

[THIRTY-SECOND CONTRIBUTION FROM THE COLOR LABORATORY, U. S. BUREAU OF CHEMISTRY.]

SYNTHESES OF *s*-XYLIDINE.

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It is well known that *s*-xylidine is the only one of the isomeric xylidines absent from commercial xylidine. It has been prepared from *m*,*4*-xylidine by successive steps involving acetylation, nitration, saponification, deamination and reduction. As a starting point in the preparation of derivatives of quinoline, it became necessary to secure *s*-xylidine absolutely free from its isomers. Since, in its preparation from *m*,*4*-xylidine, the utmost care might fail to insure this, a synthesis starting with mesitylene was undertaken. Mesitylene was oxidized to mesitylenic acid, changed to the amide and finally converted to *s*-xylidine by means of Hofmann's reaction. The synthesis from *m*,*4*-xylidine, although consisting of as many steps as involved in the foregoing process, is more satisfactory for the preparation of considerable amounts of material on account of the consistently higher yields. We found it possible to eliminate one operation from the procedure given¹ for this synthesis.

Experimental Part.

I. The Preparation of *s*-Xylidine from Mesitylene.

Mesitylene was prepared in the usual manner by the condensation of acetone with the aid of sulfuric acid. We found that the directions of Orndorff and Young² gave the most satisfactory results. After steam distillation, the crude mesitylene was washed with alkali and water, dried over calcium chloride and distilled. To remove sulfur compounds the distillate was refluxed with sodium and redistilled. The portion which distilled up to 175° was subjected to fractional distillation, and the fraction boiling from 160° to 167° was oxidized to mesitylenic acid.³

Mesitylenic Acid.—Fifty g. of mesitylene, 80 cc. of conc. nitric acid (sp. gr. 1.47) and 240 cc. of water were heated under a reflux condenser for 22 hours on a sand bath. The solution was then cooled in ice and the precipitated solid removed by filtration. The crude mass was dissolved in alkali, and the alkaline solution extracted with ether. The filtrate was also rendered alkaline and extracted with ether. From these ether extracts 10 g. of mesitylene was recovered. The alkaline solution containing the mesitylenic acid was acidified with hydrochloric acid, filtered, and the precipitate subjected to steam distillation. To remove nitro com-

¹ C. Willgerodt and F. Schmierer, *Ber.*, **38**, 1472 (1905).

² W. R. Orndorff and S. W. Young, *Am. Chem. J.*, **15**, 249 (1893).

³ R. Fittig, *Ann.*, **141**, 144 (1867). In this article the proportions of acid and mesitylene are not given, and the concentration of nitric acid used is higher than we have found desirable.

pounds, the product obtained by steam distillation was heated under a reflux condenser for several hours with tin and conc. hydrochloric acid, after which the undissolved solid was recrystallized from 50% alcohol. The yield was 9.7 g.

Mesitylenic Amide.—The conversion of mesitylenic acid to the acid chloride¹ was brought about by warming it gently with phosphorus pentachloride. After the phosphorus oxychloride had been distilled, the reaction mixture was poured into ice-cold conc. ammonia. The amide separated by filtration was washed with dil. ammonia, and recrystallized from water.

Conversion of Mesitylenic Amide with *s*-Xylidine.—The amide was converted to *s*-xylidine by means of sodium hypobromite. To a solution of 95 g. of sodium hydroxide in 400 cc. of water and cooled to 5°, 90 g. of bromine was added slowly. Forty g. of the amide was made into a paste with a 10% solution of sodium hydroxide. While the hypobromite solution was stirred, the amide was added slowly; finally the mixture was distilled with steam. The distillate was extracted with ether, the extract dried over calcium chloride and distilled. The yield of *s*-xylidine was 19 g.

The amine was converted into the acetyl derivative by heating it for half an hour on the steam-bath with an equal weight of acetic anhydride. The product was poured into water, the *s*-acet-xylide collected and recrystallized 6 times from 95% alcohol. The melting-point was 139.6° to 140.2°.

II. The Preparation of *s*-Xylidine from *m*-4-Xylidine.

To obtain *m*,4-xylidine, from commercial xylidine, it was treated with glacial acetic acid and the mixture allowed to stand for 24 to 48 hours.² The acetate which formed was filtered and recrystallized from ether. Acetylation was effected with acetic anhydride in the usual manner and the product was recrystallized from alcohol. The acet-nitro-xylide was prepared by adding the acet-xylide in small portions to "red" fuming nitric acid³ (sp. gr. 1.55 to 1.57) while the mixture was stirred and the temperature was kept between 0° and 5°. After the addition of all the acet-xylide, the reaction mixture was poured into ice-water, the precipitated acet-nitro-xylide immediately filtered, washed well with water and recrystallized from alcohol.

We have found it possible to prepare the nitro-xylene directly from nitro-acet-xylide. For this purpose 50 g. of nitro-acet-xylide was added

¹ R. Fittig and W. H. Brueckner, *Ann.*, **147**, 47 (1868).

² W. R. Hodgkinson and L. Limpach, *J. Chem. Soc.*, **77**, 65 (1900).

³ Nitrous fumes were generated by dropping conc. sulfuric acid into a concentrated solution of sodium nitrite and were passed into c. p. fuming nitric acid (sp. gr. 1.50) to the point of saturation.

to 50 g. of sulfuric acid (sp. gr. 1.84) and heated at 125° for 15 minutes. The reaction product was poured into a mixture of 300 g. of 95% ethyl alcohol and 150 g. of conc. sulfuric acid, cooled to 5°, and then diazotized with 30 g. of sodium nitrite in conc. water soln. Copper powder was added to catalyze the reaction, after which the solution was distilled with steam. The yield of the nitro-xylene was 35 g. The nitro-xylene was recrystallized from alcohol.

To a solution of 150 g. of stannous chloride in 200 g. of hydrochloric acid (sp. gr. 1.19), the nitro compound was added in small portions. Heat was necessary to start the reaction. After the addition of all the nitro-xylene, the reaction mixture was heated on the steam bath for an hour, diluted, cooled, made alkaline, and distilled with steam. The yield of *s*-xylydine was 15 g.

The acetyl derivative was prepared and purified as already described for the *s*-acet-xylide from mesitylene. The melting-point was 139.6° to 140.2°. Samples of the 2 preparations and of their mixture were attached to the same thermometer and all 3 softened and melted within 0.1° of one another.

Optical Properties (by Edgar T. Wherry). When studied by the immersion method under the microscope, these preparations have identical properties, as follows.

Habit: plates, rather irregular in outline, and often overlapping. System: apparently monoclinic, with clinopinacoid prominent.

Refractive indices (D): $\alpha = 1.45$, β -indeterminate, $\gamma = 1.69$, $\gamma - \alpha = 0.24$.

As seen in polarized light, nicols crossed: Colors around 2nd order; the overlapping and stepped variation in thickness of the plates producing striking mosaic effects; elongation negative; extinction angle (on edges most frequently present) 12°.

In convergent polarized light, nicols crossed: Shows no definite interference figures, the optic normal being apparently perpendicular to the surfaces of the plates.

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PARA CYMENE AS A SOLVENT.

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Until the discovery was made that spruce turpentine, a by-product of the manufacture of spruce pulp by the sulfite process, consisted largely of *p*-cymene this hydrocarbon was not available as an ordinary solvent. The price is now so much lower that it should be placed on the regular list of solvents.

Cymene assumes an important position as a solvent because it is a hydrocarbon of high boiling-point and, where possible, is to be preferred to such colored solvents as aniline or nitrobenzene, or an ill-smelling solvent such as pyridine. Cymene boils at 176.5° and in point of availability comes next to xylene in the benzene series. It should be useful