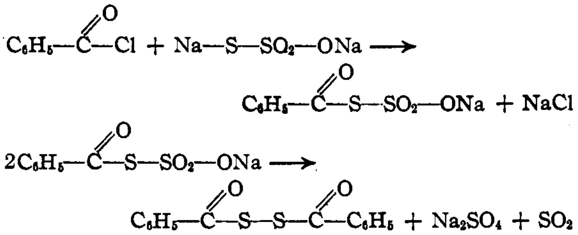
The Reaction of Benzoyl Chloride with Sodium Thiosulfate

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.



$$C_6H_5—\overset{O}{\overset{\|}{C}}—Cl + Na—S—SO_2—ONa \longrightarrow C_6H_5—\overset{O}{\overset{\|}{C}}—S—SO_2—ONa + NaCl$$

$$2C_6H_5—\overset{O}{\overset{\|}{C}}—S—SO_2—ONa \longrightarrow C_6H_5—\overset{O}{\overset{\|}{C}}—S—S—\overset{O}{\overset{\|}{C}}—C_6H_5 + Na_2SO_4 + SO_2$$

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 $C_{14}H_{10}O_2S_2$: S, 23.33. Obs.: S, 23.30.

Frick Chemical Laboratory
Princeton University
Princeton, N. J.

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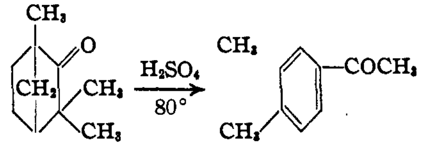
[1] Bunte, *Ber.*, **7**, 646 (1874); Purgotti, *Gazz. chim. ital.*, **20**, 24 (1890); **22**, 416 (1892); *et al.*

3,4-Dimethylaniline from Fenchone

By Harold E. Zaugg

Published methods[1] 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 oxime[3] from the crude product. A Beckmann rearrangement of this oxime gave 3,4-dimethylacetanilide[3] 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^{25}_{D} 1.4607; $[\alpha]^{24}_{D}$ + 7.60° (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 $(NH_4OH)_2·H_2SO_4$ 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-dimethylacetophenonoxime,[3] m. p. 82–85°.

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[1] Beilstein, Vol. XII, p. 1103; Suppl. Vol. XII, p. 480; Wisansky 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).

A solution of this oxime (451 g.) in a mixture of 1080 cc. of glacial acetic acid and 455 cc. of acetic anhydride was cooled in ice and saturated with gaseous hydrogen chloride. The solution was then allowed to stand at 40° for sixty to seventy hours, cooled in ice and filtered (sintered glass!) with suction, using a rubber dam to squeeze out as much of the liquid as possible. The filter cake was immediately mixed with 820 cc. of concentrated hydrochloric acid and refluxed until a homogeneous solution was obtained (two hours). The 3,4-dimethylaniline hydrochloride could be obtained merely by crystallization from the cooled reaction mixture. However, to obtain the free base, the reaction mixture was made alkaline with aqueous sodium hydroxide, extracted with ether, dried and distilled. In this manner there was obtained 238 g. (25% yield from fenchone) of pure 3,4-dimethylaniline, b. p. 132–134° (45 mm.); m. p. 50–51°

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ABBOTT LABORATORIES
NORTH CHICAGO, ILLINOIS
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NEW COMPOUNDS

p-Di-(β-chloro-*t*-butyl)-benzene

Although the preparation of (β-chloro-*t*-butyl)-benzene by the reaction of benzene with methallyl chloride in the presence of sulfuric acid[1] or hydrogen fluoride[2] has been described, the formation of a crystalline di-substituted compound analogous to *p*-di-*t*-butylbenzene has not hitherto been reported.

A solution of 300 g. (3.3 moles) of methallyl chloride in 300 g. (3.8 moles) of benzene was added during two hours to a well-stirred mixture of 500 g. (6.4 moles) of benzene and 400 g. of 96% sulfuric acid at 0–5°. After an additional one-half hour of stirring, the upper layer was separated from the 433 g. of lower layer, washed with water, dried, and distilled under reduced pressure. Neophyl chloride (*i. e.*, (β-chloro-*t*-butyl)-benzene) boiling at 90–91° at 9 mm. mercury pressure, n^{20}_{D} 1.5250, was obtained in 67% of the theoretical yield. The higher-boiling residue (55 g.) was a dark brown oil which became partly crystalline (long white needles) on standing. The mixture of oil and crystals was cooled in an ice-salt-bath and then filtered through a sintered glass plate. Recrystallization of the solid from alcohol yielded 11 g. (2.6% of the theoretical) of *p*-di-(β-chloro-*t*-butyl)-benzene, thick needles, m. p. 54.5–55°.

Anal. Calcd. for $C_{14}H_{20}Cl_2$: Cl, 27.36. Found: Cl, 27.36. No attempt was made to recover more of the compound from the filtrates.

The orientation of the chloroalkyl groups was proved by oxidizing 1 g. of the compound by refluxing it for twenty hours with a solution of 5 g. of sodium dichromate and 5 cc. of concentrated sulfuric acid in 100 cc. of water. Terephthalic acid was obtained; its identity was confirmed by means of its dimethyl ester, m. p. 140°.

Calcott, Tinker and Weinmayr,[2] using hydrogen fluoride as catalyst, obtained a 66% yield of neophyl chloride and a 20% yield of a liquid product, boiling at 140° at 4 mm., which they considered to be "di-(1′-chloro)-*t*-butylbenzene." Their product may have been a different isomer. More probably it was impure owing to loss of hydrogen chloride during distillation; the product contained only 25.6% chlorine.

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[1] F. C. Whitmore, C. A. Weisberger and A. C. Shabica, Jr., THIS JOURNAL, **65**, 1469 (1943).

[2] W. S. Calcott, J. M. Tinker and V. Weinmayr, *ibid.*, **61**, 1010 (1939).

RESEARCH LABORATORIES
UNIVERSAL OIL PRODUCTS COMPANY
RIVERSIDE, ILLINOIS
LOUIS SCHMERLING
V. N. IPATIEFF
RECEIVED JULY 20, 1945

t-Butylphthalimide[1]

t-Butylurea, m. p., 175–180°, was prepared in 86% yield by the method of Harvey and Caplan.[2] An intimate mixture of *t*-butylurea (35 g., 0.3 mole) and phthalic anhydride (100 g., 0.67 mole) is placed in a large (1000 cc.) container which is then plunged into a bath at 200°. After the initial vigorous effervescence subsides (ten minutes) the temperature of the bath is raised to 240° and maintained there for five minutes. Rapid heating is essential; the reaction is usually over in fifteen minutes. The cooled product is partially dissolved in alcohol (100 cc.) and the mixture is made alkaline (litmus) by addition of aqueous sodium carbonate. The mixture is diluted with water to a volume of 1 liter, the solid is transferred to a Büchner funnel, pressed as dry as possible, and then warmed with petroleum ether (500 cc., b. p. 60–68°). The hot mixture is filtered and, after the filtrate is separated from the water layer (if any appears), it is cooled to room temperature. Any insoluble material is removed, and the clear filtrate is concentrated by distillation to about one-third of its original volume and set aside in a refrigerator. The crystalline material is filtered with suction and pressed as dry as possible. It weighs 43.5 g. and melts at 59–60° By concentration of the filtrate, a further 3 g. may be obtained; this also melts at 59–60°. The total yield, 46.5 g., is 76%.

Anal. Calcd. for $C_{12}H_{13}O_2N$: C, 70.93; H, 6.40 Found: C, 70.95; H, 6.26.

This procedure is based upon the general procedure of Manske for conversion of alkyl ureas to phthalimides.[3] When an alcoholic solution of the phthalimide is hydrolyzed by action of hydrazine hydrate[4] and then acidified, *t*-butylamine hydrochloride can be obtained in 89% yield. The combination of the three steps from *t*-butyl alcohol to *t*-butylamine *via* the urea and phthalimide constitutes the best method for preparation of *t*-butylamine.

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[1] The work described herein was done under contract with the Office of Scientific Research and Development, which assumes no responsibility for the accuracy of the statements herein.

[2] Harvey and Caplan, U. S. Patent 2,247,495, July 1, 1941; *Chem. Abs.*, **35**, 6267 (1941).

[3] Manske, THIS JOURNAL, **51**, 1202 (1929); see also Tingle and Brenton, *ibid.*, **32**, 116 (1910).

[4] Ing and Manske, *J. Chem. Soc.*, 2348 (1926).

SCHOOL OF CHEMISTRY
INSTITUTE OF TECHNOLOGY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINN.
LEE IRVIN SMITH
OLIVER H. EMERSON
RECEIVED AUGUST 29, 1945

p-Aminobenzanilide and Derivatives

In the course of other investigations a considerable amount of *p*-aminobenzanilide was needed. Its preparation was previously described by several authors.[1,2,3] Rivier and Kunz[3] reported a yield of 70% of *p*-aminobenzanilide by reduction of *p*-nitrobenzanilide with stannous chloride and hydrochloric acid. Their method has been repeated, resulting in a yield of 90%. Other reducing agents, such as tin and hydrochloric acid, zinc and acetic acid, zinc and hydrochloric acid, or Raney nickel in alcohol,

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[1] *Friedlander*, **4**, 752 (1895).

[2] H. Kupferberg, *J. prakt. Chem.*, [2] **16**, 444 (1877).

[3] H. Rivier and S. Kunz, *Helv. Chim. Acta*, **15**, 376 (1932).