atmospheric pressure to recover the unreacted materials. As soon as this nears completion, the distillation is pursued at reduced pressure, with a carbon dioxide trap to stop the light boiling compounds. The distillation at 20 mm. gave 551 g. of chlorinated propane, boiling from 126 to 132°; this was a 49% conversion yield. The tar formation amounted to 5%, and the remainder of the ingredients was recovered unreacted. The reaction did not take place at lower temperatures, and resinification increased rapidly at higher temperatures. At 70°, resinification was complete. Consequently, the lower conversion yield was accepted, and the recovered materials were repeatedly re-treated.

Fluorination of $CCl_3CHClCCl_3$.—Two procedures were employed, to obtain products rich in mono- and in difluoride, respectively.

First Procedure.—In a 1-liter round-bottomed flask 500 g. of *s*-heptachloropropane, 120 g. of SbF_3 and 20 g. of $SbCl_5$ were placed, stirred vigorously for three hours and then heated to 70–80° for one hour, with stirring continued. The mixture was cooled, and its liquid layer, after pouring into hydrochloric acid, was washed, dried and distilled at 90 mm. The crude product amounted to 427 g., of which a little more than one-third was monofluoride.

Second Procedure.—Heptachloropropane (916 g.), SbF_3 (520 g.) and $SbCl_5$ (100 g.) were placed in a 1-liter round-bottomed flask and stirred overnight at room temperature. The mixture was then heated for ten hours on a steam-bath, cooled to separate most of the antimony chloride, decanted into acid, washed, dried and distilled at 90 mm. The crude product amounted to 630 g., of which a little more than one-half was the difluoride.

Summary

The syntheses of C_3Cl_8, $CHCl_2CCl_2CCl_3$ and $CCl_3CHClCCl_3$ have been improved. From these compounds, the mono-, di- and trifluorides have been obtained by replacement of chlorine atoms by fluorine. The formulas of the new derivatives have been established experimentally for the mono- and difluorides, and reasoned out for the trifluorides. The properties have been tabulated, together with those of three additional fluorochloropropanes which were synthesized independently for identification purposes. The course of the fluorination has thus been established.

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RECEIVED JULY 9, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Isobutene and Diisobutene with Phenol, with and without Scission of C–C Linkages

BY V. N. IPATIEFF, HERMAN PINES AND B. S. FRIEDMAN

In previous papers[1] it was shown that when diisobutene reacts with benzene in the presence of sulfuric acid, *t*-butyl-, *p*-di-*t*-butyl-, and tri-*t*-butylbenzene are formed. In view of the fact that Niederl and Natelson and co-workers[2,3] failed to notice analogous products observed by others[4] when phenol was treated with diisobutene in the presence of sulfuric acid, it was decided to investigate this reaction.

When Natelson's[3] directions were followed closely, the product contained no butylphenol. A compound not previously reported, which appears to be 2,4-di-*t*-octylphenol [2,4-di-($\alpha,\alpha,\gamma,\gamma$,-tetramethobutyl)-phenol], was isolated in addition to the expected *p*-*t*-octylphenol [*p*-($\alpha,\alpha,\gamma,\gamma$,-tetramethobutyl)-phenol].

When, however, phenol and diisobutene were treated with a large excess of sulfuric acid and the temperature allowed to rise to 85%, the product was found to contain some *p*-*t*-butylphenol.

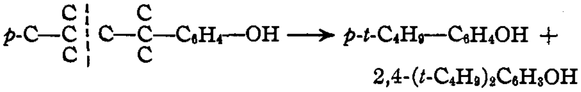
The alkylation of phenol with diisobutene in the presence of phosphoric acid required a temperature of 150°; and the yield of *p*-*t*-octylphenol was quite low. *p*-*t*-Butylphenol was isolated and identified.

The production of the *p*-*t*-butylphenol could have taken place by either of two series of reactions

$$\text{Diisobutene} \longrightarrow 2\ i\text{-}C_4H_8 \qquad \text{(A)}$$

$$i\text{-}C_4H_8 + C_6H_5OH \longrightarrow t\text{-}C_4H_9\text{-}C_6H_4OH$$

$$\text{Diisobutene} + C_6H_5OH \longrightarrow t\text{-}C_8H_{17}\text{-}C_6H_4OH \qquad \text{(B)}$$



$$p\text{-C—}\underset{C}{\overset{C}{C}}\ \vdots\ \text{C—}\underset{C}{\overset{C}{C}}\text{—}C_6H_4\text{—OH} \longrightarrow p\text{-}t\text{-}C_4H_9\text{—}C_6H_4OH + 2,4\text{-}(t\text{-}C_4H_9)_2C_6H_3OH$$

The possibility that reaction could take place by (B) is evidenced by the fact that *p*-*t*-octylphenol heated under pressure to 140° in the presence of 90% phosphoric acid was cleaved to pro-

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[1] (a) Ipatieff and Pines, THIS JOURNAL, **58**, 1056 (1936); (b) Ipatieff and Pines, *J. Org. Chem.*, **1**, 464 (1936).

[2] (a) Niederl and Natelson, THIS JOURNAL, **55**, 2571 (1933); (b) Niederl, Natelson and Beekman, *ibid.*, **53**, 272 (1931).

[3] Natelson, *ibid.*, **56**, 1584 (1934).

[4] British Patent, 453,335, Aug. 20, 1936; *C. A.*, **31**, 485 (1937). *Cf.* Smith and Rodden, THIS JOURNAL, **59**, 2353 (1937), who used aluminum chloride.

duce both *p*-*t*-butylphenol and 2,4-di-*t*-butylphenol. Cleavage also took place at the point of attachment of the octyl group to the nucleus, yielding phenol and octenes.

The alkylation of phenol with isobutene and phosphoric acid at 100° gave good yields of the expected products, *p*-*t*-butylphenol and 2,4-di-*t*-butylphenol.

Nitration of *p*-*t*-butylphenol with hot acetic–nitric acids yielded the expected 2,6-dinitro-4-*t*-butylphenol,[5] but the same reagent effected a cleavage of one of the butyl groups in 2,4-di-*t*-butylphenol to form 4,6-dinitro-2-*t*-butylphenol. The structure of the latter compound was established by its synthesis from *p*-nitrophenol by alkylation with isobutene in the presence of phosphoric acid, followed by nitration.

The replacement of a tertiary alkyl group by a nitro group corresponds to the conversion of *t*-amylphenol[6a] and *t*-butylphenol[6b] into picric acid by use of concentrated and fuming nitric acids, respectively.

Experimental Part

Phenol and Diisobutene

Experiment A. Small Quantities of Sulfuric Acid.[1]—To a rapidly stirred mixture of one mole each of phenol and diisobutene in a flask surrounded by an ice-water bath, was added dropwise 2 cc. of 96% sulfuric acid. After the mixture had become viscous, the contents of the flask were heated to 65° and stirred at that temperature for fifteen minutes.

The reaction product was placed along with 4 g. of sodium carbonate in a modified Claisen flask and the various fractions separated by vacuum distillation. The fraction (8 cc.) boiling at 210–215° (29 mm.), $n^{20}D$ 1.5040, failed to crystallize, was soluble in a solution composed of equal parts of methanol and 50% aqueous potassium hydroxide. It yielded an oil when nitrated. It probably is di-*t*-octylphenol.

Anal. Calcd. for $C_{22}H_{38}O$: C, 83.02; H, 11.94; mol. wt., 318. Found: C, 82.53; H, 12.02; mol. wt., 314.

No trace of *p*-*t*-butyl- or 2,4-di-*t*-butylphenols was found.

Experiment B. Large Quantities of Sulfuric Acid.—A mixture of two moles each of phenol and diisobutene was placed in a flask surrounded with an ice-bath. To this was added with stirring 78 g. of 96% sulfuric acid. The time of addition was one minute; the temperature inside of the flask rose to 85°. After fifteen minutes of stirring the temperature fell to 0°. The product was washed with water, dried over anhydrous sodium sulfate, and separated by vacuum distillation. The fraction (8 cc.) boiling at 141–152° (26 mm.) consisted chiefly of *p*-*t*-butylphenol, m. p. 100° after recrystallization from heptane. Mixed melting point with authentic sample was 99–100°.

Nitration.—One-half gram of *p*-*t*-butylphenol was treated with 2 cc. of a mixture of equal volumes of concentrated nitric acid and glacial acetic acid. After five seconds the vigorously reacting mixture was poured onto crushed ice. The solid product was separated by filtration, washed with water; recrystallized from dilute ethanol it yielded 2,6-di-nitro-4-*t*-butylphenol, m. p. 95–96°.

Experiment C. Phosphoric Acid.—Ninety-two grams of phenol, 57 g. of diisobutene, and 50 g. of 90% phosphoric acid were placed in the glass liner provided with a capillary[7] and heated at 150° for six hours in an Ipatieff type rotating bomb. The bomb was charged with 20 atmospheres of nitrogen in order to keep the material within the glass liner during the run. The product was washed with water, dried, and upon distillation in vacuum yielded, besides phenol, 22 g. of unreacted diisobutene, 16 g. of *p*-(α,α,γ,γ-tetramethobutyl)-phenol (b. p. 169–181° (28 mm.), m. p. 84–85°) and 4 g. of *p*-*t*-butylphenol.

Phenol and Isobutene with Phosphoric Acid.—Isobutene was passed into a rapidly stirred mixture of 94 g. of phenol and 30 g. of 89% phosphoric acid kept at 100° until 100 g. was absorbed. The product after being washed with water, dried, and distilled under reduced pressure, yielded 84 g. (40% yield based on phenol) of *p*-*t*-butylphenol, m. p. 99–101°, and 62 g. (30% yield based on phenol) of 2,4-di-*t*-butylphenol 143–147° (20 mm.), $n^{20}D$ 1.5080. The latter solidified only after being seeded with some authentic (Eastman) 2,4-di-*t*-butylphenol; m. p. and mixed m. p. 55°.

Nitration of the dialkylated phenol with acetic–nitric acid yielded 4,6-dinitro-2-*t*-butylphenol, yellow plates from dilute ethanol; m. p. 123–124°; mixed m. p. with specimen prepared from *p*-nitrophenol (see below) by alkylation and nitration was 122–123°.

Calcd. for $C_{10}H_{12}O_5N_2$: C, 50.00; H, 5.00; N, 11.66. Found: C, 50.11; H, 5.13; N, 11.35.

p-(α,α,γ,γ-Tetramethobutyl)-phenol with Phosphoric Acid. (A) At 200°.—One hundred and twenty-two grams of *p*-(α,α,γ,γ-tetramethobutyl)-phenol, b. p. 170–175° (28 mm.), and 25 g. of 90% phosphoric acid were heated for five hours at 200° under nitrogen pressure (20 kg./sq. cm.) in an Ipatieff rotating bomb equipped with a glass liner. The product was washed with a small quantity of saturated sodium sulfate solution, dried over anhydrous sodium sulfate, and distilled under reduced pressure.

The fraction (9 g.) boiling at 62–130° (30 mm.) was extracted with alkali and found to contain 4 g. of phenol and 7.5 cc. of hydrocarbons. The identity of the phenol was established by converting it to 2,4,6-tribromophenol, m. p. and mixed m. p. with authentic sample 91–92°. The hydrocarbons were separated by distillation into the following fractions: 1, 4.3 cc., 100–115°, $n^{20}D$ 1.4189; 2, 1.0 cc., 115–125°, 1.4233; 3, 0.8 cc., 126–165°, 1.4300; 4, 1.0 cc., 165–185°, 1.4446. Fraction No. 1 is probably a mixture of octenes.

Anal. Calcd. for C_8H_{16}: C, 85.63; H, 14.37. Found: C, 85.74; H, 14.15.

The fraction (32 g.) boiling at 135–143° (28 mm.) was extracted with 10% potassium hydroxide. The alkali in-

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[5] Henry and Sharp, *J. Chem. Soc.*, 2434 (1926).

[6] (a) Anschütz and Rauff, *Ann.*, **327**, 211 (1903); (b) Jedlicka, *J. prakt. Chem.* (2) **48**, 98 (1909).

[7] Grosse, This Journal, **60**, 212 (1938).

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.

RIVERSIDE, ILL.

RECEIVED JULY 8, 1938

[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).