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Polyisopropylbenzenes. I. Preparation and Properties of Two Di-, Two Tri-, and One Tetra-isopropylbenzene[1]

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Although much attention has been paid to various catalytic methods of introducing isopropyl groups into the benzene ring, comparatively little has been reported on the composition of the products. In the present work, which was carried out to prepare relatively large quantities of pure polyisopropylbenzenes for further investigation, benzene was propylated with propene in the presence of either 96% sulfuric acid[2] or anhydrous aluminum chloride.[3] The sulfuric acid product was heavily contaminated with alkyl sulfates, probably owing to the relatively high temperature (30–40°) used for propylation and to the continued propylation without intermediate purification. Attempts to remove these esters by washing with 96% sulfuric acid[2] were not successful but complete removal was obtained by distilling in a stream of steam and ammonia. Gaseous ammonia alone could also be used but sometimes gave a rather violent reaction.

Practically quantitative recovery of the individual constituents of the mixtures of isomers resulting from direct alkylation was effected by efficient fractional distillation, the composition of the products thus determined being summarized in Table I.

TABLE I

COMPOSITION OF THE ALKYLATION PRODUCTS

	H_2SO_4 catalyst at 30–40°	$AlCl_3$ catalyst at 60°
	Di-fraction	
1,3-di-, %	58.6	65.4
1,4-di-, %	41.4	34.6
	Tri-fraction	
1,2,4-tri-, %	83.7	nil
1,3,5-tri-, %	16.3	100.0
	Tetra-fraction	
1,2,4,5-tetra-, %	100	100

After recovering the greater part of the di-fraction as constant boiling 1,3- or 1,4-diisopropylbenzene, the initial, intermediate and final fractions were refractionated but no indication of the presence of a third (ortho-) isomer was obtained. Also, although all material rejected during the separation and purification of more than 10 kg. of 1,2,4,5-tetraisopropylbenzene was returned to some previous stage of the preparation, there was no indication of the accumulation of any other tetraisopropylbenzene or more highly alkylated product. It appears doubtful whether a polyisopropylbenzene containing three vicinal isopropyl groups can be prepared, at least by direct alkylation.

The presence of 1,4-diisopropylbenzene in the product from benzene, propene and 96% sulfuric acid[2] and in the product from benzene, isopropanol and 80% sulfuric acid[4] has been recorded. From the latter preparation 1,2,4-triisopropylbenzene was also obtained.[4] The only tetraisopropylbenzene which has been prepared with either sulfuric acid[2,5] or aluminum chloride[3] as catalyst is the 1,2,4,5-derivative. Both 1,3- and 1,4-diisopropylbenzenes have been observed in the diisopropylbenzene fraction using aluminum chloride. The latter was reported by Kirrman and Graves[6] using isopropanol as the propylating agent while the former was stated by Berry and Reid[3] to constitute about 65% of the diisopropylbenzene fraction obtained by propylation with propene at 70°, in close agreement with the present finding of 65.4% at 60°. The claim by Uhlhorn[7] that 1,2-diisopropylbenzene was a main constituent of the product from benzene and isopropyl chloride is considered to be in error. The hydrocarbon obtained was almost certainly the 1,4-derivative. The triisopropylbenzene obtained in the present work contained only the 1,3,5-derivative in agreement with Gustavson,[8] who used isopropyl chloride. The 1,2,4-derivative, reported by Berry and Reid[3] to occur to the extent of not more than 25%, was not present in this fraction.

Experimental

(A) Sulfuric Acid as Catalyst

(1) **Propylation.**—Benzene (constant boiling fraction from commercial pure benzol) was propylated with propene in four stages. In the first stage one liter (11.3 moles) of

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[1] Abstract from a thesis approved by the University of London for the degree of Ph.D.

[2] Ipatieff, Corson and Pines, THIS JOURNAL, **58**, 919 (1936).

[3] Berry and Reid, *ibid.*, **49**, 3142 (1927).

[4] Meyer and Bernhauer, *Monatsh.*, **53-54**, 721 (1929).

[5] Koch and Steinbrink, *Brennstoff Chem.*, **19**, 277 (1938).

[6] Kirrman and Graves, *Bull. soc. chim.*, [5] **1**, 1494 (1934).

[7] Uhlhorn, *Ber.*, **23**, 3142 (1890).

[8] Gustavson, *Compt. rend.*, **140**, 940 (1905).

benzene was stirred with 200 ml. of 96% sulfuric acid while propene (13.2 moles) was passed in at the rate of 0.775 mole per hour, the temperature being kept at 30–40° throughout this and the subsequent stages. When sufficient product had been accumulated about 60% of it was propylated in 1-liter batches using the same amount of propene as for the first stage, passed in at the same rate. In this case, however, the 96% sulfuric acid (200 ml.) was added dropwise during the first two hours of the run. About 60% of the second stage product was again propylated in exactly the same way. Finally about 50% of the third stage product was propylated until, owing to the separation of solid tetraisopropylbenzene, the mixture could no longer be stirred. As each batch of the first, second and third stage product was completed the oil was separated from the catalyst acid and washed with water and 10% sodium hydroxide. All products from the first three stages were mixed.

(2) **Removal of Sulfuric Esters.**—One liter of mixed product was heated to 110° in a 2-liter distillation flask and 20% aqueous ammonia was allowed to drip into a funnel, the stem of which extended to the bottom of the flask. The temperature was then raised at about 0.5° per minute and the rate of ammonia drip was adjusted so that there was always a smell of ammonia at the end of the condenser. When the temperature reached about 140° the liquid began to grow cloudy and at about 170° a pale brown flocculent solid, consisting chiefly of ammonium sulfate, separated. At this stage the distillation was stopped and, after cooling, the residue in the flask was washed with water, returned to the flask and distillation continued to a small residue, using ammonia only if, as was seldom the case, there were any signs of decomposition.

(3) **Separation of the Products.**—The purified product was distilled through a 12 inch bead-packed column into the following fractions: (1) up to 110°, benzene; (2) 110°–175°, isopropylbenzene; (3) 175–220°, diisopropylbenzenes; (4) 220–260°, triisopropylbenzenes; (5) residue above 260°, tetraisopropylbenzene. Fractions 3 and 4 were then systematically fractionated through a 180 × 2.5 cm. adiabatic column packed with 5-mm. glass balls, at 0.2 ml. per min. with a reflux ratio of about 40 to 1.

Fraction 3.—Three fractionations were required to separate the two isomers present. The distillation curve of the first of these is shown in Fig. 1. In the third distillation more than 95% of the charge was obtained as the separate isomers, each boiling over a range of 0.2°.

The lower-boiling isomer (8.48 g.) was refluxed for eighteen hours with 32 ml. of 96% nitric acid and 100 ml. of water and gave 5.82 g. (67%) of crude phthalic acid which was converted, by refluxing for three hours with 50 ml. of methyl alcoholic hydrogen chloride, into the dimethyl ester (5.83 g.), m. p. 62.5–66.5°. Two crystallizations from methanol gave a product, m. p. 67.6–68.2° and, in admixture with authentic dimethyl isophthalate (m. p. 67.3–68.1°), at 67.6–68.0°. Using the same procedure the higher boiling isomer (8.49 g.) gave 4.26 g. of crude dimethyl ester (42%), m. p. 137.5–139.8°, and m. p. 140.6–141.1° after one crystallization from methanol. Mixed with authentic dimethyl terephthalate (m. p. 141.0–141.4°) the m. p. was 140.9–141.4°.

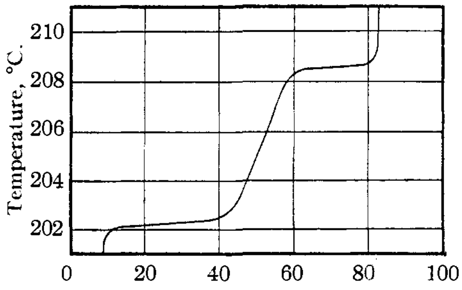

Fig. 1.—First fractionation of diisopropylbenzene fraction.

Fraction 4.—The first fractionation indicated that two constituents, boiling 3–4° apart, were present and this was confirmed on refractionation, the lower-boiling isomer constituting 16.3% by weight of the total. Eight fractionations were needed for complete separation. Distillation curves for the first and third are shown in Fig. 2.

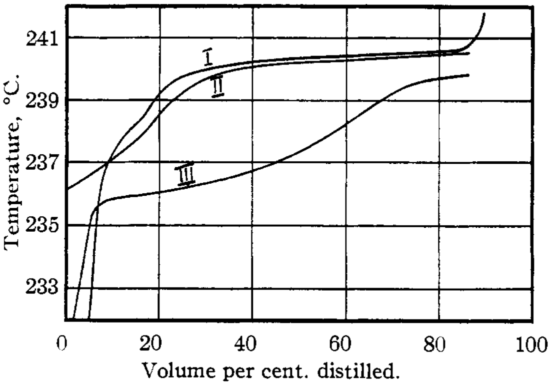

Fig. 2.—First (I) and third (II–III) fractionations of diisopropylbenzene fraction.

The lower-boiling isomer was identified as 1,3,5-triisopropylbenzene by comparison of its nitro derivative[9] with that of the triisopropylbenzene from the aluminum chloride preparation. The higher-boiling constituent was orientated as 1,2,4-triisopropylbenzene on the basis of its chemical behavior.[9]

Tetraisopropylbenzene.—The product from a fourth stage propylation was scraped out of the reaction flask into about 3 liters of cold water and the mixture stirred while heating to 90°, at which temperature the organic layer was completely liquid. After settling, the milky aqueous layer was siphoned off and the washing with water at 90° repeated until the water came away clear and practically free from acid. On cooling overnight the hydrocarbon layer formed an oily crystalline cake which was well crushed and filtered with suction until no more oil was removed, leaving a white, slightly oily solid. The filtrate was cooled to 0° overnight and again filtered, the second filtrate being used as part of a charge for fourth stage propylation. Two crystallizations from isopropanol gave long white needles, m. p. 118–119.3°. The literature[2] gives m. p. 119.0–119.4° for this product.

(B) Aluminum Chloride as Catalyst

(1) **Propylation.**—Propene (13.2 moles) was passed into a vigorously stirred mixture of isopropylbenzene (from

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(9) To be described in a later paper.

the sulfuric acid preparation) (12.2 moles) and powdered anhydrous aluminum chloride (100 g.) at 60° in the course of eighteen hours. . Absorption was practically complete. After cooling and settling for one hour the brown, viscous lower layer was discarded. The clear oil layer was washed with water, 10% sodium hydroxide and water.

About 50% of the product was propylated further in exactly the same manner.

(2) **Separation of the Products.**—This was carried out as for the sulfuric acid preparation.

Fraction 3.—The behavior of this fraction was similar to that of fraction 3 from the sulfuric acid product but the lower-boiling isomer was present to the extent of 65.4% by weight. The two isomers were identified as 1,3- and 1,4-diisopropylbenzenes by oxidation with boiling dilute nitric acid as previously described.

Fraction 4.—This fraction contained only one hydrocarbon which was obtained pure in a single distillation.

Potassium permanganate (60 g.) was added in small portions to a refluxing mixture of water (300 ml.) and the constituent of fraction 4 (8.47 g., 0.0415 mole) in the course of twenty-four hours and refluxing was continued for a further fourteen hours. The product was filtered, the filtrate acidified with hydrochloric acid, evaporated to 100 ml. and filtered. The residue on the filter was boiled with 100 ml. of 5% sodium carbonate, cooled and filtered. Acidification of the filtrate gave 1.72 g. (19.8%) of white precipitate which was esterified with boiling methyl alcoholic hydrogen chloride to 1.33 g. (65% from the acid) of white solid which, after one crystallization from methanol, melted at 142.5–143.7° and, in admixture with authentic trimethyl trimesate (m. p. 143.2–143.9°), at 142.9–143.5°.

(C) **Isomerization of 1,2,4-triisopropylbenzene.**—One liter (854 g., 4.18 moles) of the triisopropylbenzene fraction from the sulfuric acid preparation (16.3% by weight of 1,3,5- and 83.7% of 1,2,4-triisopropylbenzene) was stirred with 120 g. of finely powdered anhydrous aluminum chloride at 60° for ten hours. The product was decanted from aluminum chloride sludge, settled, a small amount of brown viscous complex removed and the oil washed with water, 10% sodium hydroxide and water. The yield was 771 g. (3.85 moles, 92.0%). Fractionation through the 180-cm. column gave the composition in mole per cent. as: benzene, trace; isopropylbenzene, 2.2%; diisopropylbenzene (containing approximately 70% of 1,3-di-), 19.3%; triisopropylbenzene, 64.3%; tetraisopropylbenzene, 14.3%. The triisopropylbenzene fraction was identified through its nitro derivative[9] as pure 1,3,5-triisopropylbenzene. The tetra- was a white solid, m. p., after one crystallization from isopropanol, 118.1–118.8°.

(D) **Physical Properties.**—Batches (900 ml.) of purified 1,3-di-, 1,4-di-, 1,2,4-tri- (sulfuric acid) and 1,3,5-tri- (aluminum chloride) were stirred vigorously with 20 g. of sodium at 150° for twelve hours, separated, washed with water, dried over calcium chloride and refractionated through the 180-cm. column taking out, in each case, a 200-ml. middle fraction. All these products contained less than 0.001% sulfur as determined by the lamp method with nephelometric estimation of sulfate. The physical properties are given below in the form of equations deduced from the experimental data by the method of least squares. A summary is given in Table II.

Densities were determined in a dilatometer of the type described by Robertson[10] but with a bulb at the bottom of one of the graduated limbs instead of a wide U-bend, and are all reported as g./ml., corrected to a vacuum basis. Vapor pressures were determined with a Cottrell boiler adapted for vacuum, temperatures being measured with a calibrated Anschütz thermometer and pressures read on a water-jacketed U-tube manometer by means of a cathetometer.

1,3-Diisopropylbenzene.—$d^t = 0.87292 - 0.000818t$ (six points from 21.0 to 71.2°, av. deviation = 0.0002, max. deviation = 0.0004). $n^t\text{D} = 1.49767 - 0.000464t$ (three points from 22.1 to 40.0°, av. deviation = nil, max. deviation = nil). $\text{Log}_{10}\, p\ (\text{mm.}) = 23.05915 - 3381.125/T - 4.88921 \log_{10} T$ (eighteen points from 152.6 to 202.9°, av. deviation = 0.24 mm., max. deviation = 0.85 mm.).

1,4-Diisopropylbenzene.—$d^t = 0.87261 - 0.000775t$ (six points from 19.6 to 71.0°, av. deviation = 0.00015, max. deviation = 0.0003). $n^t\text{D} = 1.49866 - 0.000457t$ (three points from 22.2 to 40.1°, av. deviation = 0.0001, max. deviation = 0.0001). $\text{Log}_{10}\, p\ (\text{mm.}) = 26.28825 - 3630.687/T - 5.92248 \log_{10} T$ (eighteen points from 156.7 to 210.1°, av. deviation = 0.27 mm., max. deviation = 0.73 mm.).

1,2,4-Triisopropylbenzene.—$d^t = 0.87897 - 0.000780t$ (eight points from 22.7 to 90.3°, av. deviation = 0.0001, max. deviation = 0.0003). $n^t\text{D} = 1.50115 - 0.000430t$ (three points from 22.2 to 40.2°, av. deviation = 0.0001, max. deviation = 0.0002).

1,3,5-Triisopropylbenzene.—$d^t = 0.87084 - 0.000807t$ (seven points from 20.9 to 80.8°, av. deviation = 0.0001, max. deviation = 0.0002). $n^t\text{D} = 1.49746 - 0.000461t$ (three points from 22.2 to 40.2°, av. deviation = nil, max. deviation = nil).

TABLE II

PROPERTIES OF THE POLYISOPROPYLBENZENES

	1,3-di-	1,4-di-	1,2,4-tri-	1,3,5-tri-
d^{20}	0.8566	0.8571[b]	0.8634[e]	0.8547
d^{30}	0.8484	0.8494	0.8556	0.8466
dd/dt × 10^6	818	775	780	807
$n^{20}\text{D}$	1.4884	1.4895[c]	1.4926[f]	1.4882
$n^{30}\text{D}$	1.4838	1.4850	1.4883	1.4836
dn/dt × 10^6	464	457	430	461
$MR\text{D}$ obs.	54.62	54.68	68.74	68.91
calcd. (E)[g]	54.02	54.02	67.87	67.87
calcd. (H)[h]	54.73	54.73	68.65	68.65
B. p. (760 mm.)	203.0[a]	210.3[d]	...	...
dt/dp (760) °C./mm.	0.0547	0.0560	...	...

Literature values, corrected when necessary to standard conditions, are—[a] 204°.[7] [b] 0.858,[2] 0.8555,[6] 0.8593,[11] 0.8563.[12] [c] 1.4912,[2] 1.4902,[6] 1.4903,[11] 1.4914.[12] [d] 206.3°,[2] 210°,[6] 205.9.[11] [e] 0.8620,[3] 0.8601,[6] 0.8610.[11] [f] 1.4877,[3] 1.4922,[6] 1.4918.[11] [g] Using atomic constants of Eisenlohr. [h] Using atomic constants of van der Hulst[13] for carbon (2.590) and hydrogen (1.025).

Acknowledgment.—The author is indebted to Trinidad Leaseholds, Ltd., for affording him facilities for carrying out, in the Company's research laboratories, the work described in this

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[10] Robertson, *Ind. Eng. Chem., Anal. Ed.*, **11**, 464 (1939).

[11] Slanina, Sowa and Nieuwland, THIS JOURNAL, **57**, 1547 (1935).

[12] McKenna and Sowa, *ibid.*, **59**, 470 (1937).

[13] Van der Hulst, *Rec. trav. chim.*, **54**, 518 (1935).

and subsequent papers and for permission to publish the results.

Summary

1. The composition of the di-, tri- and tetraisopropylbenzene fractions, obtained by the action of propene on benzene in presence of sulfuric acid or aluminum chloride, has been determined.

2. In presence of aluminum chloride, 1,2,4-triisopropylbenzene is converted to the 1,3,5-isomer with simultaneous formation of higher and lower homologs.

3. Two di-, two tri- and one tetra-isopropylbenzene have been isolated in a state of high purity and their physical properties determined.

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Some 5,5-Disubstituted Hydantoins

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Under the title "Some New 5,5-Disubstituted Hydantoins," Marsh and Lazzell[4] recently reported brief data for six hydantoins obtained by the Bucherer[5] method. Apparently, they were unaware of the fact that the synthesis by this method of one of these hydantoins had previously been reported.[6] Of course the mere question of priority of synthesis of 5-methyl-5-styrylhydantoin is of but little moment, but we have to offer other comments concerning their note. In the course of an extended study of the synthesis of hydantoins,[7] we had occasion to attempt the conversion of about one hundred and fifty aldehydes and ketones into the corresponding hydantoins; hence, we have investigated very nearly every common example of these two types of carbonyl compounds. Where we had tried to prepare the hydantoins listed by Marsh and Lazzell,[4] our results were not wholly corroborative of those cited. Our data suggest that Marsh and Lazzell in most cases did not succeed in their desire to obtain a pure sample of each hydantoin, and in certain instances may not have obtained the anticipated product.

We had not prepared a hydantoin from *p*-aminoacetophenone at the time of the appearance of the note by Marsh and Lazzell. However, the melting point of 100–101°, recorded by these investigators for 5-methyl-5-(*p*-aminophenyl) hydantoin seemed to us as highly improbable since it was lower than that of any hydantoin derivative which we had synthesized and, indeed, about seventy degrees below the melting point reported for a hydantoin derived from any other phenyl ketone. In our Laboratory this hydantoin has been prepared and found to melt at 186–188° (cor.).

The report of the preparation of a hydantoin, again of unexpectedly low melting point, from Michler's ketone was of particular interest to us because of the difficulty which we had in securing other than mere traces of this compound by means of the usual Bucherer procedure, in all probability because of the limited solubility of this ketone. However, using our new modification[8] of the Bucherer method we were able to synthesize the hydantoin in 38% yield. It is to be noted that we record a melting point of 276–280° (cor.) for our *white*-colored hydantoin, whereas Marsh and Lazzell reported a melting point of 136–137° for a product of *yellow* color.

Although we had not converted cyclohexyl methyl ketone into 5-cyclohexyl-5-methylhydantoin, the latter was prepared by catalytic hydrogenation of an authentic sample of 5-methyl-5-phenylhydantoin. The melting point of our crude reaction product is close to that listed by Marsh and Lazzell, but that of our purified hydantoin is significantly higher.

Considerable difficulty was encountered in our attempts[9] to obtain 5-methyl-5-(2-methylpropenyl) hydantoin in good yield from mesityl oxide, since

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[1] Parke, Davis and Company Research Fellow, 1939–1941.

[2] Research Assistant, University of Texas Research Institute, 1940–1941.

[3] Research Assistant, University of Texas Research Institute, 1941–1942.

[4] Marsh and Lazzell, This Journal, **62**, 1306 (1940).

[5] Bucherer and Lieb, *J. prakt. Chem.*, [2] **141**, 5 (1934).

[6] Before the Division of Medicinal Chemistry of the American Chemical Society at Baltimore, Md., April 9, 1939; see Henze and Long, This Journal, **63**, 1936 (1941).

[7] Henze and Speer, *ibid.*, **64**, 522 (1942); see also American Documentation Institute Document No. 1603, American Documentation Institute, 2101 Constitution Avenue, Washington, D. C.

[8] Henze and Long, *ibid.*, **63**, 1939, 1941 (1941).

[9] Henze, Thompson and Speer, *J. Org. Chem.*, in press.