NOTES

3,4-Dimethylaniline from Fenchone Using the Schmidt Reaction

BY FREDERIC R. BENSON, LAWRENCE W. HARTZEL AND WALTER L. SAVELL

One of the newer methods for the preparation of 3,4-dimethylaniline which is convenient for laboratory use is that developed by Zaugg.[1] His procedure involves conversion of fenchone to 3,4-dimethylacetophenone, isolation as the oxime, Beckmann rearrangement and subsequent hydrolysis.

In order to reduce the time required for this synthesis, investigation of an alternative method has been made. The modification developed in this laboratory consists of subjecting the crude 3,4-dimethylacetophenone obtained from fenchone to the Schmidt reaction, followed by hydrolysis of the crude 3,4-dimethylacetanilide. The present procedure eliminates the need for isolation of dimethylacetophenone as the oxime and the time consuming Beckman rearrangement. In the method described below the benzene solution of crude dimethylacetophenone, obtained according to Zaugg, is treated directly with hydrazoic acid in benzene to form crude dimethylacetanilide. Hydrolysis and distillation affords a fairly pure product which can be recrystallized to form 3,4-dimethylaniline of good purity. The over-all yield from fenchone of completely purified material is 21%.

A by-product of the Schmidt reaction was obtained in small amounts from one run. This is probably 1-(3′,4′-dimethylphenyl-5-methyltetrazole, although it is possible that it may be the isomer, 1 methyl-5-(3′,4′-dimethylphenyl)-tetrazole.

Experimental

A solution of 126 g. of crude 3,4-dimethylacetophenone in 585 ml. of dry benzene was prepared from 200 g. of commercial fenchone as described by Zaugg.[1]

To a 100-ml. portion of this solution (containing 21.4 g. of 3,4-dimethylacetophenone), mixed with 30 ml. of concentrated sulfuric acid was added with stirring 191 ml. of a 4.1% hydrazoic acid solution in benzene. The temperature was maintained at 38–41° during the addition, which took approximately fifty minutes. After all the solution had been added, the mixture was allowed to stir for five minutes longer, then cooled and poured into a separatory funnel. The sulfuric acid layer was poured into 400 ml. of water and made alkaline with ammonium hydroxide (120 ml.). The yellow oil which separated solidified on cooling. The precipitate was filtered off, washed once with water and refluxed for two hours with 75 ml. of concentrated hydrochloric acid. The solution was poured into 250 ml. of water, extracted with ether, and made alkaline with 6 *N* sodium hydroxide. The alkaline solution was extracted with ether, the ether solution dried over potassium hydroxide and distilled to yield 7.0 g. of crude 3,4-dimethylaniline, b. p. 138–143° (55 mm.), m. p. 47°. On recrystallization from light petroleum ether 5.7 g. of pure 3,4-dimethylaniline was obtained (21% yield from fenchone), m. p. 50–51°. Purity by titration with perchloric acid in glacial acetic acid, 99.1%.

In another experiment conducted as described above, except that the temperature of the Schmidt reaction was maintained at 10–15°, the ether extract of the acid hydrolysis product was allowed to evaporate. The dark, gummy crystals obtained were dissolved in boiling water and treated with charcoal. On filtration and cooling, white crystals separated. A second recrystallization from water afforded 100 mg. of white glistening crystals melting at 111–111.5°.

Anal. Calcd. for $C_{10}H_{12}N_4$: C, 63.80; H, 6.43; N, 29.77. Found: C, 63.95; H, 6.25; N (Dumas), 29.95.

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(1) Zaugg, THIS JOURNAL, **67**, 1861 (1945).

Synthesis of 1-Aminofluorene

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In view of the widespread current interest in the unusual carcinogenic properties of 2-aminofluorene,[2] we wish to report at this time the preparation of the isomeric 1-aminofluorene. The synthesis consisted essentially of the oxidation of fluoranthene to fluorenone-1-carboxylic acid, reduction of the latter to fluorene-1-carboxylic acid and replacement of the carboxyl group by an amino group.

Experimental[3]

Fluorenone-1-carboxylic Acid. I.—Fluoranthene was purchased from the Reilly Tar and Chemical Company. It had a melting point of 107.0–109.4°. Careful chromatography on alumina–celite and determination of the ultraviolet absorption spectra of the fractions showed the presence of a small quantity of pyrene and the probable presence of phenanthrene as impurities. Sulfuric acid extraction of a tetrachloroethane solution of the fluoranthene,[4] resulted in a spectrographically pure fluoranthene, m. p. 110.4–111.2°. On a large scale, the purification was more conveniently achieved by heating fluoranthene at 200° with sodium for half an hour. The fluoranthene was distilled, b. p. 180–90° (4–5 mm.) and the distillate crystallized from ethanol whereby colorless material, m. p. 110.4–111.4°, was obtained. This fluoranthene (95 g.) was oxidized with chromic acid in acetic acid according to the directions of Fieser and Seligman.[5] The procedure for the isolation of the product was simplified as follows:

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(2) Wilson, De Eds and Cox, *Cancer Research*, **1**, 595 (1941); Bielschowsky, *Brit. med. Bull.*, **4**, 382 (1947); Pinck, *Ann. New York Acad. Sci.*, **50**, 1 (1948).

(3) All melting points corrected.

(4) Compare the purification of chrysene: Fieser, "Chemistry of Natural Products Related to Phenanthrene," 2nd edition, Reinhold Publishing Corp., New York, N. Y., 1937, p. 19.

(5) Fieser and Seligman, THIS JOURNAL, **57**, 2174 (1935).