ENCLOSURE (B) 10

PREPARATION OF PURE a-METHYLNAPHTHALENE

by

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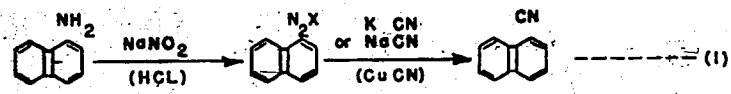
SUMMARY

a-Naphthylamine was transformed by the diazo reaction to a-Naphthonitrile and then reduced with hydrogen to a-Methylnaphthalene in the presence of reduced nickel at 250-290°C. The yield of pure a-methylnaphthalene was approximately 21% by weight.

I. INTRODUCTION

The lack of standard fuel for Diesel engines had become serious since 1941, and, consequently, the study of the following method of preparation was undertaken. The reaction was as follows:



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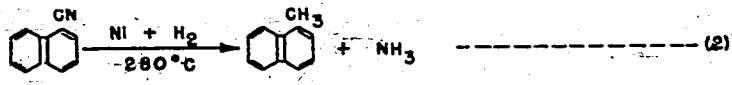

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II. DETAILED DESCRIPTION

A. Preparation of a-Naphthonitrile (Reaction 1)

To 14.3gm a-naphthylamine in 270cc water containing 10cc concentrated HCl was added 15cc concentrated HCl and 135gm of broken ice.

Then 35cc of an aqueous solution containing 7gm $NaNO_2$ was added dropwise with stirring.

The product was treated at 80°C with 100cc of an aqueous solution containing 25gm $CuSO_4.5H_2O$ and 28gm NaCN. The mixture was steam distilled and yellow, and oily, crude a-naphthonitrile was obtained. The crude a-naphthonitrile was extracted with ether, dried with $CaCl_2$, and then redistilled. The yield of pure a-naphthonitrile was 5.9gm (corresponding to approximately 40% by weight). The properties of the a-naphthonitrile formed were as follows:

B.P., 295-297°C, M.P., 35-36°C.

B. Preparation of a-Methylnaphthalene (Reaction 2)

The a-naphthonitrile was reduced in the presence of reduced nickel (prepared from nickel nitrite by ignition at about 300°C and by reduction with hydrogen at 300°C), at 270-280°C in a silica reaction tube (18mm X 1000mm). The colorless, oily product obtained (yield about 80% by weight) was distilled at atmospheric pressure into the following fractions:

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1st fraction : 233 - 240°C

2nd fraction : 240 - 250°C

3rd fraction : 250 - 285°C

The first fraction consisted mainly of a-methyl naphthalene, 3rd fraction was mainly a-naphthonitrile, and the second fraction was a mixture of a-methyl naphthalene and a-naphthonitrile.

The yield of crude a-methylnaphthalene (from first and second fractions) was about 78% by weight of a-naphthonitrile.

C. Purification of a-Methylnaphthalene

An alcoholic solution of the first and second fractions was added to the same amount of picric acid. The a-methylnaphthalene picrate was crystallized by cooling from the alcoholic solution.

The picrate, (m.p. 140-141°C) was decomposed with concentrated NH_4OH (about 28%) to a-methyl naphthalene by warming, and, after steam distillation of a-methyl naphthalene, was extracted with ether, dried with calcium chloride, and then redistilled.

The yield of a-methylnaphthalene

from 1st and 2nd fractions: approx. 84% by weight.
from a-naphthonitrile: approx. 52% by weight.
from a-naphthylamine: approx. 21% by weight.

The properties of pure a-methylnaphthalene prepared from a-naphthylamine were as follows:

B.P. (760mm Hg) : 239 - 240°C

n_D^{25} : 1.6153

n_D^{20} : 1.6173

m.p. of picrate : 140 - 141°C

Complete data relative to these experiments are not available.