[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

The Preparation of Aromatic Acids by Liquid Phase Oxidation

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While a number of procedures have been reported for the liquid phase oxidation of alkylaromatic compounds to the corresponding aromatic acids, few have shown promise as laboratory methods. They usually have involved lengthy exposures to the oxidizing agent[1b] or else the use of pressure.[2-6] However, the oxidation of *p*-cymene to *p*-toluic acid by oxygen at atmospheric pressure has been reported in conversions as high as 37.4%.[7]

We have found that in butyric acid solution in the presence of the acetates of cobalt, lead and manganese, a number of alkylaromatic compounds can be oxidized to the corresponding aromatic acids by means of oxygen at atmospheric pressure. Reaction is effected by blowing the gas through the mixture for approximately six hours at a temperature of 140–160°. The acids, thus obtained, are substantially pure.

While toluene did not react (probably partly because of its low boiling point), ethylbenzene and cumene gave benzoic acid in 42–49% conversion and 59–68% yield. With longer side chains the conversion was lower. 2-Phenyloctane and 2-phenyldecane gave 11–12% conversions to benzoic acid. In general substituted ethylbenzenes were much more readily oxidized than the corresponding toluenes. While the chlorotoluenes essentially were unattacked, the three chloroethylbenzenes gave 8–27% conversions (44–58% yields) to the corresponding chlorobenzoic acids. Similarly *p*-nitroethylbenzene gave a 14% conversion to *p*-nitrobenzoic acid, whereas *p*-nitrotoluene did not react. The presence of an additional alkyl group increased the ease of oxidation. All three xylenes gave the corresponding toluic acids in 19–30% conversion and 49–56% yield. In all cases studied the para isomer was oxidized most easily. Our yield of *o*-toluic acid (56%) compares favorably with that obtained using nitric acid (53–55%).[8]

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Experimental

Starting Materials.—The *o*-xylene, *m*-xylene, *p*-xylene, cumene, *o*-chlorotoluene, *p*-chlorotoluene, *p*-nitrotoluene and methyl *p*-cresyl ether were obtained from the Eastman Kodak Co. The toluene was Barrett nitration grade and the ethylbenzene was obtained from the Dow Chemical Co. The 1-octene and 1-decene were obtained from the Connecticut Hard Rubber Company.

2-Phenyloctane and 2-phenyldecane were prepared by the method of Ipatieff, Corson and Pines.[9] To a mixture of 390 g. of thiophene-free benzene and 100 cc. of concentrated sulfuric acid cooled in an ice-salt-bath (5–15°) was added with stirring over a one-half hour period, 280 g. of 1-octene. After the addition of the 1-octene was completed, the reaction mixture was stirred for an additional fifteen minutes. The hydrocarbon layer was then separated and washed successively with 50 cc. of concentrated sulfuric acid, 250 cc. of water, 100 cc. of 10% sodium hydroxide, and 250 cc. of water. Distillation of the hydrocarbon layer through a short Vigreux column yielded, besides recovered benzene, 350 g., b. p. 118.5–120.0° (14 mm.), n^{25}_{D} 1.4830, d^{25}_{25} 0.869 and 33 g., b. p. 121–126° at 15 mm., n^{25}_{D} 1.4825. These two fractions represented an 81% yield of 2 phenyloctane and the 33 g. residue represented 8% calculated as dioctylbenzene. The first fraction was analyzed.

Anal.[10] Calcd. for $C_{14}H_{22}$: C, 88.5; H, 11.58. Found: C, 88.6; H, 11.55.

On a larger scale (1120 g. of 1-octene) the yield rose to 84.5%, b. p. 120–128° (14–15 mm.), n^{25}_{D} 1.4823–1.4828.

2-Phenyldecane was prepared in the same way by substituting 350 g. of 1-decene for the 280 g. of 1-octene. The 88% yield was collected in two fractions: 418 g., b. p. 144–147° (14 mm.), n^{25}_{D} 1.4811, d^{25}_{25} 0.858 and 61 g., b. p. 147–150° (14 mm.), n^{25}_{D} 1.4811. The 35 g. residue represented 8% calculated as didecylbenzene. The first fraction was analyzed.

Anal. Calcd. for $C_{16}H_{26}$: C, 88.1; H, 11.91. Found: C, 88.4; H, 11.80.

***o*- and *p*-Chloroethylbenzene.**[11]—In a 5-l., three-necked, blackened flask equipped with a stirrer, condenser, thermometer and gas inlet tube was placed 2650 g. of ethylbenzene, 30 g. of powdered iron and 25 g. of ferric chloride. While the temperature of the mixture was held at 10–15°, 856 g. of chlorine was introduced over a nine-hour period. The mixture was washed with 100 cc. of concentrated hydrochloric acid and then three times with 200 cc. of water. Distillation yielded 812 g., b. p. 68–94° (87–75 mm.), n^{25}_{D} 1.5058 and 2247 g., b. p. 80–96° (30 mm.), n^{25}_{D} 1.5172 and a residue of 253 g. The second fraction was carefully redistilled through a 4 ft. by 1 in. glass helix packed column using a ten to one reflux ratio. In this way there was obtained a forerun of 45 g., b. p. < 79° (30 mm.), , n^{25}_{D} 1.5072; 1108 g. (31.5%) of *o*-chloroethylbenzene, b. p. 79.0–82.7° (30 mm.), (179°),[12] n^{25}_{D} 1.5187–1.5191 (n^{20}_{D} 1.5219),[12] 288 g. (8.2%) of intermediate, b. p. 82.7–84.2° (30 mm.), n^{25}_{D} 1.5171–1.5159;

[1a] Present address: Firestone Tire and Rubber Co., Akron, Ohio.

[1b] Ciamician and Silber, *Ber.*, **45**, 38 (1912).

(2) Pansegrau, U. S. Patent 1,815,985; *Chem. Abs.*, **52**, 5432 (1931).

(3) Loder, U. S. Patent 2,245,528; *ibid.*, **35**, 5912 (1941).

(4) Forrest and Frolich, U. S. Patent 1,902,550; *Chem. Zentr.*, **104**, I, 4038 (1933).

(5) Mares, U. S. Patent 2,120,672; *Chem. Abs.*, **32**, 5851 (1938).

(6) Henke and Benner, U. S. Patent 2,276,774; *ibid.*, **36**, 4521 (1942).

(7) Senseman and Stubbs, *Ind. Eng. Chem.*, **24**, 1184 (1932).

(8) Zaugg and Rapala, *Org. Syntheses*, **27**, 84 (1947).

(9) Ipatieff, Corson and Pines, THIS JOURNAL, **58**, 919 (1936).

(10) All of the analyses are microanalyses performed by the Oakwold Laboratories, Alexandria, Virginia.

(11) Meharg and Allen, THIS JOURNAL, **54**, 2920 (1932), describe the chlorination of ethylbenzene. They obtained two products boiling at 180° and 185°, respectively. The lower was shown to be *o*-chloroethylbenzene by oxidation to *o*-chlorobenzoic acid. They believed the higher boiling fraction was *p*-chloroethylbenzene contaminated with some of the meta isomer.

(12) Karabinos, Serijan and Gibbons, *ibid.*, **68**, 2107 (1946).

TABLE I

OXIDATION OF ALKYLBENZENES

Alkylbenzene oxidized	Acid produced	Time, hr.	Temp., °C.	Yield,[a] mole %	Conversion, mole %	M. p. of crude acid,[b] °C.	Recorded[c] m. p., °C.
Toluene	Benzoic	6	130–140	..	0	....	.....
o-Xylene	*o*-Toluic	6	140–150	55.7	19	104–105	107–108
m-Xylene	*m*-Toluic	7	140–145	48.7	20.3	95–101[d]	111–113
p-Xylene	*p*-Toluic	8	140–145	56.1	29.7[e]	181.0–182.5	181
Ethylbenzene	Benzoic	6.5	125–130	59.4	49.2	120.5–121.5	122
Cumene	Benzoic	6	130–160	67.8	41.9	119–121	122
2-Phenyloctane	Benzoic	6	150–155	40.5	10.9	116.5–118.5[f]	122
2-Phenyldecane	Benzoic	6	150–155	41.8	11.6	117.5–119.5	122
o-Chlorotoluene	*o*-Chlorobenzoic	6	150–155	..	1.4	....	.....
p-Chlorotoluene	*p*-Chlorobenzoic	6	150–155	..	0.0	....	.....
o-Chloroethylbenzene	*o*-Chlorobenzoic	6	150–160	58.2	15.7	139.5–140.5	142
m-Chloroethylbenzene	*m*-Chlorobenzoic	6	150–160	47.5	7.6	156–157	158
p-Chloroethylbenzene	*p*-Chlorobenzoic	7.5	145–155	43.6	26.9	242–244	243
p-Nitrotoluene	*p*-Nitrobenzoic	6	145–155	..	2.5	237–239	238
o-Nitroethylbenzene	*o*-Nitrobenzoic	6.5	150–155	..	0.4	....	.....
p-Nitroethylbenzene	*p*-Nitrobenzoic	6	150–160	62.3	14.1	241–243	238
Methyl *p*-cresyl ether	Anisic	4	150–160	25.3	7.2	184–185	184

[a] The percentage yield is mole per cent. of theoretical based on alkylbenzene unaccounted for. [b] All melting points are corrected. [c] The recorded melting points are all taken from Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1934 and 1943. [d] This acid had a neutral equivalent of 133.5 (theor. 136) and therefore contained about 3% of isophthalic acid. [e] In this experiment 2.2% of crude terephthalic acid was isolated by filtering the hot reaction mixture before the initial distillation, m. p. >352°, neut. equiv., 91.7 after digestion with boiling acetic acid. [f] After one recrystallization from benzene–hexane this acid melted at 120.5–121.5°.

572 g. (16.3%) of *p*-chloroethylbenzene, b. p. 84.2–84.6° (30 mm.) (184.5°),[12] n^{25}D 1.5152 (n^{20}D 1.5179)[12] and 21 g. of residue. The foreruns represented a 32.7% recovery of ethylbenzene contaminated with *o*-chloroethylbenzene and the residues represented 6.3% of dichloroethylbenzene. In subsequent runs the ratio of *o*- to *p*-chloroethylbenzene varied between 1.38 and 1.14.

Three samples of fractions from a previous, smaller run were oxidized to the corresponding acids with potassium permanganate according to the method of Clarke and Taylor.[13] The refractive indices of these fractions, together with the uncorrected melting point of the crude, dry unrecrystallized acids obtained therefrom, are shown below.

I	n^{25}D 1.5188	m. p. 134.5-135.5°
II	n^{25}D 1.5161	m. p. 233-234
III	n^{25}D 1.5153	m. p. 233-234

Pure *o*-chlorobenzoic acid melts at 142° and pure *p*-chlorobenzoic acid melts at 243°, both corrected.

m-**Chloroethylbenzene** was prepared as described previously.[14]

o- **and** *p*-**Nitroethylbenzene** were prepared by the method of Cline and Reid.[15]

Oxidations.—All of the oxidations were conducted in a 50 cm. by 45 mm. o. d. Pyrex tube in the bottom of which was sealed a perforated porcelain plate. Oxygen was introduced through this plate. The top of the tube was connected to a Dean and Stark trap, a bulb condenser and a spiral condenser in series. Heating was effected by means of an oil-bath. A safety shield always was placed in front of the reactor, although no explosions ever occurred.

In each run the charge consisted of 100 g. of the compound to be oxidized, 100 g. of *n*-butyric acid, 1.0 g. of cobalt hydrate or acetate, 1.0 g. of lead acetate and 1.0 g. of manganese acetate. Oxygen at the rate of 15-20 l. per hour was introduced under the conditions indicated in Table I. After the reaction mixture had cooled, it was transferred to a flask and distilled to remove the butyric acid. Where possible, this was separated from unreacted starting material by fractional distillation. When the boiling points were too close, the two substances were distilled together, the butyric acid washed out with alkali, and the recovered starting material redistilled. The original distillation residue was taken up in benzene, washed with hydrochloric acid to remove the catalyst, and then with sodium hydroxide to obtain the acid. Acidification of this last extract precipitated the desired acid, which was separated by filtration, washed with water and dried. These oxidations are summarized in Table I.

Summary

Catalytic oxidation in the liquid phase by oxygen using butyric acid as a solvent has been found to be a convenient method for converting certain alkylbenzenes to the corresponding aromatic acids.

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(13) Clarke and Taylor, *Org. Syntheses*, Coll. Vol. **II**, p. 135.

(14) Emerson and Lucas, THIS JOURNAL, **70**, 1180 (1948).

(15) Cline and Reid, *ibid.*, **49**, 3150 (1927).