[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VERMONT]

DERIVATIVES OF NORMAL BUTYLBENZENE[1]

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During a study of the effect on the disinfectant power of phenol of various groups in the three isomeric positions on the ring it was necessary to prepare a number of derivatives of *n*-butylbenzene as intermediates in the preparation of the three *n*-butylphenols.

Preliminary examination of these phenols[2] has shown that they have a high phenol coefficient and also that there was an apparent difference in the coefficients, the activity decreasing in the order *meta, ortho, para*. Later, more detailed examination[3] has shown that factors not taken into consideration during the preliminary tests influence these values so markedly that the order given above cannot be considered as valid.

A later paper will deal with this problem.

Johnson and Lane have pointed out[4] that in the case of methyl-, ethyl-, *n*-propyl-, and *n*-butylresorcinol the disinfectant power is a function of the weight of the side chain. More recently Leonard[5] reported that this holds only up through the hexyl group and that certain branched chains are less effective than the corresponding normal chains. In a later paper it will be shown that other factors are of even greater influence than weight in determining the disinfectant power of a phenol.

Experimental Part

Normal butylbenzene was prepared by the condensation of *n*-butyl bromide and bromobenzene with sodium.[6]

Nitration.—Five hundred g. of butylbenzene was added slowly to 500 g. of concd. sulfuric acid at 0°. To this mixture was added with stirring the nitrating acid (375 g. of concd. nitric acid and 787 g. of concd. sulfuric acid) over a period of five hours at 5–12°. External cooling was necessary. After 30 minutes at this temperature the emulsion was poured over 1.5 kg. of ice. The oil was removed and the aqueous portion extracted with benzene, the combined material washed with carbonate solution and dried over sodium sulfate. The removal of the benzene completed the drying.

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[1] The field of the effect of hydrocarbon side chains on the disinfectant power of phenols was opened by Johnson and Lane and it is to these investigators that the writers are indebted for the opening of the field to them. A preliminary version of this manuscript was submitted on September 21, 1925, but publication was withheld by request.

[2] The writers are indebted to Professor B. F. Lutman of this University for this examination.

[3] A bacteriological study involving the use of these phenols is now being made by Professor L. F. Rettger of Yale University.

[4] Johnson and Lane, THIS JOURNAL, **43**, 348 (1921).

[5] Leonard, *J. Urol.*, **12**, 585 (1924).

[6] Read and Foster, THIS JOURNAL, **48**, 1606 (1926).

Fractionation through a jacketed Clarke-Rahrs column gave a fore run of butylbenzene, then (1) a fraction boiling at 131–133° (15 mm.), followed by a small intermediate fraction at 133–143° (15 mm.), then (2) a fraction boiling at 143–145° (15 mm.). Fraction 1 yielded on oxidation an acid melting at 146°, and was therefore *o*-nitro-*n*-butylbenzene; d_4^{20}, 1.071.

Anal. Subs. 0.4281, 0.4129: 24.45 cc., 23.80 cc. of 0.01106 *N* acid. Calcd. for $C_{10}H_{13}NO_2$: N, 7.8. Found: 7.2, 7.3.

Fraction 2 yielded on oxidation an acid melting at 238–240°, and was, therefore *p*-nitro-*n*-butylbenzene; d_4^{20}, 1.065.

Anal. Subs., 0.4006, 0.4074: 23.1 cc., 24.2 cc. of 0.01106 *N* acid. Calcd. for $C_{10}H_{13}NO_2$: N, 7.8. Found: 7.3, 7.5.

Nitration of the butylbenzene in glacial acetic acid with fuming nitric acid dissolved in glacial acetic acid (in the ratio 1:1:2:1) at 10° gave a 70% yield of the *para* compound with only very small amounts of the *ortho*.

Reduction.—The reduction was carried out by the usual procedure with tin and hydrochloric acid, and the product recovered by benzene extraction of the alkaline sludge, steam vacuum distillation of the extract, and distillation through a jacketed Clarke-Rahrs column. Ordinary steam distillation can be used in place of the extraction and steam vacuum distillation but the amine comes over very slowly.

o-n-Butylaniline; b. p. 122–125° (12 mm.); d_4^{20}, 0.953.

Anal. Subs., 0.1556, 0.1626: 11.8 cc., 12.5 cc. of 0.01106 *N* acid. Calcd. for $C_{10}H_{15}N$: N, 9.4. Found: 9.6, 9.7.

The hydrochloride was prepared, crystallizing from benzene as white scales; m. p. 137°.

Anal. Subs., 0.1462, 0.1504: AgCl, 0.1136, 0.1171. Calcd. for $C_{10}H_{16}ClN$: Cl, 19.12. Found: 19.22, 19.26.

p-n-Butylaniline; b. p. 133–134° (14 mm.); d_4^{20}, 0.945. This compound has been prepared previously[7] but its boiling point under reduced pressure was not recorded.

Replacement of Amino by Hydroxyl Group.—This was accomplished by the usual procedure of diazotization of the sulfate of the amine and slow elevation of the temperature to 60°. The phenol was extracted with benzene, and purified through the sodium salt which forms intensely red solutions in water.

p-n-Butylphenol; b. p. 121–123° (9 mm.); 746–750° (751 mm.), d_4^{20}, 0.978. This compound has been described previously.[7] The *p*-nitrobenzoate crystallizes in yellow needles from alcohol; m. p. 67–68°.

Anal. Subs., 0.3160: 12.0 cc. of 0.01106 *N* acid. Calcd. for $C_{17}H_{17}NO_4$: N, 4.7. Found: 4.9.

o-n-Butylphenol; b. p. 113–115° (14 mm.); 234–237° (760 mm.); d_4^{20}, 0.975.

Anal. Subs., 0.1890: CO_2, 0.5532; H_2O, 0.1566. Calcd. for $C_{10}H_{14}O$: C, 80.0; H, 9.3. Found: C, 79.8; H, 9.2.

m-n-Butylphenol.—*p*-Butylaniline was acetylated with glacial acetic acid and crystallized from benzene-petroleum ether; m. p. 104°, corresponding with that found by Reilly and Hickenbottom. This anilide was nitrated[8] and the nitro derivative (2-nitro-4-*n*-butylacetanilide) crystallized from 50% alcohol as fine, yellow needles in radiating clusters.

Anal. Subs., 0.1560: 14.3 cc. of 0.01106 *N* acid. Calcd. for $C_{12}H_{16}N_2O_3$: N, 11.9. Found: 11.6.

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[7] Reilly and Hickenbottom, *J. Chem. Soc.*, **117**, 103 (1920).

[8] Noyes, "Organic Chemistry," H. Holt and Company, New York, **1903**.

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[9] 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_2, 0.5397; H_2O, 0.1554. Calcd. for $C_{10}H_{14}O$: 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[1] gives the crystallizing points as −10 to −11°, and in a later publication the density is given as $d_{4°}^{25°}$ = 1.15390. Perkin[2] gives the boiling point under 760 mm. as 197° (corr.), and the density at 20° as 1.1495. Jaeger[3] 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

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[9] Bigelow, THIS JOURNAL, **41**, 1559 (1919).

[1] Walden, *Z. physik. Chem.*, **55**, 220 (1906).

[2] Perkin, *J. Chem. Soc.*, **68**, 1200 (1895).

[3] Jaeger, *Z. anorg. allgem. Chem.*, **101**, 142 (1917).