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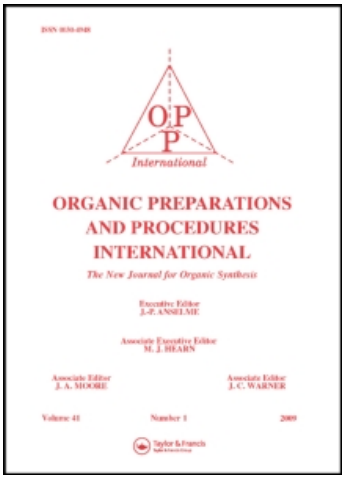


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# N-METHYLTETRAHYDROQUINOLINE AND N-METHYLINDOLINE

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ORGANIC PREPARATIONS AND PROCEDURES 1(2), 77-79 (1969)

# N-METHYLTETRAHYDROQUINOLINE AND N-METHYLINDOLINE

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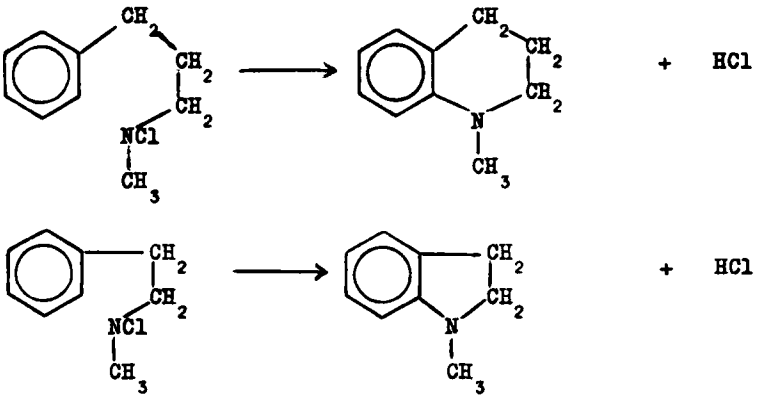

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The present procedure describes the preparation of N-methyltetrahydroquinoline (kairolin) and N-methylindoline.These are the first examples of intramolecular, free radical, aromatic amination and have been reported in a preliminary note [1].The starting materials are easily available and the experimental conditions are simple; yield is high for N-methyltetrahydroquinoline,lower for N-methylindoline owing to the side reaction:

$$C_6H_5-CH_2-CH_2-NCl-CH_3 \longrightarrow C_6H_5-CH_2Cl + CH_2=N-CH_3$$

The known methods for the preparation of kairolin are: the reduction of N-methylquinolinium iodide with tin and hydrochloric acid[2] or the methylation of tetrahydroquinoline by dimethyl sulfate[3] and for N-methylindoline the reduction of N-methylindole with tin and hydrochloric acid[4].

## Experimental

Methyl-3-phenylpropyl-N-chloroamine. A mixture of 40 g of 1-bromo-3-phenylpropane[5a] ( from hydrocinnamyl alcohol), 200 ml of 30% methylamine aqueous solution and 300 ml of ethanol is heated with stirring at 70° for 10 hrs. in 1-l autoclave.Solvent and methylamine are distilled, the residue is dissolved in 10% hydrochloric acid and extracted with ether to remove non basic products. The aqueous layer is basified with 10% sodium hydroxide solution and extracted with ether. The ethereal extract is dried over anhydrous sodium sulfate.After removal of the solvent, the residue is distilled to give 23.2 g of methyl-3-phenyl propylamine, bp 87-8° (3mm)[5b].

A solution of 23.2 g of methyl-3-phenylpropylamine in 60 ml of water and 15.5 ml of concentrated hydrochloric acid is added dropwise with vigorous stirring at 0° to a mixture of 105 ml of 14% sodium hypochlorite aqueous solution and 150 ml of ether. The ethereal layer is separated and the aqueous layer is further extracted two times with 100-ml portions of ether. The combined ethereal extracts are washed successively with 5% sulfuric acid solution, water, 5% sodium hydroxide solution, and again with water. After the ethereal solution has been dried over sodium sulfate, the solvent is removed under reduced pressure at room temperature and 27.6 g of viscous product remains. Iodometric titration indicates 98% of N-chloroamine (93%). The product is used without further purification.

N-Methyltetrahydroquinoline (kairolin). In 50 ml of concentrated sulfuric acid and 10 ml of water 11.6 g of methyl-3-phenylpropyl-N-chloroamine is dissolved at 0°. 5 g of finely powdered heptahydrate ferrous sulfate is added with stirring and nitrogen flushing. The mixture is kept at 5-8° for 30 minutes and for additional 20 minutes at room temperature. The acid solution is then poured into 100 g of ice and 300 ml of water,the diluted solution is extracted with ether(only traces of product are obtained after removal of the solvent), basified with 30%



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sodium hydroxide solution and the liberated oil is extracted with ether. The residue from the ethereal solution is distilled to give 7.6 g of kairolin (81%),bp 80-1° (0.4 mm),identical in all respects with an authentic sample[2,3].

N-Methylindoline. The preparation of the methyl-2-phenylethyl-N-chloroamine is carried out as in the preceding case from methyl-2-phenylethylamine[6]. The crude chloroamine (97%) is used without further purification. To a solution of 17 g of N-chloroamine in 130 ml of concentrated sulfuric acid is added with stirring and under nitrogen a total of 8 g of finely powdered heptahydrate ferrous sulfate in portions over a period of 1 hour, the temperature being maintained around -5° during the addition.The mixture is kept for an additional 15 minutes at room temperature, then poured onto 200 g of ice and 500 ml of water. The diluted solution is extracted with ether; after removal of the solvent the residue is distilled to give 5.6 g of benzyl chloride (44%). The acid solution is basified with 30% sodium hydroxide solution and extracted with ether; the solvent is removed and the residue is distilled to give 3.7 g of N-methylindoline (27%), bp 98-9° (20 mm).The product[4] and its picrate[7] (mp 164°) are identical with authentic samples.

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