

The nitro-anilide was hydrolyzed in alcoholic potassium hydroxide from which water precipitated the 2-nitro-4-*n*-butylaniline. The amino group was removed by the reduction of the diazonium sulfate<sup>9</sup> and the resulting *m*-nitro-*n*-butylbenzene reduced as previously noted; b. p., 133° (18 mm.). The melting point of its benzoate (67–68°) checked that previously recorded (68°).

The phenol, *m*-*n*-butylphenol, was prepared and purified as in the case of the other isomers; b. p. 247–249° (758 mm.);  $d_4^{20}$ , 0.974.

*Anal.* Subs., 0.1853: CO<sub>2</sub>, 0.5397; H<sub>2</sub>O, 0.1554. Calcd. for C<sub>10</sub>H<sub>14</sub>O: C, 80.0; H, 9.3. Found: C, 79.4; H, 9.3.

### Summary

Various derivatives of *n*-butylbenzene have been synthesized including the three isomeric phenols. The phenols are powerful disinfectants.

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[CONTRIBUTION FROM THE LABORATORIES OF THE MONSANTO CHEMICAL WORKS]

## THE PHYSICAL PROPERTIES OF SALICYLALDEHYDE

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In connection with some work on salicylaldehyde, the writers recently had occasion to prepare a highly purified sample of this material. We found that the physical properties were quite different from those given in the most recent literature and for this reason our results are reported here in detail.

As is frequently the case with compounds of this nature, the data given in the literature are quite conflicting. Walden<sup>1</sup> gives the crystallizing points as –10 to –11°, and in a later publication the density is given as  $d_4^{25} = 1.15390$ . Perkin<sup>2</sup> gives the boiling point under 760 mm. as 197° (corr.), and the density at 20° as 1.1495. Jaeger<sup>3</sup> purified the commercial aldehyde by fractionation, and obtained a boiling point of 192.5°, crystallizing point of –7° and density as  $d_4^{25} = 1.1525$ . The International Critical Tables (1926) give the melting point as –7°, the boiling point as 196.5° and the density as 1.167.

In preparing our purified product we started with a commercial sample of aldehyde, which already had a crystallizing point of –7°. This material was carefully fractionated in vacuum, using a column about four feet long packed with 1/8-inch Raschig rings. The middle fraction of the aldehyde obtained by this fractionation had a crystallizing point of 1°. This fraction was further purified by the following treatment.

Three hundred g. of the fraction with 1° crystallizing point was slowly

<sup>9</sup> Bigelow, *THIS JOURNAL*, **41**, 1559 (1919).

<sup>1</sup> Walden, *Z. physik. Chem.*, **55**, 220 (1906).

<sup>2</sup> Perkin, *J. Chem. Soc.*, **68**, 1200 (1895).

<sup>3</sup> Jaeger, *Z. anorg. allgem. Chem.*, **101**, 142 (1917).

added, with agitation, to an alcoholic solution of sodium bisulfite. A slight excess of bisulfite was used. In a short time a voluminous yellow precipitate of the bisulfite compound separated. The precipitate was filtered off and washed with alcohol and ether, after which it became nearly white in color. The precipitate was then recrystallized once from 10% alcohol, after which the bisulfite compound was obtained as pure white crystals.

An attempt was made to hydrolyze the bisulfite compound with sodium carbonate. However, when the bisulfite compound was mixed with sodium carbonate solution, an abundant yellowish-white precipitate was formed. This precipitate was filtered off, sludged up with water and treated with hydrochloric acid until acid to congo red. There was considerable effervescence and the aldehyde separated as a yellowish oil. The oil was fractionated under vacuum and the middle fraction was refractionated under atmospheric pressure.

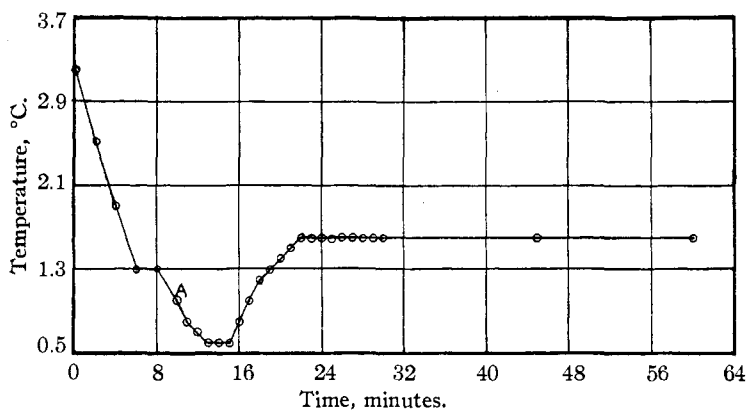


Fig. 1.—Cooling curve of salicylaldehyde (seeded at A).

The purified product so obtained had the following properties: boiling point under 751 mm., 196.4–196.5°; boiling point under 25 mm., 93°; crystallizing point, 1.6°;  $d_{20}^{20} = 1.1690$ . The temperatures were measured with thermometers calibrated by the Bureau of Standards and the density was taken in a bottle type pycnometer.

The crystallizing point was determined by slowly cooling 30 g. of the product and observing the temperature as crystallization proceeded. To prevent excessive supercooling, the sample was seeded when the temperature was about 1° below the crystallizing point. The time-temperature data are given in Fig. 1.

The constancy of the crystallizing point as crystallization proceeded shows that our preparation was quite pure.

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