

4,5-DIAZAFLUOREN-9-ONE FROM THE OXIDATION OF 1,10-PHENANTHROLINE BY PERMANGANATE

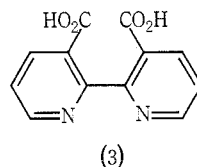
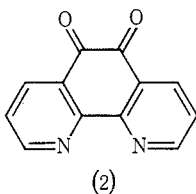
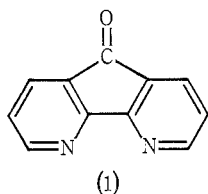
By I. F. ECKHARD* and L. A. SUMMERS*

[Manuscript received 28 June 1973]

Abstract

4,5-Diazafluoren-9-one is a co-product of the oxidation of 1,10-phenanthroline with alkaline potassium permanganate along with 2,2'-bipyridyl-3,3'-dicarboxylic acid.

4,5-Diazafluoren-9-one (1) has hitherto been a difficultly accessible compound, its only synthesis^{1,2} being from the action of aqueous alkali on 1,10-phenanthroline-5,6-quinone (2) by way of a benzylic acid type rearrangement analogous to the formation of fluorenone from phenanthrenequinone.³ 1,10-Phenanthroline-5,6-quinone (2), however, is much less readily prepared than phenanthrenequinone⁴ and is obtained at best in 15% overall yield by a tedious three-step synthesis from 1,10-phenanthroline.⁵ Consequently, the chemistry of 4,5-diazafluoren-9-one (1) has been neglected apart from studies of its reduction,^{1,5} its lack of participation in the Schmidt reaction,⁶ and exploratory chelation experiments.⁵ We now report a facile one-step synthesis of 4,5-diazafluoren-9-one (1) in about 20% yield by the oxidation of 1,10-phenanthroline with alkaline permanganate.



The oxidation of 1,10-phenanthroline by aqueous alkaline potassium permanganate to give 2,2'-bipyridyl-3,3'-dicarboxylic acid (3) has been recorded several times, the acid (3) being the only product described in yields varying from

* Department of Chemistry, University of Newcastle, N.S.W. 2308.

¹ Druey, J., and Schmidt, P., *Helv. chim. Acta*, 1950, **33**, 1080.

² Inglett, G. E., and Smith, G. F., *J. Am. chem. Soc.*, 1950, **72**, 842.

³ Badger, G. M., and Cook, J. W., in "Chemistry of Carbon Compounds," (Ed. E. H. Rodd) Vol. IIIB, p. 1446 (Elsevier: Amsterdam 1956).

⁴ Kermack, W. O., and McKail, J. W., in "Heterocyclic Compounds," (Ed. R. C. Elderfield) Vol. 7, p. 344 (John Wiley: New York 1961).

⁵ Dickeson, J. E., and Summers, L. A., *Aust. J. Chem.*, 1970, **23**, 1023.

⁶ Coombs, M. M., *J. chem. Soc.*, 1958, 4200.

50 to 85%.^{2,7-11} By using conditions similar to those adopted previously, however, we have found that 4,5-diazafluoren-9-one (1) is consistently a co-product of the reaction in about 20% yield along with the acid (3) from which it is easily separated. The formation of (1) is readily explained since the quinone (2), which is presumably an intermediate in the oxidation of 1,10-phenanthroline to give the acid (3), can as well undergo the benzylic acid type rearrangement with the formation of (1) in alkaline reaction conditions.

Experimental

Oxidation of 1,10-Phenanthroline

1,10-Phenanthroline hydrate (20 g) and potassium hydroxide (10 g) were dissolved in water (1.5 l.) and the solution heated to boiling. A hot solution of potassium permanganate (50 g) in water (800 ml) was then added over 15 min. Throughout the addition, the mixture was stirred vigorously and was kept boiling. After further boiling for 10 min the hot mixture was filtered to remove the precipitate of manganese dioxide. The orange filtrate was cooled and extracted with chloroform (3 × 500 ml). The extract was dried (MgSO₄) and the solvent removed under reduced pressure. The pale yellow solid residue (4.0 g) was crystallized from acetone to afford 4,5-diazafluoren-9-one (1), with m.p. and spectroscopic properties (i.r., n.m.r.) identical to those of an authentic sample.⁵ The aqueous solution was evaporated to dryness and the residue treated as described by Smith and Richter.⁹ The acid (3) (20 g), m.p. 264–268° (dec.), was also obtained.

Acknowledgment

This research was supported by a grant from the Ciba-Geigy organization.

⁷ Smith, C. R., *J. Am. chem. Soc.*, 1930, **52**, 397.

⁸ Willink, H. D. T., and Wibaut, J. P., *Recl Trav. chim. Pays-Bas*, 1935, **54**, 275.

⁹ Smith, G. F., and Richter, F. P., "Phenanthroline and Substituted Phenanthroline Indicators," p. 20 (G. F. Smith Chemical Co.: Columbus, Ohio, 1944).

¹⁰ Aziz, D., and Breckenridge, J. G., *Can. J. Res. (B)*, 1950, **28**, 26.

¹¹ Ellis, P., Wilkins, R. G., and Williams, M. J. G., *J. chem. Soc.*, 1956, 3975.