flux condenser, and gas inlet tube. Dry hydrogen chloride gas was passed into the rapidly stirred mixture for two and one-half hours with an increase in weight of 3.5 g. The temperature was kept between 65 and 70° during the addition. The mixture was washed with hydrochloric acid, water, sodium carbonate solution, again with water, and dried over calcium chloride. Distillation gave two fractions. The high boiling fraction had the following constants: b. p. 68–71° at 49 mm.; $n^{25}\text{D}$ 1.4369; d^{25} 1.0137. Literature values[7] for 2,2-dichlorohexane are: b. p. 68° at 49 mm.; $n^{25}\text{D}$ 1.4353; d^{25} 1.0150. The lower boiling fraction had the following constants: b. p. 117–118°; $n^{25}\text{D}$ 1.4300; d^{25} 0.8937; % chlorine, obsd. 26.15; calcd. 29.89. Permanganate oxidation of this material, as described above, produced *n*-butyric acid whose *p*-bromophenacyl ester was identical with that obtained from an authentic sample.

Isomerization of 1,2-Hexadiene.—Ten grams of 1,2-hexadiene was added to 5 g. of sodium under 100 ml. of moist ether and heated to gentle reflux. Eight grams of water was added, a few drops at a time, over a period of two days. Distillation of the ether layer gave about 2 g. of 1-hexyne, whose mercury derivative[11] melted correctly at 96–97°. Three grams of unreacted 1,2-hexadiene was also recovered.

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Summary

1. 1,2-Hexadiene has been prepared by a three-step synthesis starting with *n*-butyraldehyde and sodium acetylide.

2. The reactions of 1,2-hexadiene are very similar to those undergone by the higher acetylenes and give products corresponding to those secured from either 1- or 2-hexyne.

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[11] Vaughn, THIS JOURNAL, **55**, 3453 (1933).

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

o-t-Butylphenol

BY HAROLD HART

In several recent papers[1,2,3] the effect of bulky groups in the ortho positions upon the spectra and reactivity of phenols has been investigated. It is to be noted, however, that in nearly all of the compounds studied, there was a substituent present in the para as well as the ortho position. Since both electrical and steric factors probably play a role in the effect of ortho substituents, it was desirable to have available for study compounds which contain groups in the ortho position only. It was the purpose of this investigation to devise a method of synthesizing such compounds. *o-t*-Butylphenol was selected as a typical example.

o-t-Butylphenol has been reported previously by several workers.[4,5,6] Direct alkylation of phenol, however, is not satisfactory for the laboratory synthesis of *o-t*-butylphenol.[5,7]

p-Bromophenol was alkylated with isobutylene using a procedure similar to that of Stillson, Sawyer and Hunt.[3] The 4-bromo-2-*t*-butylphenol obtained was reduced to *o-t*-butylphenol with Raney nickel–aluminum alloy and aqueous alkali.[8] This reduction, carried out in alkaline solution yields essentially no rearranged product. The over-all yield of *o-t*-butylphenol was 68%. Some of its physical and chemical properties are described in the Experimental Part.

The ultraviolet absorption spectrum of *o-t*-butylphenol in cyclohexane was determined and is shown in Fig. 1, with the spectra of phenol and *p-t*-butylphenol for comparison. It is seen that the spectrum of *o-t*-butylphenol is very similar to that of phenol, with peaks of almost identical extinction coefficients at 271 and 278 mμ and an incipient peak at 265 mμ corresponding to the peak at that wave length in the phenol spectrum. The peaks are somewhat broader, as one might expect, for the substituted phenol. *p-t*-Butylphenol has a spectrum which is almost identical with that of the ortho isomer, with the exception that the entire spectrum is shifted about 6 mμ toward the red (peaks at 277 and 283 mμ and an incipient peak at 271 mμ). The spectrum of *p*-cresol as determined by Wolf and Herold[9] shows a similar shift toward the red, whereas *o*-cresol has its maxima at almost

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[1] N. D. Coggeshall, THIS JOURNAL, **69**, 1620 (1947).

[2] N. D. Coggeshall and E. M. Lang, *ibid.*, **70**, 3283 (1948).

[3] G. H. Stillson, D. W. Sawyer and C. K. Hunt, *ibid.*, **67**, 303 (1945).

[4] G. Vavon and N. Zaharia, *Compt. rend.*, **187**, 347 (1928).

[5] R. P. Perkins, A. J. Dietzler and J. T. Lundquist, U. S. Patent 1,972,599 (1934).

[6] W. A. Pardee and W. Weinrich, *Ind. Eng. Chem.*, **36**, 595 (1944).

[7] A. E. Chichibabin, *Bull. soc. chim.*, [5] **2**, 497–520 (1935); *Compt. rend.*, **198**, 1239 (1934). Chichibabin reported the synthesis of certain *o*-alkylphenols in good yields from tertiary alcohols, phenols and a phosphoric acid catalyst. The alkylation of phenol itself is not described by Chichibabin, but there is some reason to doubt the validity of the assignment of structure made by him to the mono-*t*-butyl-*o*-cresol. Dr. Donald R. Stevens of the Mellon Institute has kindly made available to us the boiling points which were obtained by Dr. Victor J. Anhorn of the Gulf Research and Development Company, Pittsburgh, Pa., for 6-*t*-butyl-*o*-cresol and 4-*t*-butyl-*o*-cresol. They are 110° and 124° (14 mm.), respectively. The mono-*t*-butyl-*o*-cresol described by Chichibabin is reported to boil at 122.5° (14 mm.) and is probably the 4-*t*-butyl- and not the 6-*t*-butyl-*o*-cresol as claimed.

[8] D. Papa, E. Schwenk and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942); E. Schwenk, D. Papa, B. Whitman and H. Ginsberg, *ibid.*, **9**, 1 (1944).

[9] K. L. Wolf and W. Herold, *Z. physik. Chem.*, [B] **13**, 201 (1931).

identical wave lengths as phenol. Thus it is likely that the size of the para alkyl group is not the determining factor in this shift. An entirely satisfactory explanation for this shift is not apparent, although the shift is quite common.

Since the method of synthesis outlined above makes *o*-alkylphenols, phenolic ethers and related compounds readily available, a re-investigation of some aspects of the "ortho effect" is now under way.

Experimental

4-Bromo-2-*t*-butylphenol.—A mixture of *p*-bromophenol (121 g. or 0.7 mole), 200 ml. of benzene and 4 ml. of 98% sulfuric acid was treated at 65 ± 5° over a period of five hours with slightly over one mole of isobutylene in an alkylation vessel similar to that shown in Fig. 1 of ref. 3. After neutralization, the benzene solution was dried over anhydrous sodium sulfate and the solvent removed *in vacuo*. The residue, fractionated through a Vigreux column at 6 mm., distilled at 123–131° and, upon redistillation, at 128–130°; yield 118.4 g. (74.0%).

Anal.[10] Calcd. for $C_{10}H_{13}OBr$: C, 52.5; H, 5.72; Br, 34.9. Found: C, 51.6, 51.8; H, 5.67, 5.72; Br, 35.3, 35.7.

The discrepancies in these analyses can be accounted for by assuming that 5% of the starting material (*p*-bromophenol) was present in the product. It was not possible to carry out a slow fractionation of the product, because of its instability.

When treated with sodium hydroxide and chloroacetic acid according to the usual procedures the compound yielded 4-bromo-2-*t*-butylphenoxyacetic acid, m. p. 183.5–184.0° recrystallized from ligroin.

Anal.[11] Calcd. for $C_{12}H_{15}O_3Br$: C, 50.2; H, 5.27; Br, 27.8; neut. equiv., 287.2. Found: C, 50.4; H, 5.54; Br. 27.7; neut. equiv., 286.8, 287.2.

***o-t*-butylphenol.**—A mixture of 4-bromo-2-*t*-butylphenol (10 g. or 0.0437 mole), 50 ml. of 95% ethanol and 30 g. of Raney nickel–aluminum alloy in a 1-l. flask equipped with a reflux condenser was treated, over a period of thirty minutes, with 300 ml. of 10% aqueous sodium hydroxide. The mixture was refluxed for an additional hour, filtered and the nickel washed with 10% alkali followed by benzene. The cooled aqueous layer was poured into 250 ml. of concentrated hydrochloric acid. After extraction with benzene, combination of the washings and drying over anhydrous sodium sulfate, the solvent was stripped using a Vigreux column. The residue distilled at 217–220° at atmospheric pressure; yield 6.0 g. (91.4%), $n^{20}{}_D$ 1.5160, $d^{20}{}_4$ 0.9783.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.9; H, 9.39. Found: C, 80.1; H, 9.57.

With ferric chloride the product gave a light brown color which gradually darkened. A deep blue color was obtained with phosphomolybdic acid and ammonium hydroxide.[12] With sodium hydroxide and chloroacetic acid, *o-t*-butylphenoxyacetic acid was obtained, recrystallized from ligroin, m. p. 145.5–146.5°; lit. value for *p-t*-butylphenoxyacetic acid 86°.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.2; H, 7.75; neut. equiv., 208.3. Found: C, 69.0; H, 7.87; neut. equiv., 210.6.

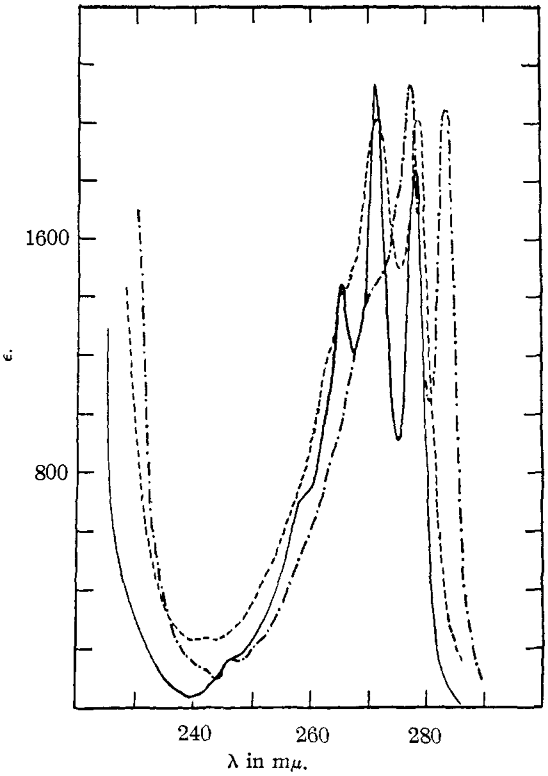

Fig. 1.—Ultraviolet absorption spectra: —, 2.37 × 10^{-4} *M* phenol; ----, 2.29 × 10^{-4} *M* *o-t*-butylphenol; —·—·—, 2.10 × 10^{-4} *M* *p-t*-butylphenol, all in cyclohexane solvent.

The ultraviolet absorption spectra were determined with a Beckman spectrophotometer (model DU) using 1-cm. quartz cells. The cyclohexane solvent was freed of benzene by passage through silica gel, followed by fractionation.

Rearrangement of *o-t*-Butylphenol.—The warm solution of 5 drops of 98% sulfuric acid in 1 ml. of *o-t*-butylphenol was further heated for two or three minutes, then poured into cold water. After extraction with petroleum ether, neutralization and evaporation of the solvent, the crystals, recrystallized from ligroin, melted at 98.0–98.5°; mixed with known *p-t*-butylphenol at 98–99°.

Treatment with 85% phosphoric acid yielded no rearranged product. However, vigorous boiling for five to ten minutes of the heterogeneous mixture obtained with 98% phosphoric acid (the alkylation catalyst employed by Chichibabin[7]) yielded considerable amounts of *p-t*-butylphenol.

Summary

o-t-Butylphenol has been synthesized in good yields and characterized. Its ultraviolet absorption spectrum in cyclohexane has been determined and is discussed. It is shown that the *t*-butyl group readily rearranges to the para position in the presence of acid catalysts. This work is being extended to related compounds and to a study of the "ortho" effect.

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[10] The author is indebted to Mr. J. S. Mihina for this analysis.

[11] The remainder of the analyses, with the exception of the neutralization equivalents, were performed by the Clark Microanalytical Laboratory, Urbana, Illinois.

[12] V. M. Platkovskaya and S. G. Vatkina, *J. Applied Chem. (U. S. S. R.)*, **10**, 202 (1937); *C. A*, **31**, 4232 (1937).