

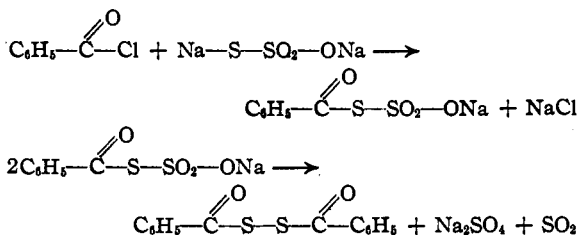
The Reaction of Benzoyl Chloride with Sodium Thiosulfate

BY HARRY E. WESTLAKE, JR., AND GREGG DOUGHERTY

The formation of sodium alkyl thiosulfates, or Bunte salts, from alkyl halides and thiosulfate is well known,¹ but the corresponding reaction between thiosulfate and an acyl halide appears not to have been reported.

When an aqueous-alcoholic solution of benzoyl chloride and sodium thiosulfate is allowed to stand, benzoyl disulfide crystallizes therefrom and the solution smells strongly of sulfur dioxide. More benzoyl disulfide can be isolated from the mother liquor along with benzoic acid. The mother liquor also contains chloride, sulfate, and thiosulfate.

Probably the first step in the formation of the disulfide is analogous to the Bunte reaction; the unstable product then decomposes at room temperature in the same way in which Bunte salts do on heating.



Since benzoyl chloride reacts not only with thiosulfate but also with ethanol and with the water which is necessary to dissolve the thiosulfate, only 60% of the benzoyl groups are recovered in the form of the disulfide; the rest of the benzoyl group appears in the form of benzoic acid and ethyl benzoate.

p-Nitrobenzoyl chloride and 3,5-dinitrobenzoyl chloride are too reactive to give the disulfides, as they react with the alcohol used as a solvent, or, when aqueous dioxane is employed, with the water present.

Experimental

A solution of 24.8 g. of sodium thiosulfate in 30 cc. of water was mixed with a solution of 12 cc. of benzoyl chloride in 60 cc. of alcohol. After standing for forty-eight hours, the disulfide was filtered off. Evaporation of a good part of the alcohol caused the precipitation of more disulfide and of benzoic acid. Washing with sodium carbonate solution removed the acid. The crude disulfide (m. p. 128°) was recrystallized twice from ether, giving a melting point of 134–135°. Fifty-eight and four-tenths per cent. of the benzoyl groups were recovered as disulfide, 29% as benzoic acid, and the remainder as an oil which, in an experiment using a large excess of benzoyl chloride, was identified as ethyl benzoate (b. p. 212–213°).

Anal. Calcd. for C₁₄H₁₀O₂S₂: S, 23.33. Obs.: S, 23.30.

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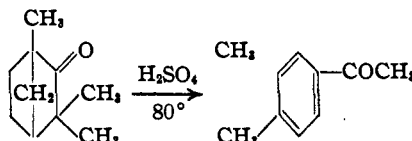
(1) Bunte, *Ber.*, **7**, 646 (1874); Purgotti, *Gazz. chim. ital.*, **20**, 24 (1890); **22**, 416 (1892); *et al.*

3,4-Dimethylaniline from Fenchone

BY HAROLD E. ZAUGG

Published methods¹ for the synthesis of the riboflavin intermediate, 3,4-dimethylaniline, employ either toluene, *o*-xylene or derivatives of them as starting materials. The present paper describes a method starting from commercial fenchone which is obtained by oxidation of fenchyl alcohol, one of the constituents of pine oil.

The method is based on the interesting dehydrogenation rearrangement reaction of fenchone first observed by Marsh.² He reported a



yield of 70% for this reaction but, using a variety of conditions in the present work, the best yields obtained from the commercial fenchone were only 40–45%. Pure 3,4-dimethylacetophenone could be obtained by careful fractionation, but it was found more advantageous to prepare the oxime³ from the crude product. A Beckmann rearrangement of this oxime gave 3,4-dimethylacetanilide³ which on hydrolysis resulted in pure 3,4-dimethylaniline in a 25% over-all yield from fenchone.

Experimental

To 1600 cc. of concentrated sulfuric acid heated to 80° was added with vigorous stirring over a period of fifteen minutes, 400 g. of commercial fenchone [n_D^{20} 1.4607; $[\alpha]_D^{20} + 7.60^\circ$ (without solvent)]. The temperature was not allowed to rise above 110° and was kept between 100 and 110° for ten minutes after completion of addition. The hot solution was then poured into six liters of ice water, and extracted with benzene. Two more identical runs were carried out and the combined benzene extracts (from 1200 g. of fenchone) were steam-distilled. Distillation of the benzene from the organic layer of the steam-distillate gave 750 g. of residual deep yellow oil containing the 3,4-dimethylacetophenone.

To a solution of this oil (750 g.) in two liters of 95% ethanol was added with stirring 672 g. of solid (NH₄OH)₂·H₂SO₄ followed by a cold solution of 912 g. of potassium hydroxide in 2400 cc. of 50% ethanol. Stirring was continued without external heating for twenty-four hours and then 780 cc. of concentrated hydrochloric acid was added slowly with stirring and cooling. Precipitated inorganic salts were filtered with suction and the filtrate was boiled with Norit for ten to fifteen minutes and filtered by gravity. The temperature of the filtrate was adjusted to 50–55° and just enough 95% ethanol was added to make a homogeneous solution (no undissolved oil) at this temperature. Any inorganic salt precipitated at this point was filtered off, the filtrate (50–55°) was seeded with some oxime and allowed to stand at room temperature overnight. Refrigeration for several hours followed by filtration gave 451 g. (35% yield from fenchone) of crystalline 3,4-dimethylacetophenone oxime, $m. p.$ 82–85°.

(1) Beilstein, Vol. XII, p. 1103; Suppl. Vol. XII, p. 480; Wisnisky and Ansbacher, *This Journal*, **63**, 2532 (1941); U. S. Patent 2,347,652; Weinmayr, U. S. Patent 2,373,438; Barclay, Burawoy and Thomson, *Nature*, **151**, 615 (1943); British Patents 539,747 and 545,382; *J. Chem. Soc.*, 109 (1944); Cripps and Hey, *ibid.*, 14 (1943); Karrer *et al.*, *Helv. Chim. Acta*, **18**, 1435 (1935).

(2) Marsh, *J. Chem. Soc.*, **75**, 1058 (1899).

(3) Armstrong and Kipping, *ibid.*, **63**, 75 (1893).