

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF VERMONT]

DERIVATIVES OF SECONDARY BUTYLBENZENE<sup>1</sup>

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During a study of some relationships of the germicidal activity of certain phenols<sup>2</sup> it became necessary to prepare a number of derivatives of secondary butylbenzene. It has seemed desirable to report this work separately.

## Experimental

Normal butyl alcohol was dehydrated by heated aluminum oxide in the furnace described previously<sup>3</sup> and the butylene condensed and dissolved in kerosene. This was extracted twice in the cold with 50% sulfuric acid to remove the isobutylene that might have been formed. No attempt was made to prove the presence of this isomer.

The butylene was distilled out of the kerosene through a cooled refluxing column, dried by passing through a calcium chloride column, and converted into secondary butylbenzene by the usual procedure; 1818 g. of butylene yielded 2150 g. of *sec.*-butylbenzene, b. p. 172–175°.

This was nitrated as in the case of *n*-butylbenzene and fractionated through a packed (glass tubes 5 × 10 mm.) refluxing column one meter long.

*o*-Nitro-*sec.*-butylbenzene, b. p. 123–126° (12 mm.),  $d_4^{20}$  1.065. *Anal.* Calcd.: N, 7.8. Found: N, 8.2.

*p*-Nitro-*sec.*-butylbenzene, b. p. 142–144° (12 mm.),  $d_4^{20}$  1.065. *Anal.* Calcd.: N, 7.8. Found: N, 8.2.

The nitro derivatives were reduced by tin and hydrochloric acid and by iron and hydrochloric acid.

*o*-Amino-*sec.*-butylbenzene, b. p. 120–122° (16 mm.),  $d_4^{20}$  0.957. *Anal.* Calcd.: N, 9.4. Found: N, 9.2.

*p*-Amino-*sec.*-butylbenzene, b. p. 130–133° (26 mm.).<sup>4</sup>

The benzoate melted at 130° as reported previously.<sup>4</sup>

The corresponding phenols were prepared from the amines by the usual procedure, the previously described para derivative melting at 61–62°; previous value 59–60°.

*o*-*Sec.*-butylphenol, b. p. 116° (21 mm.), 227–228° (corr.). *Anal.* Calcd.: C, 80.0; H, 9.3. Found: C, 79.6; H, 9.2.

These two phenols were later prepared by condensing *sec.*-butyl alcohol with phenol in the presence of zinc chloride. The phenol mixture so obtained was freed from non-phenolic material by extraction of the alkali solution with ligroin. Repeated fractionation through a 90-cm. packed column heated to about 200° produced the separation of the two isomers: *o*-*sec.*-butylphenol, 227–228°, and *p*-*sec.*-butylphenol, 240–242°, m. p. 61–62°. A later report will give the details of the condensation of the secondary and tertiary alcohols with phenols.

The *p*-*sec.*-butylaniline was acetylated with glacial acetic acid and the anilide air dried. This was nitrated<sup>5</sup> at 12°, and the product hydrolyzed. The crude nitro-

<sup>1</sup> Read and Mullin, *THIS JOURNAL*, **50**, 1763 (1928).

<sup>2</sup> A report of a portion of this is included in a paper by Rettger, Plastridge and Valley, *Centr. Bakt., Parasitenk.*, 287 (1929).

<sup>3</sup> Read and Prisley, *THIS JOURNAL*, **46**, 1512 (1924).

<sup>4</sup> Reilly and Hickenbotton, *J. Chem. Soc.*, **117**, 103 (1920).

<sup>5</sup> Noyes "Organic Chemistry," H. Holt and Company, New York, 1903.

aniline was converted into the *m*-nitro-*sec*-butylbenzene in the usual manner by diazotization in alcohol:<sup>6</sup> *m*-nitro-*sec*-butylbenzene; b. p. 132–134° (19 mm.). *Anal.* Calcd.: N, 7.8. Found: N, 8.0. This was reduced to the amine with tin and hydrochloric acid: *m*-*sec*-butylaniline, b. p. 120° (18 mm.). *Anal.* Calcd.: N, 9.4. Found: N, 8.8.

<sup>6</sup> Bigelow, *THIS JOURNAL*, **41**, 1559 (1919).

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## SOME SUBSTITUTED PHENOLS AND GERMICIDAL ACTIVITY

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An increasing interest in the germicidal activity of substituted phenols led the writers to undertake a study of the relation between this property and the nature of certain substituted groups as well as their positions on the ring.

Since it was found, in the case of the alkylresorcinols<sup>1,2,3</sup> that the weight of the hydrocarbon side chain determined the degree of germicidal activity, it seemed desirable to study the influence of weight alone by comparing the effects of differing groups of approximately the same molecular weight. For this purpose a series of substituted phenols, containing oxygen in the side chain, was prepared and compared with normal, secondary and tertiary butylphenols. The activity of a number of other phenols is also included for comparative purposes.

Also in order to study the influence of position in the ring, the ortho, meta and para isomers were prepared in several instances. These compounds and their phenol coefficients are listed in the accompanying table.

### Experimental

The preparation of the three normal butylphenols<sup>4</sup> and of the ortho and para secondary butylphenols from secondary butylbenzene<sup>5</sup> has been reported previously.

The various ethers were all prepared by the usual procedure. One mole of sodium was dissolved in about 15 moles of absolute alcohol and one mole of the phenol added to the solution. The solution was refluxed on a steam-bath while one mole of the alkyl chloride or chlorohydrin was added during one hour. Heating was continued during two hours. The precipitated salt was filtered off and the alcohol removed under reduced pressure. The

<sup>1</sup> Johnson and Lane, *THIS JOURNAL*, **43**, 348 (1921).

<sup>2</sup> Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926).

<sup>3</sup> See also the work of Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930), which appeared since the work here described was completed.

<sup>4</sup> Read and Mullin, *THIS JOURNAL*, **50**, 1763 (1928).

<sup>5</sup> Read, Hewitt and Pike, *ibid.*, **54**, 1194 (1932).