2,3-Diphenyl-6,7-dimethoxyquinoxaline.—A mixture of equimolecular quantities of 4,5-diaminoveratrole and benzil, dissolved in alcohol, was warmed for ten minutes. Lustrous plates promptly separated. The mixture when cold was further cooled in an ice-pack and filtered. The crude product was crystallized from dilute acetic acid and washed with a small amount of Skellysolve D. Pale yellow plates were thus obtained, m. p. 251–252°; yield, over 50%.

Anal. Calcd. for $C_{22}H_{18}O_2N_2$: C, 77.2; H, 5.3. Found: C, 77.3; H, 5.3.

Summary

1. 3-Nitro-4-aminoveratrole, when subjected to an ordinary Skraup reaction, yields no quinoline derivative, but rearranges to 5-nitro-4-aminoveratrole.

2. The same change can be brought about by digestion of the 3-nitro compound for one and one-half hours at 140–160° with a mixture of phosphoric and glacial acetic acids.

3. It may be explained by the migration of the nitro group, or of one of the methoxyls.

4. A number of veratrole derivatives are described, some new, others old but prepared by new methods.

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Polyisopropylbenzenes. II.[1a] Nitro and Amino Derivatives[1b]

BY A. NEWTON

The nitration of an isopropyl substituted aromatic hydrocarbon has been studied extensively only in the case of *p*-cymene,[2,3] where it was found that, in addition to the main product, 2-nitrocymene, *p*-nitrotoluene was formed in about 8% yield. Many other cases have been reported in which an alkyl group in a polymethylbenzene,[4,5,6] polyethylbenzene,[7] polychlorocymene[8,9] or polychlorocumene[8,9] is replaced by an entering substituent, usually a nitro group. In almost all these cases, however, the replacement was effected by the use of rather severe conditions and led to the formation of a penta- or hexa-substituted benzene. The present study of the nitration of five polyisopropylbenzenes has provided three cases in which, under relatively mild conditions, the main product of mononitration is formed by replacement of an isopropyl group.

The nitrations described in the experimental part may be divided into three types.

Type 1.—Reactions in which the main product was formed by replacement of an isopropyl group by the entering nitro group. Mononitro derivatives from 1,4-diisopropylbenzene with acetyl nitrate contained the replacement product —4-nitroisopropylbenzene (X)—and the normal product—2-nitro-1,4-diisopropylbenzene (XI)—in the mole ratio 1.44 to 1. With mixed acids at 0–6° the ratio was 4.78 to 1. Tetraisopropylbenzene gave only 15% of the normal products—3-nitro-1,2,4,5-tetraisopropylbenzene (XXVII)—and 83% of 5-nitro-1,2,4-triisopropylbenzene at 45°, while at 80° the latter was the sole product. Nitration of 5-amino-1,2,4-triisopropylbenzene (XVIII) gave only 6-nitro-4-amino-1,3-diisopropylbenzene (VIB). In all three cases the condition obtained that a pair of para isopropyl groups was present, one of which occupied a position favorable, with respect to the directing effect of all other groups present, for the entry of the nitro group.

Type 2.—Reactions in which no replacement was observed though the above condition was fulfilled. This type comprises the nitration of 1,2,4-triisopropylbenzene which gave 5-nitro-1,2,4-triisopropylbenzene (XVIIIA) and of 2-amino-1,4-diisopropylbenzene which gave a nitroaminodiisopropylbenzene (XVI). The condition, while probably necessary, is evidently not sufficient.

Type 3.—Reactions in which the condition was not fulfilled and in which no replacement was observed. The reactions were the mononitration of 1,3-di- and 1,3,5-triisopropylbenzenes, the dinitration of the former and the trinitration of the latter and the nitration of 4-amino-1,3-diisopropylbenzene (V) and of 2-amino-1,3,5-triisopropylbenzene (XXIV).

The main relationships among these substances are summarized in Chart I. The constitutions of the derivatives are those that would be expected on the basis of known orientating effects and are confirmed or supported by the following additional evidence. The acetyl and benzoyl derivatives of 4-aminoisopropylbenzene (XII) have melting points corresponding with the known products. Tetraisopropylbenzoquinone (XXIX) was obtained by oxidation of 3-amino-1,2,4,5-tetraisopropylbenzene (XXVIII). Oxidation of 2-nitro- (I), 4-nitro- (II) and 4,6-dinitro-1,3-diisopropylbenzene (III) and of 2-nitro-1,4-diisopropylbenzene gave acids that formed methyl or ethyl esters

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[1a] Abstract from a thesis approved by the University of London for the degree of Ph.D.: Paper No. 1, THIS JOURNAL, **65**, 320 (1943).

[1b] Original manuscript received July 6, 1942.

[2] Mann, Montonna and Larian, *Ind. Eng. Chem.*, **28**, 598 (1936).

[3] Kobe and Doumani, *ibid.*, **31**, 257 (1939).

[4] Smith and Harris, THIS JOURNAL, **57**, 1289 (1935).

[5] Tohl and Tripke, *Ber.*, **28**, 2463 (1895).

[6] Smith and Kiess, THIS JOURNAL, **61**, 989 (1939).

[7] Smith and Guss, *ibid.*, **62**, 2635 (1940).

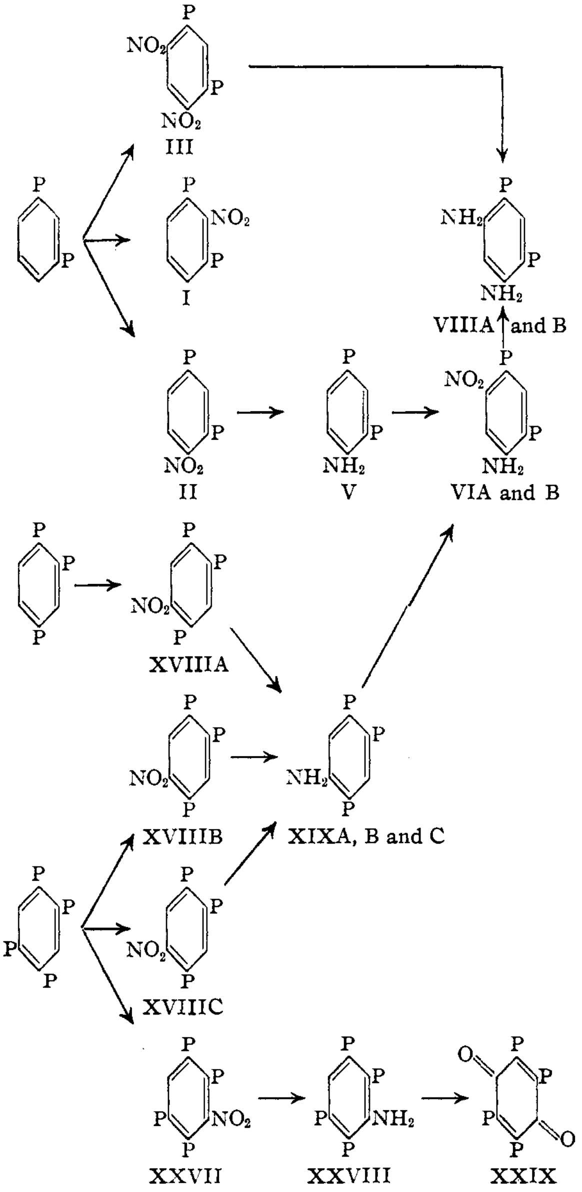
[8] Qvist and Holmberg, *Acta Acad. Aboensis, Math. et Phys.*, **6**, No. 14, 3 (1932); *C. A.*, **27**, 5726 (1933).

[9] Qvist and Salo, *ibid.*, **8**, No. 4, 310 (1934); *C. A.*, **29**, 6884 (1935).

with the correct melting points for derivatives of known nitrophthalic acids. No definite oxidation product could be obtained from 5-nitro-1,2,4-triisopropylbenzene (XVIIIA or B). However, the constitution of XVIIIA is established by the conversion of the corresponding amine (XIXA) into 6-nitro-4-amino-1,3-diisopropylbenzene (VIB), the orientation of which follows from its relation to 4,6-dinitro-1,3-diisopropylbenzene (III) through the diamine (VIIIA and B). Two forms of 5-nitro-1,2,4-triisopropylbenzene were obtained. The first (XVIIIA), from 1,2,4-triisopropylbenzene, was a homogeneous liquid as indicated by the constancy of refractive index of its distillation fractions. The second (XVIIIB), a low melting solid, was obtained from 1,2,4,5-tetraisopropylbenzene together with a product (XVIIIC) which appeared to be a mixture of the two. Both gave the same amine (XIXA and B) on reduction. These two products are being investigated further.

CHART I

—P ≡ —CH(CH_3)$_2$



Experimental

Experimental Methods

Mononitration of Hydrocarbons.—The following method was used for all hydrocarbons unless otherwise stated. An excess (1.24–2.05 equivalents) of 96% nitric acid was added to a mechanically stirred solution of the hydrocarbon (110–350 g.) in acetic acid (400 ml.) containing enough acetic anhydride (100–300 ml.) to ensure absence of free water throughout the reaction. The reaction mixture was cooled in running water and the nitric acid was added at such a rate that the maximum temperature was 45–50°. After standing for twenty-four hours (unless otherwise noted) the product was diluted with a large excess of water, petroleum ether was added to decrease the density of the nitro derivative and the solution was washed thoroughly with dilute sodium hydroxide or ammonia and finally with water. The dried product was distilled to remove solvent and the residue fractionated at 5–10 mm. pressure through a 180 × 2.5 cm. adiabatic column. In all fractionations the distillate was collected in small fractions which were recombined on the basis of refractive index and, if two substances were found to be present, each was separately refractionated. Samples for analysis and determination of physical constants were taken as middle fractions on plateaux of constant refractive index.

Oxidation of Nitro Derivatives.—The substance (2.5 g.) was heated with 70% nitric acid (20 ml.) and water (12 ml.) at 180° for ten hours in a flask with a capillary stopper.[10] The flask was contained in a rotating autoclave charged with hydrogen to an initial pressure of 1000 lb./sq. in. The residual liquid in the flask was evaporated to dryness and the solid esterified with methanol or ethanol. The yield of crude acid was 50–60% for the mononitrodiisopropylbenzenes and 13% for dinitrodiisopropylbenzene.

Reduction of Nitro Derivatives.—The purified nitro compound, dissolved in about twice its weight of 99% isopropanol, was reduced with hydrogen (initial pressure about 1200 lb./sq. in., maximum temperature 100°) in presence of 5–10% by weight of Raney nickel in a rotating autoclave. Reduction was continued for four to ten hours after the pressure ceased to fall. The product was filtered, isopropanol removed by distillation and, in the case of liquid monoamines, the product was fractionated at 5–10 mm. through the 180 cm. column at 0.33 ml./min. with a reflux ratio of about 20 to 1.

Nitration of Amines.—About 10 g. of amine was dissolved in 100 ml. of 98% sulfuric acid, the solution cooled to 0–5° and about 1.1 equivalents of 70% nitric acid added at 5–10°. After standing for one hour the product was poured onto 500 g. of shaved ice, the nitroamine sulfate filtered off, shaken with excess 2% ammonia and benzene, the benzene layer washed with water and the crude nitroamine recovered by evaporation of the solvent.

Physical Properties.—The following physical properties are reported for all liquid products: (1) d^{20}, g./ml. *in vacuo*, (2) $-\mathrm{d}d/\mathrm{d}t \times 10^6$ (20–30°), (3) $n^{20}\mathrm{D}$, (4) $-\mathrm{d}n/\mathrm{d}t \times 10^6$ (20–45°). M. p.'s are corrected unless otherwise stated.

Derivatives of 1,3-Diisopropylbenzene

Nitration of 1,3-Diisopropylbenzene: 2-(I) and 4-(II) Nitro-1,3-diisopropylbenzene.—The nitration was rapid, being apparently finished about one hour after completing the addition of nitric acid, and gave 95.1% of orange oil containing 1% of unnitrated hydrocarbon, 74% of lower-boiling and 25% of higher-boiling mono nitro derivative and traces of poly nitro compounds.

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[10] Grosse, THIS JOURNAL, 60, 212 (1938).

Lower-boiling isomer (II). Physical properties: (1) 1.0387, (2) 846, (3) 1.5308, (4) 420.

Anal. Calcd. for $C_{12}H_{17}O_2N$: C, 69.53; H, 8.27. Found: C, 69.6, 69.3; H, 8.16, 8.28.

The oxidation product from this substance gave a methyl ester, m. p. 86.0–86.8°; literature[11] value for 4-nitro-dimethylisophthalate is 87–88.5°.

Higher-boiling isomer (I). Physical properties: (1) 1.0243, (2) 878, (3) 1.5161, (4) 419.

Anal. Calcd. for $C_{12}H_{17}O_2N$: C, 69.53; H, 8.27. Found: C, 69.8, 69.6; H, 8.29, 8.00.

The oxidation product gave a methyl ester, m. p. 135.3–135.9°; literature[12] value for 2-nitro-dimethylisophthalate is 135°.

Nitration of 1,3-Diisopropylbenzene: 4,6-Dinitro-1,3-diisopropylbenzene (III).—A mixture of the hydrocarbon (18.7 g.) and 98% sulfuric acid (120 ml.) was stirred at 70° while 16.0 ml. of 96% nitric acid (3.17 equivalents) was added in the course of eighty minutes. After stirring for a further ten minutes the product was cooled and poured onto ice. The resulting finely divided, pale yellow solid was filtered off after two hours, washed with water, 20% ammonia and water and dried *in vacuo* over calcium chloride. It weighed 14.5 g. and melted indefinitely over a wide range. One crystallization from isopropanol gave 8.2 g. of pale yellow flakes, m. p. 76.9–77.7°. The melting point was not changed on recrystallization. A further 3.7 g. of less pure product was recovered from the filtrate.

Anal. Calcd. for $C_{12}H_{16}O_4N_2$: C, 57.13; H, 6.39. Found: C, 57.4, 57.2; H, 6.22, 6.20.

The oxidation product of III gave an ethyl ester, m. p. 124.5–125.2°. The literature[13] value for 4,6-dinitrodiethylisophthalate is 124°.

2-Amino-1,3-diisopropylbenzene (IV).—From 2-nitro-1,3-diisopropylbenzene (I) the crude amine was obtained in 94.9% yield. After purification it was a colorless oil. Physical properties: (1) 0.9367, (2) 790, (3) 1.5330, (4) 429.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.29; H, 10.81. Found: C, 81.3, 81.3; H, 10.63, 10.83.

All attempts to prepare an acetyl derivative gave only a colorless, viscous oil, apparently a diacetyl compound.

Benzoyl Derivative.—White crystalline powder from isooctane, m. p. 106.0–106.7°. This substance frequently separated as a liquid which crystallized on standing.

Anal. Calcd. for $C_{19}H_{23}ON$: C, 81.10; H, 8.23. Found: C, 80.9, 81.2; H, 8.01, 8.34.

4-Amino-1,3-diisopropylbenzene (V).—Reduction of 4-nitro-1,3-diisopropylbenzene (II) gave 95.8% of crude amine as a dark brown oil. The distilled material was colorless but soon became pale brownish-yellow. Physical properties: (1) 0.9285, (2) 812, (3) 1.5275, (4) 454.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.29; H, 10.81. Found: C, 81.3, 81.3; H, 10.65, 10.77.

Acetyl Derivative.—White needles from iso-octane, m. p. 108.3–109.0°. Fourteen per cent. of the crude product of acetylation at room temperature was a colorless, viscous oil which was hydrolyzed back to the amine by refluxing with 30% hydrochloric acid and was apparently a diacetyl derivative. At higher temperatures the amount of this material increased greatly.

Anal. Calcd. for $C_{14}H_{21}ON$: C, 76.66; H, 9.65. Found: C, 76.4, 76.4; H, 9.59, 9.56.

Benzoyl Derivative.—Fine white needles from iso-octane–isopropanol, m. p. 162.8–163.4°.

Anal. Calcd. for $C_{19}H_{23}ON$: C, 81.10; H, 8.23. Found: C, 81.4, 81.0; H, 8.46, 8.42.

Nitration of 4-Amino-1,3-diisopropylbenzene (V), 6-Nitro-4-amino-1,3-diisopropylbenzene-A (VIA).—From 11.0 g. of amine there was obtained 9.9 g. of very oily, dark red crystals which, after draining on a filter, left 6.95 g. of dry product, m. p. 69.5–74.5°. Two crystallizations from petroleum ether gave shining brownish orange flakes, m. p. 75.3–76.1°.

Anal. Calcd. for $C_{12}H_{18}O_2N_2$: C, 64.84; H, 8.16. Found: C, 65.0, 64.6; H, 8.23, 8.02.

Acetyl Derivative (VIIA).—Very pale yellow needles from 50% acetic acid, m. p. 116.2–117.0°.

Anal. Calcd. for $C_{14}H_{20}O_3N_2$: C, 63.61; H, 7.63. Found: C, 63.8, 63.7; H, 7.69, 7.65.

4,6-Diamino-1,3-diisopropylbenzene-A (VIIIA).—Reduction of 49.6 g. of 6-nitro-4-amino-1,3-diisopropylbenzene-A (IX) gave 41.5 g. (96.9%) of dark green, crystalline diamine, m. p. 67–71°. Filtration of a petroleum ether solution of the crude diamine through activated bauxite removed 2.2 g. of brownish yellow material mainly consisting of unreduced nitroamine. The pale yellow purified diamine (38.7 g.) crystallized from petroleum ether in very pale yellow flakes, m. p. 72.6–72.9°.

Anal. Calcd. for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48. Found: C, 74.8, 74.9; H, 10.62, 10.60.

Diacetyl Derivative (IXA).—Small white needles from glacial acetic acid, m. p. 320.5–321.5° (uncor.).

Anal. Calcd. for $C_{16}H_{24}O_2N_2$: C, 69.53; H, 8.75. Found: C, 69.6, 69.2; H, 8.90, 8.88.

4,6-Diamino-1,3-diisopropylbenzene-B (VIIIB).—In reducing 4,6-dinitro-1,3-diisopropylbenzene (III), hydrogen corresponding to one nitro group was absorbed at room temperature, the second nitro group requiring a temperature of 60°. The crude, dark green product was obtained in 91.4% yield and was purified by filtration through bauxite followed by crystallization from petroleum ether to give pale yellow flakes, m. p. 72.6–73.0° alone and 72.6–73.0° in admixture with the A compound (VIIIA).

Diacetyl Derivative (IXB).—M. p. 320.5–321.5° (uncor.) alone and 320.5–322° (uncor.) in admixture with the A compound (IXA).

Derivatives of 1,4-Diisopropylbenzene

Nitration of 1,4-Diisopropylbenzene: 4-Nitroisopropylbenzene (X) and 2-Nitro-1,4-diisopropylbenzene (XI).—Nitration was comparatively slow, heat of reaction being still detectable after six hours of standing at 30–35°. Much acidic material was removed by the sodium hydroxide washes, leaving 88.6% of orange-yellow oil which contained 65 mole % of unchanged hydrocarbon, 49.7% of a low-boiling mono nitro derivative (X), 33.7% of a high-boiling mono nitro derivative (XI) and 10.1% of heavy material.

Lower-boiling mono nitro derivative, physical properties: (1) 1.0830, (2) 892, (3) 1.5361, (4) 478.

Anal. Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71. Calcd. for $C_{12}H_{17}O_2N$: C, 69.53; H, 8.27. Found: C, 65.7, 65.6; H, 6.62, 6.89.

Higher-boiling mono nitro derivative, physical properties: (1) 1.0267, (2) 858, (3) 1.5177, (4) 437.

Anal. Calcd. for $C_{12}H_{17}O_2N$: C, 69.53; H, 8.27. Found: C, 69.8, 69.5; H, 8.02, 8.08.

The oxidation product of XI gave a methyl ester, m. p. 72.5–73.7°. The literature[14] value for 2-nitro-dimethylterephthalate is 76°.

Nitration of 1,4-Diisopropylbenzene with Mixed Acids.—A mixture of 70% nitric acid (37 ml., 1.11 equivalents) and 98% sulfuric acid (52 ml.) was added in forty minutes to 100 ml. (0.523 mole) of hydrocarbon, the mixture being kept at 0–6° in a freezing mixture. The product was stirred for a further thirty minutes at 6° and poured onto 500 g. of ice. Petroleum ether (50 ml.) was added and the organic layer washed with water, three times with 10% ammonia, six times with 10% sodium hydroxide and finally with water. Large amounts of acidic material were removed by the alkali washes but the product dark-

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[11] Axer, *Monatsh.*, **41**, 159 (1920).

[12] Wohl, *Ber.*, **43**, 3480 (1910).

[13] Ruggli and Schmid, *Helv. Chim. Acta*, **18**, 247 (1935).

[14] Kauffmann and Weissel, *Ann.*, **393**, 10 (1912).

ened during the subsequent removal of petroleum ether and deposited sludge on cooling. It was steam distilled from 10% sodium hydroxide and gave 67.9 g. (61.9%) of stable, orange-red oil. Fractionation of the combined product from several runs gave the following composition: 17.2 mole per cent. of unchanged hydrocarbon, 65.0% of low-boiling mono nitro derivative, 13.6% of high-boiling mono nitro derivative and 4.2% of residue. The amines from the mono nitro derivatives gave derivatives identical by m. p. and mixed m. p. with those from X and XI.

4-Aminoisopropylbenzene (XII).—The nitro derivative (X) was converted into the crude, dark brown amine in 97.5% yield. Fractionation gave a colorless, mobile oil; physical properties: (1) 0.9507, (2) 811, (3) 1.5415, (4) 417.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69. Calcd. for $C_{12}H_{19}N$: C, 81.29; H, 10.81. Found: C, 80.1, 79.8; H, 9.61, 9.56.

Hydrochloride.—Long white needles from dilute hydrochloric acid. The sample for analysis was dried *in vacuo* over solid sodium hydroxide. Calcd. for $C_9H_{13}N \cdot HCl$: neut. equiv., 171.7. Found: neut. equiv., 171.6.

Acetyl Derivative.—Shining white scales from isooctane, m. p. 105.8–106.6°. Sterling and Bogert[15] give m. p. 102.5°; Ipatieff, Pines and Schmerling,[16] m. p. 106°.

Benzoyl Derivative.—Small white needles from isooctane–isopropanol, m. p. 161.4–162.0°. Sachs and Wiegert[17] give m. p. 162°.

2-Amino-1,4-diisopropylbenzene (XV).—Reduction of the nitro derivative (XI) gave 94.1% of dark brown oil. The fractionated product was a colorless, mobile oil; physical properties: (1) 0.9315, (2) 769, (3) 1.5293, (4) 417.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.29; H, 10.81. Found: C, 81.0, 81.1; H, 10.94, 11.09.

Hydrochloride.—Small white plates from dilute hydrochloric acid. Calcd. for $C_{12}H_{19}N \cdot HCl$: neut. equiv., 213.7. Found: neut. equiv., 213.7.

Acetyl Derivative.—White crystalline powder from isooctane, m. p. 80.8–81.5°. The substance rapidly acquired a brick red color on exposure to light.

Anal. Calcd. for $C_{14}H_{21}ON$: C, 76.66; H, 9.65. Found: C, 77.1, 77.1; H, 9.70, 9.88.

Benzoyl Derivative.—Tufts of small white needles from iso-octane–isopropanol, m. p. 124.6–125.0°.

Anal. Calcd. for $C_{19}H_{23}ON$: C, 81.10; H, 8.23. Found: C, 80.9, 81.0; H, 8.25, 8.02,

Nitration of 2-Amino-1,4-diisopropylbenzene (XV): 6-Nitro-2-amino-1,4-diisopropylbenzene (XVI).—The yield of crude nitroamine was low, only 24.2 g. of soft, slightly oily brown solid being obtained from 38.0 g. of amine. Filtration of a benzene solution of the product through activated bauxite gave a filtrate containing 19.2 g. of yellow-orange crystals, m. p. 93.5–95.5°. A 10% solution of methanol in benzene subsequently removed 4.2 g. of viscous, reddish-brown oil from the column. Two crystallizations from benzene–petroleum ether gave large, flat, intensely yellow hexagonal tables, m. p. 95.2–96.3°.

Anal. Calcd. for $C_{12}H_{18}O_2N_2$: C, 64.84; H, 8.16. Found: C, 65.2, 65.0; H, 8.24, 8.23.

2,6-Diamino-1,4-diisopropylbenzene (XVII).—Reduction of 6-nitro-2-amino-1,4-diisopropylbenzene (XVI) gave 71.4% of crude diamine which, after filtration through bauxite and crystallization from petroleum ether, formed thin, very faintly brown tinted flakes, m. p. 77.9–78.3°.

Anal. Calcd. for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48. Found: C, 75.1, 75.2; H, 10.50, 10.48.

Derivatives of 1,2,4-Triisopropylbenzene

Nitration of 1,2,4-Triisopropylbenzene: 5-Nitro-1,2,4-triisopropylbenzene-A (XVIIIA).—The yield was 92.5% of orange oil containing 3% of unchanged hydrocarbon and 97% of mono nitro derivative. Refractive indices of all distillation fractions from 5 to 95% distilled were n^{30}D 1.5135 ± 0.0002. Physical properties: (1) 1.0047, (2) 842, (3) 1.5179, (4) 426.

Anal. Calcd. for $C_{15}H_{23}O_2N$: C, 72.25; H, 9.30. Found: C, 72.0, 72.0; H, 9.20, 9.31.

When the mixture was allowed to stand for only two hours the product contained about 50% of unchanged hydrocarbon.

5-Amino-1,2,4-triisopropylbenzene-A (XIXA).—Reduction of XVIIIA gave 97.6% of dark brown product, the pure substance being a rather viscous, very faintly yellow tinted oil; physical properties, (1) 0.9175, (2) 792, (3) 1.5215, (4) 448.

Anal. Calcd. for $C_{15}H_{25}N$: C, 82.12; H, 11.49. Found: C, 82.3, 82.0; H, 11.51, 11.53.

Acetyl Derivative (XXA).—Shining white flakes from isooctane, m. p. 141.9–142.5°. About 8% of the product prepared by acetylation at 30–40° was a colorless, viscous oil.

Anal. Calcd. for $C_{17}H_{27}ON$: C, 78.11; H, 10.41. Found: C, 78.0, 77.9; H, 10.48, 10.56.

Benzoyl Derivative (XXIA).—Small white needles from 99% isopropanol, m. p. 159.2–159.8°.

Anal. Calcd. for $C_{22}H_{29}ON$: C, 81.68; H, 9.04. Found: C, 81.6, 81.5; H, 9.16, 9.29.

Nitration of 5-Amino-1,2,4-triisopropylbenzene (XVIIIA). 6-Nitro-4-amino-1,3-diisopropylbenzene-B (VIB).—A bright orange powder, m. p. 72–75.5°, was obtained in 86.3% yield. Crystallization from petroleum ether gave shining reddish-orange flakes, m. p. 75.8–76.4° alone and 75.3–76.2° in admixture with the A compounds (VIA).

Anal. Calcd. for $C_{12}H_{18}O_2N_2$: C, 64.84; H, 8.16. Calcd. for $C_{15}H_{24}O_2N_2$: C, 68.15; H, 9.15. Found: C, 65.1, 65.0; H, 8.34, 8.00.

Acetyl Derivative (VIIB).—Pale yellow silky needles from 50% acetic acid, m. p. 116.1–117.0° alone and 116.4–117.2° in admixture with the A compound (VIIA).

Anal. Calcd. for $C_{14}H_{20}O_3N_2$: C, 63.61; H, 7.63. Calcd. for $C_{17}H_{26}O_3N_2$: C, 66.64; H, 8.55. Found: C, 63.7, 63.6; H, 7.79, 7.61.

Derivatives of 1,3,5-Triisopropylbenzene

Nitration of 1,3,5-Triisopropylbenzene: 2-Nitro-1,3,5-triisopropylbenzene (XXII).—After standing for two hours the nitration product was poured into water when the nitro derivative separated as a pale yellow, granular solid which held much enclosed water. It was filtered off, washed with water, melted on the water-bath and allowed to cool overnight. The dried crude product (98.6%) had m. p. 72.0–73.4°. After two crystallizations from isopropanol, the m. p. was 74.6–75.5°.

Anal. Calcd. for $C_{15}H_{23}O_2N$: C, 72.25; H, 9.30. Found: C, 72.1, 72.2; H, 9.33, 9.31.

Variation in the amount of nitric acid from 1.5 to 4.0 equivalents, in reaction temperature from 30° to 70°, and in time of standing from one to twenty-four hours did not affect the yield or purity appreciably.

In the above run, the triisopropylbenzene prepared by propylation in presence of aluminum chloride was used. Similar runs on the lower-boiling triisopropylbenzene from the sulfuric acid preparation and that prepared by isomerization of 1,2,4-triisopropylbenzene[18] gave similar yields of identical product.

Nitration of 2-Nitro-1,3,5-triisopropylbenzene: 2,4,6-Trinitro-1,3,5-triisopropylbenzene (XXIII).—Finely ground mono nitro derivative (29.5 g., 0.118 mole) was added all at once to a stirred mixture of 60 ml. of 96% nitric acid and 180 ml. of 98% sulfuric acid at 35°. The temperature rose to 53° in eight minutes. After one hour the mixture, which at this stage appeared to contain mono, di and tri nitro derivatives, was heated on a boiling water-bath until the nitro derivative, which had melted on heat-

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[15] Sterling and Bogert, *J. Org. Chem.*, **4**, 20 (1939).

[16] Ipatieff, Pines and Schmerling, *ibid.*, **6**, 253 (1941).

[17] Sachs and Wiegert, *Ber.*, **40**, 4360 (1907).

ing, became a pasty solid (two hours) and the cooled product was then poured onto excess of ice. The pale yellow solid was filtered off, washed with water, 20% ammonia and water and dried at 100°. It weighed 38.1 g. (0.112 mole, 94.9%), softened at 169° and melted at 177–184°. Three crystallizations from isopropanol gave 30.7 g. of large, very pale yellow crystals, m. p. 190.8–191.6°.

Anal. Calcd. for $C_{16}H_{21}O_6N_3$: C, 53.09; H, 6.24. Found: C, 53.1, 53.3; H, 6.45, 6.48.

The remainder of the product (5.2 g.) apparently contained both di and tri nitro derivatives which could not be separated further.

2-Amino-1,3,5-triisopropylbenzene (XXIV).—The crude amine was obtained in 99.7% yield by reduction of the nitro derivative (XXII). The product of vacuum fractionation was a pale yellow, viscous oil; physical properties: (1) 0.9168, (2) 821, (3) 1.5189, (4) 458.

Anal. Calcd. for $C_{15}H_{25}N$: C, 82.12; H, 11.49. Found: C, 82.5, 82.3; H, 11.56, 11.40.

Hydrochloride.—Long fine white needles from boiling dilute hydrochloric acid, very sparingly soluble in cold water, freely soluble in benzene. In absence of excess hydrochloric acid the free base began to separate from the aqueous solution on warming. Calcd. for $C_{15}H_{25}N{\cdot}HCl$: neut. equiv., 255.8. Found: neut. equiv., 255.1.

Acetyl Derivative.—White flakes from iso-octane, m. p. 177.3–178.1°.

Anal. Calcd. for $C_{17}H_{27}ON$: C, 78.11; H, 10.41. Found: C, 78.0, 78.0; H, 10.24, 10.30.

Benzoyl Derivative.—White needles from 99% isopropanol, m. p. 286.5–287.2° (uncor.).

Anal. Calcd. for $C_{22}H_{29}ON$: C, 81.68; H, 9.04. Found: C, 81.7, 81.5; H, 9.17, 9.00.

Nitration of 2-Amino-1,3,5-triisopropylbenzene (XXIV). 4-Nitro-2-amino-1,3,5-triisopropylbenzene (XXV).—The crude product, which was a slightly oily, brownish-yellow solid, m. p. 69.5–73°, was obtained in 92% yield. A petroleum ether solution of 36.6 g. filtered through bauxite gave 34.2 g. of orange-yellow crystals, m. p. 73–75.5° which, after crystallization from 60% isopropanol, gave yellow crystals, m. p. 75.9–76.5°.

Anal. Calcd. for $C_{15}H_{24}O_2N_2$: C, 68.15; H, 9.15. Found: C, 68.3; H, 9.27, 9.03.

Acetyl Derivative.—Very pale yellow long blunt needles from glacial acetic acid, m. p. 157.1–157.9°.

Anal. Calcd. for $C_{17}H_{26}O_3N_2$: C, 66.64; H, 8.55. Found: C, 66.4, 66.6; H, 8.61, 8.46.

2,4-Diamino-1,3,5-triisopropylbenzene (XXVI).—The crude product from 4-nitro-2-amino-1,3,5-triisopropylbenzene (XXV) (100% yield) was a pale brown, viscous oil which began to crystallize after two weeks at room temperature. It was filtered through bauxite and crystallized twice from petroleum ether by chilling to give faintly brown tinted flakes, m. p. 71.9–72.7°.

Anal. Calcd. for $C_{15}H_{26}N_2$: C, 76.86; H, 11.18. Found: C, 76.5, 76.7; H, 11.22, 11.06.

Acetyl Derivative.—A white powder practically insoluble in all ordinary solvents. It showed no signs of melting at 360°.

Derivatives of 1,2,4,5-Tetraisopropylbenzene

Nitration of 1,2,4,5-Tetraisopropylbenzene: 3-Nitro-1,2,4,5-tetraisopropylbenzene (XXVII) and 5-Nitro-1,2,4-triisopropylbenzenes-B (XVIIIB) and -C (XVIIIC).—When a mixture of the hydrocarbon (80 g.), acetic acid (300 ml.) and acetic anhydride (100 ml.) was stirred at 30° a considerable proportion of the hydrocarbon remained undissolved. Nitric acid (25 ml. of 96%, 1.76 equivalents) was added in ten minutes keeping the temperature below 45°. Ten minutes later all the solid had passed into a clear, pale yellow solution which, after a further forty-five minutes, began to deposit fine, pale yellow needles. The product was kept in ice for eighteen hours, the solid (XXVII) filtered off, washed with water and dried *in vacuo* over calcium chloride. The yield was 14.3 g. (15.1%), m. p. 190.5–193.5° after sintering at 185°, and m. p. 192.6–193.8° after one crystallization from isopropanol (700 ml.).

Anal. Calcd. for $C_{18}H_{29}O_2N$: C, 74.18; H, 10.03. Calcd. for $C_{15}H_{23}O_2N$: C, 72.25; H, 9.30. Found: C, 74.1, 73.9; H, 10.23, 10.16.

The filtrate from XXVII worked up after dilution with water gave 67.6 g. (83.4%) of yellow-orange oil which began to crystallize after standing at room temperature for three days and was converted to an oily solid by cooling in ice for twelve hours. Two filtrations, first at room temperature, then after cooling to 5° for two weeks, gave slightly oily crystals (42.5 g.) which were pressed between filter paper and then had m. p. 35–40° (41.0 g.). Two crystallizations by cooling a solution in petroleum ether to −40° gave very pale yellow material, m. p. 40.9–41.9°. This substance was designated 5-nitro-1,2,4-triisopropylbenzene-B (XVIIIB).

Anal. Calcd. for $C_{15}H_{23}O_2N$: C, 72.25; H, 9.30. Found: C, 72.3, 72.3; H, 9.15, 9.33.

The filtrate from XVIIIB still contained solid matter in solution. Vacuum fractionation gave slight but definite separation, the earlier fractions being crystallizable at 5° while the later ones were not. No satisfactory method of separation was found. The mixture was designated 5-nitro-1,2,4-triisopropylbenzene-C (XVIIIC).

The yield of XXVII could not be increased by variation of conditions. Nitration of the hydrocarbon at 80° gave no XXVII and very little XVIIIB, the main product being XVIIIC.

Reduction of 5-Nitro-1,2,4-triisopropylbenzene-B (XVIIIB). 5-Amino-1,2,4-triisopropylbenzene-B (XIXB).—The crude amine was obtained in 95.5% yield and on distillation gave a pale yellow, viscous oil; physical properties: (1) 0.9177, (2) 796, (3) 1.5213, (4) 445.

Anal. Calcd. for $C_{15}H_{25}N$: C, 82.12; H, 11.49. Found: C, 82.0, 81.7; H, 11.56, 11.46.

Acetyl Derivative (XXB).—White flakes from iso-octane, m. p. 140.3–141.2°, and, in admixture with the A compound (XXA), m. p. 140.8–141.6°.

Anal. Calcd. for $C_{17}H_{27}ON$: C, 78.11; H, 10.41. Found: C, 78.5, 78.2; H, 10.66, 10.52.

Benzoyl Derivative (XXIB).—Tufts of white needles from isopropanol, m. p. 159.5–160.4°, and, in admixture with the A compound (XXIA), m. p. 159.2–160.2°.

Anal. Calcd. for $C_{22}H_{29}ON$: C, 81.68; H, 9.04. Found: C, 81.1, 81.6; H, 9.07, 9.23.

Reduction of 5-Nitro-1,2,4-triisopropylbenzene-C (XIXC). 5-Amino-1,2,4-triisopropylbenzene-C (XVIIIC).—Distillation of the crude amine (94.0% yield) gave a pale yellow, viscous oil; physical properties: (1) 0.9172, (2) 788, (3) 1.5210, (4) 443.

Anal. Calcd. for $C_{15}H_{25}N$: C, 82.12; H, 11.49. Found: C, 82.0, 81.9; H, 11.55, 11.63.

Acetyl Derivative (XXC).—White flakes from iso-octane, m. p. 141.2–141.7°, and, in admixture with the A compound (XXA), m. p. 141.1–141.9°; with the B compound (XXB), m. p. 140.6–141.6°.

Anal. Calcd. for $C_{17}H_{27}ON$: C, 78.11; H, 10.41. Found: C, 78.2, 78.2; H, 10.36, 10.45.

3-Amino-1,2,4,5-tetraisopropylbenzene (XXVIII).—The crude reduction product (97.2%) from XXVII was a pale yellow crystalline solid, m. p. 149–151°. Crystallization from isopropanol gave almost white material, m. p. 150.5–151.3°.

Anal. Calcd. for $C_{18}H_{31}N$: C, 82.69; H, 11.95. Found: C, 82.2, 82.5; H, 11.94, 12.00.

Oxidation of 3-Amino-1,2,4,5-tetraisopropylbenzene (XXVIII). Tetraisopropylbenzoquinone (XXIX).—To a mechanically stirred solution of potassium bichromate (70 g.) in a mixture of water (800 ml.) and 96% sulfuric 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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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).