acid (200 ml.) at 30°, a solution of the amine (20 g.) in acetone (100 ml.) was added dropwise during thirty minutes. Oxidation appeared to be almost instantaneous with slight evolution of heat. After standing at 30° for eighteen hours, the liquid was filtered and the solid residue washed with water until free from bichromate and dried *in vacuo* over calcium chloride. The resulting yellow-orange powder (19.5 g., 92.3%) had m. p. 157.5–159° and, after crystallization from 99% isopropanol, formed golden yellow needles, m. p. 159.5–160.4°.

Anal. Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 77.9, 78.3; H, 10.25, 10.34.

Summary

1. A study of the nitration of five polyisopropylbenzenes is described together with the conversion of the nitro derivatives to amines and meta nitration of the amines.

2. With acetyl nitrate in acetic acid at 30–45° extensive replacement of an isopropyl group takes place with 1,4-di- and 1,2,4,5-tetraisopropylbenzenes. The nitration proceeds normally with 1,3-di-, 1,2,4-tri- and 1,3,5-triisopropylbenzenes.

3. The product of nitrating 5-amino-1,2,4-triisopropylbenzene in 98% sulfuric acid is 6-nitro-4-amino-1,3-diisopropylbenzene which is also obtained from 4-amino-1,3-diisopropylbenzene by nitration in sulfuric acid.

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RECEIVED AUGUST 17, 1943

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TRINIDAD LEASEHOLDS, LTD.]

Polyisopropylbenzenes. III.[1] Sulfonyl Chlorides and Nitrosulfonyl Chlorides

BY A. NEWTON

The susceptibility to replacement of isopropyl groups in certain polyisopropylbenzenes, encountered in the nitration of these hydrocarbons and of their amino derivatives, is demonstrated even more markedly in the behavior of 1,2,4,5-tetraisopropylbenzene toward chlorosulfonic acid and in the nitration of 1,4-diisopropylbenzene-2-sulfonyl chloride and of 1,2,4-triisopropylbenzene-5-sulfonyl chloride. In all three cases very high yields of replacement products, containing no detectable amounts of normal products, were obtained.

The same product—1,2,4-triisopropylbenzene-5-sulfonyl chloride—was obtained from both 1,2,4-tri- and 1,2,4,5-tetraisopropylbenzenes, the effect of the isopropyl group displacement being clearly evident in the latter case by a much smaller evolution of heat. Both these hydrocarbons, and also 1,3,5-triisopropylbenzene, gave intense but transient red colorations with the first portions of chlorosulfonic acid. A similar coloration was observed by Kirrman and Graves[2] when the first two hydrocarbons were treated with fuming sulfuric acid. The product of nitration of 1,3-diisopropylbenzene-4-sulfonyl chloride was 6-nitro-1,3-diisopropylbenzene-4-sulfonyl chloride and was identical with the nitration product of 1,2,4-triisopropylbenzene-5-sulfonyl chloride.

All the nitration products contained small quantities of impurities which were extremely difficult to remove by crystallization but were preferentially adsorbed on activated alumina. In the nitration of 1,3,5-triisopropylbenzene-2-sulfonyl chloride this by-product amounted to about 4% of the total products. After purification its analysis corresponded fairly closely with a dinitrohexaisopropyldiphenyldisulfone.

Experimental Part

A. Chlorosulfonation of the Hydrocarbons.—Three equivalents of chlorosulfonic acid were added in the course of about ten minutes to a solution of about 85 g. of the hydrocarbon in 250 ml. of carbon tetrachloride (initially at 30–32°) with shaking. There was usually a temperature rise of 15–20°. After standing for thirty minutes the product was poured onto a large excess of crushed ice. The mixture was allowed to warm to room temperature, more carbon tetrachloride added when necessary to get the sulfonyl chloride into solution and the organic layer separated, washed with water and then shaken with water to which small quantities of 10% sodium hydroxide were added until, after vigorous shaking, the aqueous layer was just alkaline to methyl orange. The greater part of the solvent was distilled off and the residue evaporated to constant weight on a boiling water-bath. No sulfone could be detected in any of the sulfonyl chlorides.

Sulfonamides and Sulfonanilides.—In agreement with the experience of Huntress and Autenrieth,[3] the sulfonyl chloride from 1,2,4,5-tetraisopropylbenzene failed to react with aqueous ammonia or solid ammonium carbonate but reacted readily when a benzene solution was shaken with aqueous ammonia or treated with excess of aniline. All sulfonamides and sulfonanilides were prepared in this way. Analyses and melting points of these derivatives are listed in Table I.

Chlorosulfonation of 1,3-Diisopropylbenzene: 1,3-Diisopropylbenzene-4-sulfonyl Chloride (I).—The crude product (97.4% yield) was a clear, pale yellow oil which could not be crystallized by cooling to −20°. The liquid (93 g.; 0.357 mole) was hydrolyzed by heating to 80° with 465 ml. of 10% sodium hydroxide. Reaction took place quite suddenly at 60°. The solution was cooled, neutralized to phenolphthalein with 30% hydrochloric acid and 31 g. of sodium chloride added. After heating to complete solution and standing overnight, the white, silky needles which formed were filtered off, sucked as dry as possible and dehydrated at 120°; the yield was 50 g. (52.9%). One hundred grams of the sodium sulfonate was covered with 100 g. of phosphorus pentachloride and the reaction regulated by gentle shaking and cooling. After ten minutes the fluid mixture was heated to 100° for two hours, cooled and the pasty solid decomposed with excess of shaved ice. A pale brown oil separated and, on cooling

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[1] Paper No. II, THIS JOURNAL, 65, 2434 (1943).

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

[3] Huntress and Autenrieth, THIS JOURNAL, 63, 3446 (1941).

TABLE I

DERIVATIVES OF POLYISOPROPYLBENZENE SULFONYL CHLORIDES

Parent compound, -sulfonyl chloride	Formula	M. p., °C.	Per cent. composition Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
			Sulfonamides			
1,3-Diisopropylbenzene-4-	$C_{12}H_{19}O_2NS$[b,f]	144.2–144.9	59.72	59.9 59.8	7.94	8.02 7.98
1,4-Diisopropylbenzene-2-	$C_{12}H_{19}O_2NS$[d,f]	110.2–110.8	59.72	59.8 59.7	7.94	7.91 7.94
1,2,4-Triisopropylbenzene-5-	$C_{15}H_{25}O_2NS$[e,h]	154.8–155.7	63.57	63.9 63.5	8.89	9.10 8.91
1,3,5-Triisopropylbenzene-2-	$C_{15}H_{25}O_2NS$[d,i]	119.0–119.6	63.57	63.8 63.8	8.89	8.79 8.68
6-Nitro-1,3-diisopropylbenzene-4-	$C_{12}H_{18}O_4N_2S$[a]	192.4–192.8	50.33	50.5 50.4	6.34	6.39 6.13
4-Nitroisopropylbenzene-2-	$C_9H_{12}O_4N_2S$[k]	172.5–173.5	44.25	44.5 44.5	4.95	4.91 4.85
4-Nitro-1,3,5-triisopropylbenzene-2-	$C_{15}H_{24}O_4N_2S$	165.9–166.3	57.85	54.6 54.5	7.37	7.25 7.30
			Sulfonanilides			
1,3-Diisopropylbenzene-4-	$C_{18}H_{23}O_2NS$[c,g]	113.9–114.5	68.11	68.4 68.3	7.30	7.38 7.45
1,4-Diisopropylbenzene-2-	$C_{18}H_{23}O_2NS$	124.1–125.0	68.11	67.9 67.9	7.30	7.27 7.45
1,2,4-Triisopropylbenzene-5-	$C_{21}H_{29}O_2NS$	187.8–188.8	70.15	70.0 70.1	8.13	8.21 8.22
1,3,5-Triisopropylbenzene-2-	$C_{21}H_{29}O_2NS$	163.6–164.2	70.15	70.2 70.0	8.13	8.19 8.27
6-Nitro-1,3-diisopropylbenzene-4-	$C_{18}H_{22}O_4N_2S$[j]	169.8–170.6	59.64	59.7 59.7	6.12	6.18 6.04
4-Nitroisopropylbenzene-2-	$C_{15}H_{16}O_4N_2S$	192.8–193.7	56.23	56.4 56.5	5.03	5.18 5.24
4-Nitro-1,3,5-triisopropylbenzene-2-	$C_{21}H_{28}O_4N_2S$[j]	182.4–183.3	62.34	62.6 62.5	6.98	7.11 7.22

All of the nitro compounds are pale yellow in color, except as noted; the other derivatives are colorless. Crystallizations were carried out in 99% isopropanol, unless otherwise stated. [a] Greenish-yellow leaflets. [b] Crystallized from 67% isopropanol. [c] Crystallized from 75% isopropanol by seeding. [d] Crystallized from 50% isopropanol. [e] Crystallized from iso-octane. [f] Flakes. [g] Thick needles. [h] Small silky needles. [i] Fine needles. [j] Hexagonal tables. [k] Square tables.

to 5°, crystallized. It was filtered off, washed with water and dried *in vacuo* over calcium chloride. The product (92.3%), which was not purified further, had m. p. 35–40°.

Chlorosulfonation of 1,4-Diisopropylbenzene: 1,4-Diisopropylbenzene-2-sulfonyl Chloride (II).—Removal of the solvent left 95.3% of a very pale yellow, viscous liquid which, on cooling in ice for a few minutes, gave a white crystalline mass, m. p. 48.5–53°. This crystallized from iso-octane in rosets of white needles, m. p. 52.5–53.0°.

Anal. Calcd. for $C_{12}H_{17}O_2SCl$: C, 55.27; H, 6.57; Cl, 13.60. Found: C, 55.4, 55.2; H, 6.60, 6.62; Cl (by hydrolysis), 13.68, 13.65.

Chlorosulfonation of 1,2,4-Triisopropylbenzene: 1,2,4-Triisopropylbenzene-5-sulfonyl Chloride-A (III).—On addition of the first few drops of chlorosulfonic acid to the hydrocarbon solution an intense purple-red color developed which faded to salmon-pink and then to pale orange as more acid was added. The color remained unchanged until two equivalents of acid had been added when it became red and finally reddish purple. There was a temperature rise of 25°. The crude product (99.3%) had m. p. 139–141.5°, and crystallized from iso-octane in compact balls of white needles, m. p. 141.5–142.2°.

Anal. Calcd. for $C_{15}H_{23}O_2SCl$: C, 59.47; H, 7.66; Cl, 11.71. Found: C, 59.2, 59.5; H, 7.72, 7.69; Cl (by hydrolysis), 11.72, 11.73.

Chlorosulfonation of 1,3,5-Triisopropylbenzene: 1,3,5-Triisopropylbenzene-2-sulfonyl Chloride (IV).—The first few drops of chlorosulfonic acid developed a bright cherry red color which faded and then deepened to dark purple-red with further addition. The crude product (98%) was a white crystalline mass, m. p. 92–95.5°. Two crystallizations from iso-octane gave long colorless prisms, m. p. 97.2–98.4°.

Anal. Calcd. for $C_{15}H_{23}O_2SCl$: C, 59.47; H, 7.66; Cl, 11.71. Found: C, 59.6, 59.6; H, 7.44, 7.62; Cl (by hydrolysis), 11.64, 11.70.

Chlorosulfonation of 1,2,4,5-Tetraisopropylbenzene: 1,2,4-Triisopropylbenzene-5-sulfonyl Chloride-B.—This hydrocarbon gave initially an intense crimson with the reagent. The temperature rise under conditions closely similar to those for 1,2,4-triisopropylbenzene was 10°. On shaking, after diluting the reaction product, a persistent creamy emulsion was formed, presumably because of the presence of isopropyl hydrogen sulfate in the aqueous layer. The crude product (97.0%, mol. wt. 303) melted at 137–140°. After crystallization from iso-octane the m. p. was 141.0–141.9° and 140.8–141.6° in admixture with the A compound (III). This compound, incorrectly described as 1,2,4,5-tetraisopropylbenzene-3-sulfonyl chloride, was prepared by Huntress and Autenrieth,[3] who found m. p. 141.5–142°.

Anal. Calcd. for $C_{15}H_{23}O_2SCl$: Cl, 11.71. Calcd. for $C_{18}H_{29}O_2SCl$: Cl, 10.28. Found: Cl (by hydrolysis), 11.74, 11.70.

The sulfonamide and sulfonanilide of this compound gave identical melting points with similar derivatives from III and mixed melting points showed no depression. The literature[3] gives m. p. 154.5–155° for the sulfonamide of the B compound.

B. Nitration of the Sulfonyl Chlorides.—The sulfonyl chloride was added in the course of about ten minutes to a large excess (17–40 equivalents) of well-stirred 96% nitric acid at 0–5°. After stirring for about ten minutes longer the product was poured in a thin stream onto a large quantity of shaved ice with thorough mixing to prevent local overheating. The resulting suspension was kept for two to three hours, filtered, the solid washed very thoroughly with cold water and dried *in vacuo* over calcium chloride.

Nitration of 1,3-Diisopropylbenzene-4-sulfonyl Chloride (*I*): 6-Nitro-1,3-diisopropylbenzene-4-sulfonyl Chloride-A (V).—The reaction product was a clear yellow liquid which, on dilution, deposited a very pale yellow solid (80.8%), m. p. 91–99°. Two crystallizations from iso-octane gave pale yellow flakes, m. p. 102.1–103.0°. The hot solution of the crude product deposited a small amount of flocculent solid on cooling and before crystallizing.

Anal. Calcd. for $C_{12}H_{16}O_4NSCl$: C, 47.13; H, 5.28; Cl, 11.60. Found: C, 47.3, 47.2; H, 5.21, 5.25; Cl (by hydrolysis), 11.63, 11.55.

Nitration of 1,4-Diisopropylbenzene-2-sulfonyl Chloride (II). 4-Nitroisopropylbenzene-2-sulfonyl Chloride.—The clear yellow-orange reaction product deposited pale yellow granules on dilution (100%, mol. wt. 264), m. p. 95–100°. It was necessary to grind this product to a smooth paste with water to get rid of nitric acid completely. On crystallizing from hot iso-octane a thin layer of crystals contaminated with a trace of sparingly soluble, yellow-orange impurity separated first, followed by a thick layer of very pale, greenish-yellow crystals which, on recrystallization, had m. p. 101.6–102.1°. The mixed m. p. with 6-nitro-1,3-diisopropylbenzene-4-sulfonyl chloride-A (V) was 70–81°.

Anal. Calcd. for $C_{12}H_{16}O_4NSCl$: C, 47.13; H, 5.28; Cl, 11.60. Calcd. for $C_9H_{10}O_4NSCl$: C, 40.99; H, 3.82; Cl, 13.45. Found: C, 41.2, 41.0; H, 3.85, 3.80; Cl (by hydrolysis), 13.30, 13.33.

Nitration of 1,2,4-Triisopropylbenzene-5-sulfonyl Chloride (III). 6-Nitro-1,3-diisopropylbenzene-4-sulfonyl Chloride-B.—The yield of crude product, m. p. 87–98°, was 100% (mol. wt., 306). A cold solution of this material (20.2 g.) in 50–90° petroleum ether (100 ml.) was poured through a 28 × 2 cm. column of 40–60 mesh activated bauxite. The column was washed with 200 ml. of petroleum ether followed by acetone, the filtrate being collected altogether until the acetone, the movement of which was indicated by a warm zone, had nearly reached the bottom of the column. Evaporation of the petroleum ether solution gave pale greenish-yellow crystals (17.9 g.), m. p. 101.5–102.5° or 101.8–102.3° after recrystallization from iso-octane. In admixture with the A compound (V) the m. p. was 101.9–102.8°.

Anal. Calcd. for $C_{15}H_{22}O_4NSCl$: Cl, 10.19. Calcd. for $C_{12}H_{16}O_4NSCl$: Cl, 11.60. Found: Cl (by hydrolysis), 11.62, 11.59.

The sulfonamide and sulfonanilide of this compound gave the same melting points as similar derivatives from V and mixed melting points showed no depression.

Nitration of 1,3,5-Triisopropylbenzene-2-sulfonyl Chloride. 4-Nitro-1,3,5-triisopropylbenzene-2-sulfonyl Chloride.—The reaction product was a suspension of pale yellow granular solid which on dilution gave 98.5% of pale yellow powder, m. p. 150.5–156.5°. Two crystallizations from iso-octane gave material of sharp, constant m. p., 152.4–153.4°, which contained only 8.70% of hydrolyzable chlorine (calcd., 10.19%). A solution of 45.2 g. of crude product in 700 ml. of 50–90° petroleum ether was filtered through a column of activated bauxite as described for the nitro derivative from 1,2,4-triisopropylbenzene-5-sulfonyl chloride. The petroleum ether filtrate and washings gave 40.3 g. of very faintly yellow tinted crystals, m. p. 157.5–158.0°, which crystallized from petroleum ether in colorless rhombic tables, m. p. 157.8–158.4°.

Anal. Calcd. for $C_{15}H_{22}O_4NSCl$: C, 51.79; H, 6.37; Cl, 10.19. Found: C, 51.5, 51.7; H, 6.45, 6.28; Cl (by hydrolysis), 10.19, 10.10.

Subsequent washing of the adsorption column with acetone gave 1.7 g. of pale yellow crystals slightly contaminated with a yellow resinous material. The m. p. was 144.5–152°. The combined product from a number of runs was boiled with 1% sodium hydroxide for two hours, filtered off, washed with water and crystallized from 99% isopropanol. There were obtained pale yellow crystals, m. p. 150.2–151.1°.

Anal. Calcd. for $C_{30}H_{44}O_8N_2S_2$: C, 57.67; H, 7.10. Found: C, 58.2, 57.8; H, 6.84, 6.87.

Summary

1. The chlorosulfonation of 1,4-diisopropylbenzene (in contrast to nitration) gives only the normal product—the 2-sulfonyl chloride. Both 1,2,4-tri- and 1,2,4,5-tetraisopropylbenzenes give almost the theoretical yields of the 5-sulfonyl chloride of the former hydrocarbon.

2. On nitration both 1,3-diisopropylbenzene-4-sulfonyl chloride and 1,2,4-triisopropylbenzene-5-sulfonyl chloride give high yields of 6-nitro-1,3-diisopropylbenzene-4-sulfonyl chloride and no other product. The 2-sulfonyl chloride of 1,4-diisopropylbenzene nitrates to give 4-nitroisopropylbenzene-2-sulfonyl chloride.

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RECEIVED MAY 17, 1943

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TRINIDAD LEASEHOLDS, LTD.]

Polyisopropylbenzenes. IV. Bromo Derivatives, Nitriles, Amides and Carboxylic Acids[1]

BY A. NEWTON

In connection with an investigation of the aluminum chloride-catalyzed reaction of polyisopropylbenzenes with acetic anhydride, it was necessary to have available polyisopropylbenzene carboxylic acids of known orientation. This paper describes the preparation of these substances from the hydrocarbons via the bromo derivatives, nitriles and amides.

Bromination of 1,3-di-, 1,4-di-, 1,2,4-tri-, 1,3,5-tri- and 1,2,4,5-tetraisopropylbenzenes was carried out by the procedure of Fuson and Horning.[2] Two monobromo derivatives were formed from 1,3-diisopropylbenzene and were separated by vacuum fractionation. The lower-boiling (77% of the monobromides) were shown to be the 4-isomer by conversion to an amide (III) identical with that (VII) obtained from 4-amino-1,3-diisopropylbenzene.[3] No indication of isopropyl group replacement was obtained in the bromination of 1,4-diisopropylbenzene. The monobromo derivative (A) from 1,2,4-triisopropylbenzene had physical constants agreeing well with those of a monobromo derivative (B) prepared from 1,2,4-triisopropylbenzene-5-sulfonic acid. A monobromo derivative (C) from 1,2,4,5-tetraisopropylbenzene could not be freed completely from a small amount of unchanged hydrocarbon by efficient fractional distillation. The three compounds, A, B and C, were carried separately through the same series of reactions and gave identical amides (VIII, X and XII) and carboxylic acids (IX, XI, XIII), establishing the orientation of the bromide atom at the expected 5-position.

Bromo derivatives were converted into nitriles

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(1) Paper No. III, Newton, THIS JOURNAL, 65, 2439 (1943).

(2) Fuson and Horning, *ibid.*, 62, 2962 (1940).

(3) Newton, *ibid.*, 65, 2434 (1943).