

Graeme Butt and Ronald D. Topsom

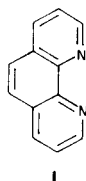
Department of Organic Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083

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The reaction of *o*-phenylenediamine with  $\alpha,\beta$ -unsaturated ketones in the presence of hydrochloric acid smoothly affords alkyl substituted 1,10-phenanthrolines in a one step synthesis.

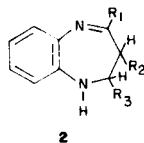
*J. Heterocyclic Chem.*, **18**, 641 (1981).

1,10-Phenanthrolines can be synthesized by the Skraup reaction on 8-aminoquinolines, which themselves are prepared by a Skraup reaction on 2-nitroanilines and subsequent reduction of the nitroquinoline obtained. The synthesis of 1,10-phenanthroline itself **1**, has been achieved (1,2) in one step by the double Skraup reaction between *o*-phenylenediamine and glycerol under various conditions.



Several syntheses have also been reported (3,4) of substituted 1,10-phenanthrolines by the double Skraup reaction but these gave lower yields and were less reproducible than with the parent compound. Our attempts with such syntheses using either sulfuric or phosphoric acid gave viscous products from which small yields of difficult to purify product were obtained.

The use of Doebner-Miller reaction conditions does not appear to have been reported. Here the *o*-phenylenediamine is reacted with an  $\alpha\beta$ -unsaturated ketone in the presence of concentrated hydrochloric acid alone. In the reaction between aniline and crotonaldehyde, it has been suggested (5) that a Schiff's base by-product acts as the oxidising agent for the reduction of the intermediate hydroquinoline. We suggest that in the case of reactions with the *o*-phenylenediamine, a possible oxidising agent is the substituted benzo-diazacycloheptadiene **2**, formed



from the diamine and one mole of the unsaturated ketone. The presence of the reduced form of **2**, the benzodiazepine, in crude reaction mixtures was confirmed by <sup>1</sup>H nmr. The spectra were compared with that of an authentic sample synthesised by the reaction (6) between *o*-phenylenediamine and methyl isopropenyl ketone to yield **2** and subsequent reduction with Adams catalyst in absolute ethanol. The maximum yield of phenanthroline by this

Doebner-Miller synthesis is thus 50% based on *o*-phenylenediamine. The reaction however proceeds smoothly to give easily obtainable products in reasonable yields. The 2,4,7,9- and 3,4,7,8-tetramethyl and 4,7-dimethyl-1,10-phenanthrolines have been prepared by this method.

An attempt to synthesise 2,9-dimethyl-1,10-phenanthroline from *o*-phenylenediamine and crotonaldehyde, under the same conditions, was unsuccessful even though crotonaldehyde reacts with 8-amino-2-methylquinoline to give this product under the normal Skraup conditions. The product of the attempted double ring closure was apparently 7-methyl-2,3-benzo-1,4-diazacycloheptadiene (2,4) (**2**, R<sub>1</sub> = R<sub>2</sub> = H, R<sub>3</sub> = Me) (6).

#### EXPERIMENTAL (7)

##### General Procedure.

The *o*-phenylenediamine (0.06 mole) was heated to reflux in concentrated hydrochloric acid (50 ml.). To this stirred solution was added the unsaturated ketone (or  $\beta$ -hydroxy ketone) (25 ml.) over a period of 45 minutes. Heating was then continued at 80° for 16 hours. The reaction mixture was cooled, diluted with water (25 ml.), and then extracted with chloroform. Basification of the aqueous extract with "880" ammonia gave an oil which was extracted into chloroform. After evaporation of the chloroform, the residue was dissolved in the minimum volume of dry methanol and the hydrochloride precipitated by saturation with dry hydrogen chloride gas. The hydrochloride was washed with a cold mixture of methanol-ether and after drying afforded the phenanthroline by neutralisation of an aqueous solution with ammonia.

##### 1,10-Phenanthrolines.

4,7-Dimethyl-1,10-phenanthroline was obtained as above in 37% yield from methyl vinyl ketone, m.p. 188-190 [lit. (5) m.p. 188-190°]; pmr: 2.85 (s), 7.40 (d), 7.95 (s), 8.95 (d). 2,4,7,9-Tetramethyl-1,10-phenanthroline was similarly obtained in 28% yield from 3-penten-2-one (8), m.p. 195-197 [lit. (5) m.p. 199-200°]; pmr: 2.78 (s), 2.92 (s), 7.30 (s), 7.90 (s). 3,4,7,8-Tetramethyl-1,10-phenanthroline was similarly prepared in 48% yield, m.p. 270-274° [lit. (5), 284-285°]; pmr: 2.50 (s), 2.62 (s), 7.95 (s), 8.92 (s).

#### REFERENCES AND NOTES

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