soluble material (12 g.) consisted chiefly of 2,4-di-*t*-butylphenol identified by conversion into the nitro derivative described in the preceding experiment. The alkali soluble material, recrystallized from heptane, melted at 101°. Mixed with an authentic sample of *p*-*t*-butylphenol, it melted at 100–101°.

(B) **At 140°.**—One hundred grams of *p*-($\alpha,\alpha,\gamma,\gamma$-tetramethobutyl)-phenol and 25 g. of 90% phosphoric acid heated six hours at 140° in an autoclave under 20 atmospheres of initial nitrogen pressure yielded 2 g. of phenol, 5.6 cc. of hydrocarbons, a 6-g. fraction containing 2,4-di-*t*-butylphenol, and a 12-g. fraction containing *p*-*t*-butylphenol.

Synthesis of 4,6-Dinitro-2-*t*-butylphenol.—Fifteen grams (0.107 mole) of *p*-nitrophenol, 18.6 g. (0.33 mole) of isobutene and 17.5 g. of 90% phosphoric acid was placed in a glass liner and heated at 100° for four hours in an Ipatieff type rotating bomb. All of the isobutene reacted to yield a product containing, besides unreacted *p*-nitrophenol, a tarry substance. The reaction mixture was diluted with water and extracted with ether. The ether solution was treated with 10% potassium hydroxide; the 2-*t*-butyl-4-nitrophenol was precipitated by bubbling carbon dioxide through the yellow alkali solution. The precipitate was separated by filtration and washed with water. When purified by recrystallization from dilute alcohol (norite), it formed colorless flakes, m. p. 138.5–139.5°, yield 15%.

Anal. Calcd. for $C_{10}H_{13}NO_3$: N, 7.17. Found: N, 7.22.

Forty milligrams of the 2-*t*-butyl-4-nitrophenol was heated on a water-bath for two minutes with 0.5 cc. of concentrated nitric acid and 1.0 cc. of acetic acid. The reaction mixture was diluted with crushed ice and water, and the product taken up with ether. The ether solution was washed with water and evaporated on a water-bath. The residue, recrystallized from dilute alcohol, formed yellow plates, m. p. 122–123°; mixed m. p. with a specimen formed by nitration of 2,4-di-*t*-butylphenol was 122–123°. Mixed m. p. with picric acid was 95°.

Summary

4-*t*-Butylphenol and 2,4-di-*t*-butylphenol have been obtained in the alkylation of phenol with diisobutene at higher temperatures either with phosphoric acid or a large excess of sulfuric acid as catalyst.

When *p*-($\alpha,\alpha,\gamma,\gamma$-tetramethobutyl)-phenol was heated under pressure with phosphoric acid, the side chain was cleaved to produce phenol, octenes, *p*-*t*-butylphenol, and 2,4-di-*t*-butylphenol.

Phenol was readily alkylated by isobutene in the presence of phosphoric acid at 100° to produce *p*-*t*-butylphenol and 2,4-di-*t*-butylphenol in 40 and 30% yields, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA]

Preparation of Some Lower Alkyl Chlorides from the Corresponding Alcohols Using Zinc Chloride and Concentrated Hydrochloric Acid

BY ATHERTON M. WHALEY AND J. E. COPENHAVER

Because of the importance of the alkyl chlorides, this study was undertaken to determine the best procedure for the zinc chloride and hydrochloric acid method. This paper deals principally with *n*-propyl, *n*-butyl and *s*-butyl chlorides. Excellent reviews of the preparation of alkyl chlorides by this method are given by Dehn and Davis,[1] Norris and Taylor[2] and Clark and Streight.[3] The procedure of Norris and Taylor generally has been used and requires six to seven hours to produce 64–66% yield of butyl chloride, for example, from three moles of butyl alcohol. By the method described below, the yield was raised to 76–77% and the time shortened to one hour.

The above investigators, as well as Guyer, Bieler and Hardmier,[4] have found that approximately two moles of zinc chloride for each mole of alcohol, which conclusion was confirmed in this investigation. It was found that long contact of the alkyl chlorides with the zinc chloride–hydrochloric acid mixture caused decomposition and polymerization, and better results were obtained by removing them from the reaction flask as soon as formed. Many catalysts have been tried by other workers but none seemed to be more effective than zinc chloride, hence it has been used throughout this investigation.

Experimental

The reaction flask for a one-mole run was a one-liter round-bottomed, short-necked flask, attached to an up-

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[1] Dehn and Davis, THIS JOURNAL, **29**, 1328 (1907).

[2] Norris and Taylor, *ibid.*, **46**, 753 (1924); *Org. Syntheses*, **5**, 27 (1925).

[3] Clark and Streight, *Trans. Roy. Soc. Can.*, [3] **23**, Sec. 3, 77 (1929).

[4] Guyer, Bieler and Hardmier, *Helv. Chim. Acta.*, **20**, 1462 (1937).

right water-jacketed condenser, which acted as a fractionating column. This must be efficient and long enough to give ease of control of the reflux. The top of this carried a thermometer and a goose-neck connecting an efficient downward condenser. This condenser was attached to a 200-cc. trap, surrounded by an ice-salt mixture, from which the hydrogen chloride escaped into a water absorber. A second trap, similarly cooled, increased the yield from 3–5%. Rubber stoppers were used throughout.

Two moles of zinc chloride was dissolved completely in two moles of concentrated hydrochloric acid, cooling if necessary to prevent the loss of hydrogen chloride. This solution and one mole of alcohol were mixed thoroughly in the reaction flask and heated on a paraffin-bath. It usually required from ten to fifteen minutes for the reaction to start, which was determined by vigorous boiling. The best average bath temperatures for the three chlorides were as follows: *n*-propyl, 138–140°; *n*-butyl, 150–155°; *s*-butyl, 125–130°. This temperature was kept as low as possible to reduce polymerization. By the water in the jacket, the reflux temperature was controlled so that it was approximately the boiling point of the alkyl chloride and never allowed to rise higher than 1–2° above that point. For the three chlorides, these temperatures were respectively: 45–50, 68–80 and 65–69°. When evolution of the chlorides slackened, the temperature of the bath was raised to 160°. The reaction time averaged from fifty to sixty minutes for *n*-propyl and *n*-butyl and thirty minutes for *s*-butyl chloride.

The crude alkyl chloride, which averaged from 90–95% yield, was washed with cold water, repeatedly with small portions of concd. sulfuric acid[6] and finally with very dilute sodium carbonate, the latter being added very little at a time to prevent emulsions. The alkyl chlorides were dried over calcium chloride.[6]

Distillation was made from a 200-cc. flask with a 23-inch (58 cm.) punched-in column, at a rate of one to two drops per second and the product collected at a maximum over a 2° range. The foreshot usually contained some unsaturated derivatives and a slight residue remained in the flask. The yields averaged as follows: *n*-propyl, 70–72%; *n*-butyl, 76–77% and *s*-butyl, 83%.

Discussion

Our results agree with those of Dehn and Davis, that all of the zinc chloride must be dissolved before the reaction is started and with Norris,[7] that more than 1.25 moles of zinc chloride per mole of alcohol is necessary, and, further, that too large an excess of hydrochloric acid decreases the yield. Too much zinc chloride causes polymerization and less prolongs the reaction time. Dry-Ice around the receivers produces larger crude yields, due principally to dissolved hydrogen chloride. *i*-Butyl alcohol was used in one experiment but excessive rearrangement and polymerization cut the yield to 10%, the bath being held at 130° and the reflux temperature at 60–70°. The crude product boiled from 55–180°. One three-mole run with *n*-butyl alcohol gave the same consistent percentage yield. It was shown that the mechanical loss from washing and distilling averaged from 5–8% by running a blank on known quantities of propyl alcohol, propyl chloride and water. This loss was less for butyl chloride because of its lower vapor pressure.

The authors wish to express their sincere appreciation to Dr. E. Emmet Reid, Research Advisor at the University of South Carolina, for his valuable suggestions and help in the course of this investigation.

Summary

A procedure is given for the preparation of *n*-propyl, *n*-butyl and *s*-butyl chlorides, by the zinc chloride–hydrochloric acid method, in better yields and in a much shorter time than has been reported previously.

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(5) McCullough and Cortese, THIS JOURNAL, **51**, 225 (1929); Sherrill, *ibid.*, **52**, 1982 (1930).

(6) "Org. Syntheses, John Wiley and Sons, New York, N. Y., Vol. I, 1921, p. 11.

(7) Norris, *Ind. Eng. Chem.*, **16**, 184 (1924).