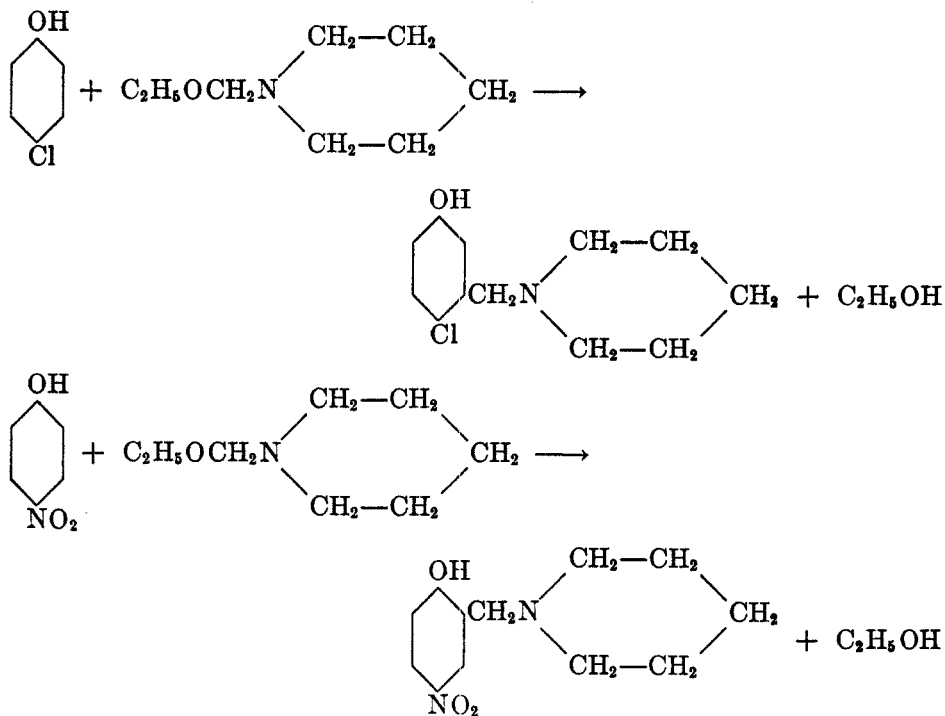


CONDENSATION OF AMINO ETHER WITH *p*-CHLOROPHENOL AND
p-NITROPHENOL¹

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In a previous paper the author, in collaboration with Dr. Heou-feo Tseou, reported a series of condensation reactions of piperidinomethyl ethyl ether with naphthols, cresols, and naphthylamines (1). In every case alcohol is eliminated, which is formed by the combination of the ethoxyl group of the ether and the reactive hydrogen atom in the benzene nucleus. The present paper is a continuation of the preceding one. The condensation of the amino ether with compounds containing active hydrogen atoms is extended to negatively substituted phenols. With *p*-chlorophenol and *p*-nitrophenol the results of the condensation reactions can be represented by the equations:



The lack of electric facilities renders the estimation of carbon and hydrogen content of the reaction products impossible, and only the nitrogen content is

¹ Received through the U. S. Department of State. While no proof of structure of the products described is offered, this article is published as supplementing the previous communication on the same subject. Editor.

determined by the Kjeldahl method. The estimation of molecular weights by the Rast camphor method has also been carried out and good checks are observed.

EXPERIMENTAL

1-Hydroxy-3-piperidinomethyl-4-chlorobenzene. Nine grams of *p*-chlorophenol was slowly added to 10 g. of piperidinomethyl ethyl ether in a 50-cc. flask. The mixture was then heated on a water-bath under a reflux condenser protected from moisture by a calcium chloride tube. At the end of two hours the flask was allowed to cool and solid separated out. It was powdered and extracted repeatedly with a 5% sodium hydroxide solution to remove any unreacted phenol, filtered under suction, washed until free from alkali, and dried in a desiccator. It was then dissolved in 20 cc. of hot toluene, from which the solid separated as plate crystals on cooling. It was filtered, washed with toluene, and dried by suction. The yield amounts to 70% of the theoretical. It melts at 55°. It is basic in nature, soluble in most organic solvents, and insoluble in water.

Anal. Calc'd for $C_{12}H_{16}ClNO$: N, 6.21; Mol. wt., 225.6.

Found: N, 6.03; Mol. wt., 218.6. (A 0.0103-g. sample in 0.0785 g. of camphor gave a depression in m.p. of 24°)

1-Hydroxy-2-piperidinomethyl-4-nitrobenzene. Ten grams of *p*-nitrophenol was added to 10 g. of piperidinomethyl ethyl ether in a 50-cc. flask. The mixture was refluxed on the water-bath for four hours and allowed to cool. After standing for two days, solid separated out. It was ground into powder and extracted with a 5% sodium hydroxide solution to remove any unreacted *p*-nitrophenol, filtered, and washed until free from alkali. It was dried in a desiccator and then recrystallized from acetone. Light yellow needles were obtained, m.p. 134°. It is soluble in acetone, chloroform, alcohol, benzene, and toluene.

Anal. Calc'd for $C_{12}H_{16}N_2O_3$: N, 13.19; Mol. wt., 212.2.

Found: N, 12.95; Mol. wt., 203. (A 0.0087-g. sample in 0.0926 g. of camphor gave a depression in m.p. of 18.5°.)

SUMMARY

1. Piperidinomethyl ethyl ether reacts with *p*-chlorophenol and *p*-nitrophenol to form 1-hydroxy-3-piperidinomethyl-4-chlorobenzene and 1-hydroxy-2-piperidinomethyl-4-nitrobenzene respectively.

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REFERENCE

- (1) TSEOU AND YANG, *J. Org. Chem.*, **4**, 123 (1939).