[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS CO.]

Dealkylation of Dialkylbenzenes

BY V. N. IPATIEFF AND B. B. CORSON

It is well known that dialkylbenzenes are converted into monoalkylbenzenes by the action of benzene in the presence of aluminum chloride.[1] Aluminum chloride catalyzes the removal of primary, secondary and tertiary groups.

Inasmuch as it is desirable to differentiate between the different classes of alkyl groups, we have studied the action of a number of catalysts upon the reaction of dealkylation. It was found that di-*t*-alkylbenzenes are dealkylated in the presence of ferric chloride to give high yields of the corresponding mono derivatives whereas di-*s*- and di-*prim*-alkylbenzenes are not dealkylated under the same conditions. It is possible to isolate pure mono-*t*-butylbenzene from a mixture of di-*t*- and di-*s*-butylbenzenes.

Hydrogen chloride is liberated during the reaction and ferric chloride is reduced to the ferrous state. We hope to gain an insight into the mechanism of alkylation reactions by further study of this reaction.

Sulfuric, phosphoric, and perchloric acids were also tested as dealkylating catalysts. 1,4-Di-*t*-butylbenzene reacts with benzene in the presence of sulfuric acid to give mono-*t*-butylbenzene and *p*-*t*-butylbenzenesulfonic acid. The para position of the sulfonic acid group indicates that dealkylation preceded sulfonation. The dealkylation of di-*t*-butylbenzene is also catalyzed by phosphoric acid but not by perchloric acid.

Experimental

Ferric Chloride and Di-*t*-butylbenzene.—A mixture of 50 g. of 1,4-di-*t*-butylbenzene, 500 g. of benzene, and 30 g. of anhydrous ferric chloride was stirred for four hours at 83°. Sixty grams of mono derivative (85% yield) and 4 g. of di derivative were obtained. The fraction containing mono derivative (b. p. 165–175°; $n^{20}\mathrm{D}$ 1.4929; d^{20}_4 0.869) was free from polymer as evidenced by its inability to decolorize alcoholic permanganate.

Ferric Chloride and Di-*t*-amylbenzene.—1,4-Di-*t*-amylbenzene,[2] under the same conditions, gave a 70% yield of mono-*t*-amylbenzene (b. p. 185–195°, $n^{20}\mathrm{D}$ 1.4950) which did not decolorize alcoholic permanganate. Its identity was established by converting it into its 2,4-diacetamino derivative; m. p. 181°.[3]

Ferric Chloride Plus Secondary and Primary Dialkylbenzenes.—1,4-Diisopropyl-, 1,4-di-*s*-butyl-,[4] 1,4-methylisopropyl-, and diethylbenzenes were treated in the same manner. Dealkylation was negligible in all cases, 60–75% of the original dialkylbenzenes being recovered unchanged.

Ferric Chloride Plus Mixture of Tertiary and Secondary Dibutylbenzenes.—A mixture of 25 g. of 1,4-di-*t*-butylbenzene, 25 g. of 1,4-di-*s*-butylbenzene, 500 g. of benzene, and 30 g. of ferric chloride was stirred four hours at 83°. The 11 g. fraction boiling at 165–175° ($n^{20}\mathrm{D}$ 1.4930) was pure mono-*t*-butylbenzene. Its purity was established by converting it into its 2,4-diacetamino derivative. Recrystallization and microscopic examination of the crystals showed the absence of the isomeric secondary compound.[3] Unchanged di-*t*-butylbenzene crystallized from the recovered di-*s*-butylbenzene. A second treatment of the recovered di derivative with the same benzene and a fresh portion of ferric chloride gave an additional yield of 7 g. of pure mono-*t*-butylbenzene. The total yield was 51% of the theoretical amount.

Sulfuric Acid and Di-*t*-butylbenzene.—A mixture of 95 g. of 1,4-di-*t*-butylbenzene, 177 g. of benzene, and 96 g. of 96% sulfuric acid was stirred for four hours at 15°. The acid weight increased 4 g. Seven grams (5% yield) of mono derivative and 85 g. of di derivative were isolated.

A mixture of 95 g. of di-*t*-butylbenzene, 156 g. of benzene, and 122 g. of 96% sulfuric acid was stirred for five hours at 50°. The acid weight increased 25 g. Forty-one grams (31% yield) of mono derivative and 48 g. of di derivative were isolated. The fraction (b. p. 165–175°; d^{20}_4 0.869; $n^{20}\mathrm{D}$ 1.4922) containing mono derivative did not decolorize alcoholic permanganate. Forty-four grams of sodium para-*t*-butylbenzenesulfonate was precipitated from the diluted catalyst acid by sodium hydroxide. The salt was crystallized from absolute ethyl alcohol.

Anal. Calcd. for $C_{10}H_{13}SO_3Na$: Na, 9.74. Found: Na, 9.87.

t-Butylphenol[5] (m. p. 98–99°) was obtained by fusing the sodium salt with sodium hydroxide and decomposing the melt with hydrochloric acid. Nitration of the phenol gave 2,4-dinitro-4-*t*-butylphenol[6] melting at 91–92°.

A mixture of 95 g. of di-*t*-butylbenzene, 156 g. of benzene, and 184 g. of 96% sulfuric acid was stirred four hours at 50°. The acid weight increased 40 g. Fifty-four grams (40% yield) of mono derivative and 33 g. of di derivative were obtained. The catalyst acid was diluted, made alkaline, and distilled. The distillate (d^{20}_4 0.998) did not separate an alcohol layer when saturated with potassium carbonate. The catalyst acid, therefore, did not contain butyl sulfate.

Phosphoric Acid and Di-*t*-butylbenzene.—Experiments were made in a rotating Ipatieff bomb equipped with a glass liner. The yields of mono derivative obtained by heating mixtures of 95 g. of 1,4-di-*t*-butylbenzene, 156 g. of ben-

---

[1] Radziewanowski, *Ber.*, **27**, 3235 (1894); see also Boedtker and Halse, *Bull. soc. chim.*, [4] **20**, 444 (1916); Milligan and Reid, THIS JOURNAL, **44**, 208 (1922).

[2] Prepared by Dr. H. Pines by the interaction of benzene and trimethylethylene in the presence of sulfuric acid.

[3] Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937).

[4] Ipatieff, Corson and Pines, *ibid.*, **58**, 919 (1936).

[5] Senkowski, *Ber.*, **23**, 2418 (1890).

[6] Studer, *ibid.*, **14**, 1474 (1881).

zene, and 187 g. of 100% orthophosphoric acid under an initial nitrogen pressure of 10 kg./sq. cm. for six hours at 90, 150, 200, 250, and 300° were 0, 0, 2, 19, and 23%, respectively.

Perchloric Acid and Di-*t*-butylbenzene.—A mixture of 50 g. of 1,4-di-*t*-butylbenzene, 84 g. of 70–72% perchloric acid and 500 g. of benzene was stirred six hours at 85°. The acid became dark and viscous. Mono derivative was not obtained; 36 g. of di derivative was recovered.

Acknowledgment.—The authors express their thanks to Dr. Louis Schmerling for identifying the *t*-butyl and *t*-amylbenzenes and to Mr. Wilbur Shand for assistance in the experimental work.

Summary

Di-*t*-butyl- and di-*t*-amylbenzenes are dealkylated in the presence of ferric chloride and benzene to the corresponding mono derivatives. Di-*s*- and di-*prim*-alkylbenzenes are not dealkylated under the same conditions.

Hydrogen chloride is liberated during the reaction and ferric chloride is reduced to the ferrous state.

Di-*t*-butylbenzene reacts with benzene in the presence of sulfuric acid to give mono-*t*-butylbenzene and *p*-*t*-butylbenzenesulfonic acid. Di-*t*-butylbenzene is dealkylated in the presence of phosphoric acid and benzene, but mono derivative was not obtained in the presence of perchloric acid.

RIVERSIDE, ILLINOIS RECEIVED MAY 13, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Dielectric Properties of Acetylenic Compounds. VIII.[1] Propiolyl Chlorides and Some Other Acid Chlorides

BY S. MERCEDES KOEHL AND H. H. WENZKE

The acid chloride group contains two linkages quite polar in character. These are the C—Cl bond and that of the C=O group. Assuming the classical structure (see A below) for acetyl chloride and using the method of bond moments, the moment is calculated to be 2.28. In these calculations the values of the bond moments are assumed to be C—H, 0.4; C=O, 2.3; and C—Cl, 1.5. Interactions between the bond moments are neglected and the valence angles are those calculated for an undistorted tetrahedral structure. The valence angles in acetyl chloride have been determined by Dornte[2] using the method of electron diffraction. This author gives the compound a Y structure with the angle between the carbon–carbon bond and the carbon–halogen bond 110 ± 10° and the other two angles each 125 ± 10°.

Preparation of Compounds.—Butylpropiolyl chloride was synthesized from butyl bromide and a liquid ammonia solution of sodium acetylide. The butylacetylene thus obtained was refluxed with ethylmagnesium bromide. Carbon dioxide was bubbled through the acetylenic Grignard reagent to form the magnesium bromide complex of butylpropiolic acid. This complex was acidified with dilute hydrochloric acid. The butylpropiolic acid thus obtained was converted to the acid chloride by refluxing with thionyl chloride. The product was purified by fractional distillation.

The method of preparing amylpropiolyl chloride differed from that of the butyl homolog insofar as the respective acetylenic Grignard reagent was refluxed with ethyl chlorocarbonate. The ester was treated with alcoholic potassium hydroxide; the potassium amylpropiolate acidified with dilute hydrochloric acid. The amylpropiolic acid was chlorinated with thionyl chloride.

The best grades of acetyl, propionyl, butyryl and benzoyl chlorides, and the practical grade of cinnamoyl chloride were obtained from the Eastman Kodak Co. The first four chlorides were purified by distillation. The cinnamoyl chloride was recrystallized from petroleum ether solutions until a constant melting point was obtained.

The solvent used for dielectric constant determinations was Baker thiophene-free chemically pure analyzed benzene. It was dried over metallic sodium and then distilled within a 0.2° temperature range. A heterodyne beat method was employed for the determination of dielectric constants. The indices of refraction were read on an Abbé refractometer. The measurements were made at 25°.

TABLE I

PHYSICAL CONSTANTS OF ACID CHLORIDES

Compound	B. p., °C.	d	n_D
Acetyl	51.8	1.0983	1.3878
Propionyl	80	1.0469	1.4057
Butyryl	102	1.0154	1.4115
Benzoyl	197	1.2071	1.5520
Cinnamoyl	35 (m. p.)	1.1632[a]	1.6202[a]
Butylpropiolyl	65 (13 mm.)	1.0609	1.4695
Amylpropiolyl	88.5 (13 mm.)	1.0568	1.4797

[a] These data were obtained at 37.6°.

Table III shows that the moment of acetyl chloride when determined in the liquid state is

---

[1] Article VII of this series, Curran and Wenzke, THIS JOURNAL, **59**, 943 (1937).

[2] Dornte, *ibid.*, **55**, 4126 (1933).