1802.