into an isoöctane solution of the amine. It was readily hydrolyzed. The neut. equiv. was 154.5 (calcd. 153.7).

Sulfonyl Chlorides.—A liquid mixture (106 g.) was obtained from 86 g. of fraction 6. A separation was effected by hydrolysis to the sulfonic acids, fractional crystallization of the sodium salts, and reconversion to the sulfonyl chlorides by treating with phosphorus pentachloride. The first crop of sodium salts gave a sulfonyl chloride (white crystals) melting at 64.9–65.4°, which corresponded, by analysis, to a dodecylbenzenesulfonyl chloride.

Anal. Calcd. for $C_{18}H_{29}O_2SCl$: C, 62.7; H, 8.51; Cl, 10.3. Found: C, 62.9; H, 8.5; Cl (by hydrolysis), 10.3.

The sulfonamide from this formed white flakes, m. p. 135.5–136.5°. In admixture with *t*-butylbenzene-4-sulfonamide (m. p. 139.1–139.5°),[22] the m. p. was depressed to 110–115°.

Anal. Calcd. for $C_{18}H_{31}O_2NS$: C, 66.4; H, 9.6. Found: C, 66.4; H, 9.7.

The second crop of sodium salts gave a mixture of liquid sulfonyl chlorides.

Anal. Calcd. for $C_{14}H_{21}O_2SCl$: Cl, 12.3. Calcd. for $C_{15}H_{23}O_2SCl$: Cl, 11.7. Found: Cl (by hydrolysis) 11.9.

1-*t*-Amyl-2-*t*-butylbenzene-5-sulfonamide.—The mixed sulfonamides from the second crop sodium salts formed a brown viscous mass. By triturating with petroleum ether a white granular solid separated.

Fractions 7–12.—Each fraction was oxidized (6–8 ml., 58 ml. of 50% nitric acid, 180°, five hours) and each gave terephthalic acid in yields of 10–20%. The dimethyl esters (85–95%) all melted between 139.5 and 141.0°. There was no depression when in admixture with authentic dimethyl terephthalate, but in every case the m. m. p. with trimethyl trimesate (m. p. 144°) was depressed to 110–120°.

Acknowledgment.—The author expresses his thanks to Trinidad Leaseholds Ltd., for permission to publish this and following papers; to Dr. F. Morton and to Dr. A. Newton, for their interest in the progress of this work.

Summary

Benzene has been alkylated with isobutane in the presence of aluminum chloride. The following hydrocarbons were isolated from the complex reaction product: *t*-amyl benzene, 1-isopropyl-2-*t*-butylbenzene, 1-isopropyl-3-*t*-butylbenzene, 1,4-di-*t*-butylbenzene, 1-*t*-amyl-2-*t*-butylbenzene and *t*-octylbenzenes. The higher boiling material consisted mainly of *p*-dialkylbenzenes. No tri-*t*-butylbenzene was detected. *t*-Amylbenzene and 1-isopropyl-3-*t*-butylbenzene were also formed when sulfuric acid was the catalyst.

The probable course of the reaction is outlined on the basis of modern electronic concepts.

POINTE-A-PIERRE, TRINIDAD, B. W. I.

RECEIVED JULY 25, 1946

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(22) Huntress and Autenrieth, THIS JOURNAL, **63**, 3446 (1941).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TRINIDAD LEASEHOLDS LIMITED]

Alkylbenzenes from Benzene and Isobutene. II.[1] 1,4-Di-*t*-butylbenzene

BY D. I. LEGGE[1a]

Although 1,4-di-*t*-butylbenzene has been known for many years[2] its chemical behavior has received little attention and definite proof of its structure has been lacking. Attempts to oxidize the hydrocarbon to terephthalic acid have failed[3] and proof of orientation has rested mainly on the claim by Boedtker[4] of its oxidation to 4-*t*-butylbenzoic acid by chromic oxide in acetic acid. Baur[5] sulfonated the compound and described the product as 1,4-di-*t*-butylbenzene-2-sulfonic acid. Huntress and Autenrieth[6] used chlorosulfonic acid and described their product as 1,4-di-*t*-butylbenzene-2-sulfonyl chloride, from which they also prepared a sulfonamide (m. p. 135.5–136.5°). The only other known derivative has been the dinitro compound. As prepared by Baur[5] using hot nitrosylsulfuric acid this compound melted at 167–168° and smelt of musk. Verley[3] also used nitrosylsulfuric acid but obtained a product melting at 177° which did not smell of musk. The homogeneity of both these products was questioned by Boedtker[7] who nitrated the hydrocarbon at room temperature with fuming nitric acid and obtained almost odorless crystals melting at 190–191°. Subsequent workers,[8a] have reported m. p's. from 190 to 192°. Potts and Carpenter[8b] used a mixture of nitric and sulfuric acids in their preparation. The compound has been described as 2,6-dinitro-1,4-di-*t*-butylbenzene in view of the known orientating effect of the nitro group.

In the present work,[1] 1,4-di-*t*-butylbenzene (I) was prepared by the reaction of isobutene with benzene in the presence of aluminum chloride or more conveniently in the presence of 96% sulfuric acid. The white solid was purified readily by crystallization and melted at 77.8–78.4° in agreement with recorded values. It could not be oxidized by chromic oxide in acetic acid, by aqueous potassium permanganate or by any concentration of nitric acid (10–100%) under reflux. It was finally oxidized with 50% nitric acid at 180° giving a 30% yield of terephthalic acid.

On sulfonation or chlorosulfonation 1,4-di-*t*-butylbenzene partially underwent an abnormal Jacobsen rearrangement giving 1-isopropyl-3-*t*-butyl-

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(1) Previous paper, THIS JOURNAL, **68**, 2079 (1947).

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(2) (a) Goldschmitt, *Ber.*, **15**, 1066, 1425 (1882); (b) Senkowski, *ibid.*, **23**, 2413 (1890).

(3) Verley, *Bull. soc. chim.*, [3] **19**, 72 (1898).

(4) Boedtker, *ibid*, [3] **31**, 969 (1904).

(5) Baur, *Ber.*, **27**, 1608 (1894).

(6) Huntress and Autenrieth, THIS JOURNAL, **63**, 3446 (1941).

(7) Boedtker, *Bull. soc. chim.*, [3] **35**, 835 (1906).

(8a) Ipatieff, Corson and Pines, THIS JOURNAL, **58**, 919 (1936).

(8b) Potts and Carpenter, *ibid.*, **61**, 663 (1939).

benzene, but the main product was *t*-butylbenzene-4-sulfonic acid (or sulfonyl chloride).

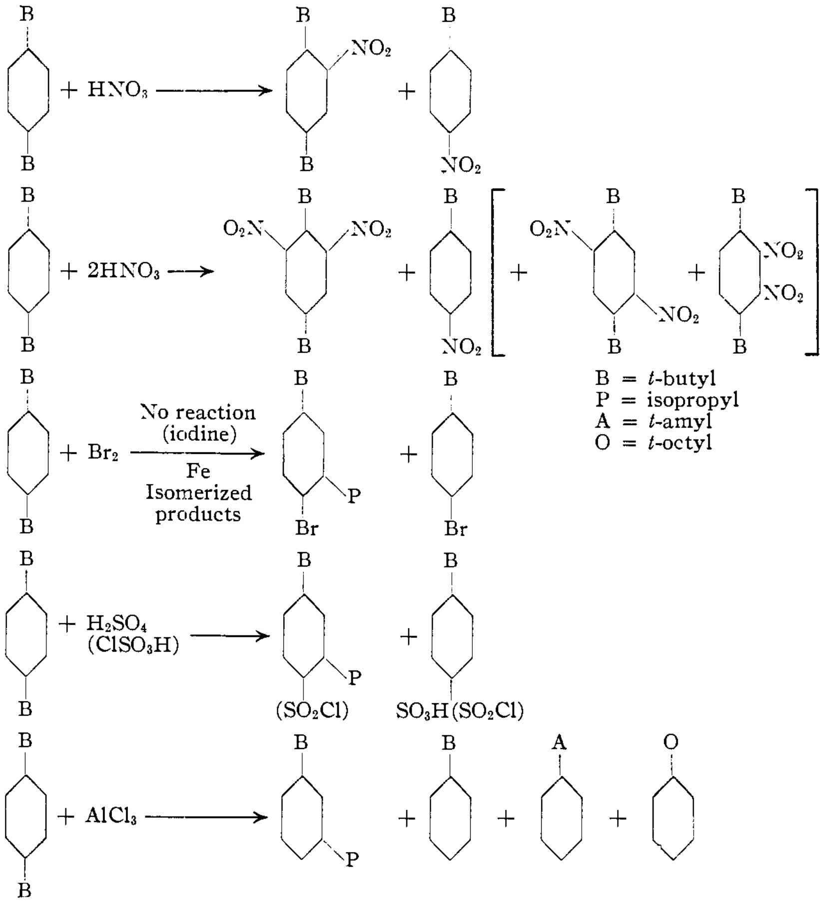

Fig. 1.—Reactions of 1,4-di-*t*-butylbenzene (main products).

With 96% nitric acid at room temperature, alone or in acetic acid solution, an 80% yield of solid (m. p. 88.0–88.7°) and a 20% yield of oil was obtained. The solid was shown to be 2-nitro-1,4-di-*t*-butylbenzene (II) by oxidation to 2-nitroterephthalic acid[9] and reduction to 2-amino-1,4-di-*t*-butylbenzene (III), a white solid m. p. 104.5–104.8°, whose hydrochloride had the expected neutral equivalent. The oil was identified as 4-nitro-*t*-butylbenzene (IV) by its oxidation to 4-nitrobenzoic acid and by conversion to 4-acetylamino-[2b,10] and 4-benzoylamino-*t*-butylbenzene.[10] After refluxing (II) with benzene and aluminum chloride for twenty-four hours and standing for four days, the whole of the nitro compound was recovered unchanged.

With 96% nitric acid at 60°, alone or mixed with 98% sulfuric acid, 53% of 2,6-dinitro-1,4-di-*t*-butylbenzene (V) (m. p. 191.4–192.4°) was obtained. About 8% each of two other dinitro-di-*t*-butylbenzenes, one solid (m. p. 138.7–139.7°) and one liquid were also formed. These are believed to be 2,5- and 2,3-dinitro-1,4-di-*t*-butylbenzene, respectively. Elementary analysis is in agreement with these formulas and neither could be identified with any likely isomerization product. Oxidation gave no identifiable acid products. 4-Nitro-*t*-butylbenzene was again about 20% of the product, the remainder (11%) being 2-nitro-1,4-di-*t*-butylbenzene. Orientation of (V) was proved by oxidation to 2,6-dinitroterephthalic acid[11] and the neutral equivalent of the diamine dihydrochloride prepared from it was that expected for this compound.

Iodine did not catalyze any reaction between 1,4-di-*t*-butylbenzene and bromine. When iron filings were used reaction took place readily giving, mainly, 4-bromo-*t*-butylbenzene (55%), a lesser amount of 2-bromo-1,4-di-*t*-butylbenzene mixed with an unidentified bromohydrocarbon (32%) and some *t*-butylbenzene (5%) together with unreacted starting material (6%). The formation of *t*-butylbenzene must result from the action of ferric bromide on 1,4-di-*t*-butylbenzene, analogous to the action of aluminum chloride.[1] An appreciable amount of side chain bromination took place.

Aluminum chloride treatment of 1,4-di-*t*-butylbenzene or *t*-butylbenzene gave the same products, namely: benzene, *t*-butyl and *t*-amylbenzene, 1-isopropyl-3-*t*-butylbenzene and 1,4-di-*t*-butylbenzene. While these products were definitely identified, all the other constituents of the alkylation product appeared to be present. Hence the reversible reactions[12]

$$\text{benzene} + [t\text{-C}_4\text{H}_9]^+ \rightleftharpoons t\text{-butylbenzene} + \text{H}^+ \quad (1)$$

$$t\text{-butylbenzene} + [t\text{-C}_4\text{H}_9]^+ \rightleftharpoons 1,4\text{-di-}t\text{-butylbenzene} + \text{H}^+ \quad (2)$$

are accompanied by the irreversible reaction[1]

$$1\text{-}4\text{-di-}t\text{-butylbenzene} + [t\text{-C}_4\text{H}_9]^+ \longrightarrow \text{isopropyl-}t\text{-butylbenzene} + [t\text{-C}_4\text{H}_9]^+ + [\text{CH}_3]^+$$

and by irreversible addition reactions of the methyl ion giving *t*-amylbenzene and homologs.

A number of derivatives were prepared from *t*-butylbenzene (fraction 1[1]) for comparison with the corresponding derivatives obtained from 1,4-di-*t*-butylbenzene.

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(9) Kauffmann and Weissel, *Ann.*, **393**, 10 (1912).

(10) Du Toit Malherbe, *Ber.*, **52**, 319 (1919).

(11) Haeussermann and Martz, *ibid.*, **26**, 2983 (1893).

(12) Boedtker and Halse, *Bull. soc. chim.*, [4] **19**, 447 (1916); Ipatieff and Corson, THIS JOURNAL, **59**, 1417 (1937).

Discussion

Replacement of an alkyl group by electrophilic reagents frequently has been observed when the benzene nucleus contained no unsubstituted position and less frequently with other highly substituted benzenes. 1,4-Dialkylbenzenes which contain an isopropyl group[13a] may have this group replaced during nitration, but the replacement of an alkyl group in a dialkylbenzene by bromine or sulfuric acid has not been observed except in the present work with 1,4-di-*t*-butylbenzene.

The ready replacements of the *t*-butyl group are considered to be a result of the electronic state of the molecule and of steric hindrance caused by these bulky groups. The strong inductive effect which can be transmitted by them[14] makes electrons readily available throughout the nucleus of 1,4-di-*t*-butylbenzene. The availability will be greatest at the carbon atoms holding the *t*-butyl groups, since these are subject to both the inductive displacement of the attached groups and to the electromeric displacements of the group in the para position.

Whilst nitration of 1,4-diisopropylbenzene[13b] causes 50% replacement of an isopropyl group, under similar conditions only 20% replacement of a *t*-butyl group in 1,4-di-*t*-butylbenzene takes place. This difference is due to the relatively greater availability of electrons at the 2 position in the latter molecule and to the more effective hindrance exerted by the *t*-butyl groups against the access of reagent molecules to the 1 or 4 positions. The absence of any alkyl group replacement when 2-nitro-1,4-di-*t*-butylbenzene (II) is converted to the dinitro derivative (V) indicates a stabilization of the alkyl group attachments due to the withdrawal of electrons from the nucleus by the first nitro group.

More replacement takes place with bromine (iron catalyst). Access of this bulky reagent to the 2-position is more difficult than access of the nitro group and, on the other hand, position 4 is available for substitution since the catalyst causes dealkylation. This is shown by the isolation of *t*-butylbenzene. Side chain bromination is facilitated by the electronic displacements of the para *t*-butyl group which can be transmitted through the nucleus to the methyl carbons of the other *t*-butyl radical.[1]

Sulfuric and chlorosulfonic acid do not react directly with 1,4-di-*t*-butylbenzene, and none of the 2-sulfonic derivative is formed. Attack on the hydrocarbon is by proton from the acid solution, which replaces a *t*-butyl group, allowing the formation of *t*-butylbenzene-4-sulfonic acid (or sulfonyl chloride). In the presence of sulfuric acid the displaced *t*-butyl group may alkylate an unreacted molecule of 1,4-di-*t*-butylbenzene. As previously described,[1] this will result in the formation of 1-isopropyl-3-*t*-butylbenzene. When the reaction is performed without stirring this hydrocarbon can be isolated (4%). With stirring, it is completely sulfonated and cannot be recovered by hydrolysis of the sulfonic acid. There can be little doubt that this Jacobsen type rearrangement is due to an intermolecular reaction and not simply an intramolecular migration in the hypothetical 1,4-di-*t*-butylbenzene-2-sulfonic acid. The migrating fragment is a positively charged *t*-butyl ion.

Experimental

***t*-Butylbenzene.**—Oxidation (3.4 g., 60 ml. of 15% nitric acid, 1 g. of vanadium pentoxide, 160°, five hours) gave a green solution and most of the oil was unchanged. It was neutralized with solid sodium carbonate, extracted twice with benzene, filtered and made acid with hydrochloric acid. Benzoic acid (0.2 g., 8%) was precipitated, m. p. and m. m. p. with an authentic specimen 121°. 4-Acetylamino-*t*-butylbenzene[2b,10] (from benzene containing isoöctane) (75%) melted at 174.6–175.2°. The benzoylamine[10] (76%) melted at 143.1–143.7° (white needles from the same solvent). The sulfonyl chloride[6] (91%) m. p. 81.0–82.0°, gave the sulfonamide[6] (98%) m. p. 139.1–139.5°. *t*-Butylbenzene-4-sulfonanilide (6.4 g., 86%) was prepared from 6 g. of the sulfonyl chloride. It gave white flakes from 60% isopropyl alcohol, m. p. 132.8–133.4°.

Anal. Calcd. for $C_{16}H_{19}O_2NS$: C, 66.4; H, 6.6. Found: C, 66.6; H, 6.7.

1,4-Di-*t*-butylbenzene (I).—Oxidation (4.5 g., 38 ml. of 50% nitric acid, 180°, nine hours) by the method previously described,[1] gave 1.2 g. (30%) of terephthalic acid. It was filtered off and esterified with methyl alcohol. The dimethyl terephthalate melted at 141.5–141.8°. It did not depress the m. p. of an authentic specimen.

Nitration. 2-Nitro-1,4-di-*t*-butylbenzene, 4-Nitro-*t*-butylbenzene.—A solution of 1,4-di-*t*-butylbenzene (380 g.) in 400 ml. of glacial acetic acid and 300 ml. of acetic anhydride was nitrated with 159 g. (1.27 equivalents) of 96% nitric acid added gradually with stirring at 30–42°. The mixture was allowed to stand for twenty-two hours and then poured into one liter of ice-water. The pale yellow solid which precipitated was filtered and washed with 10% sodium hydroxide and water. The filtrate, containing some yellow oil, was extracted twice with petroleum ether. After washing until neutral, evaporation of the petroleum ether left 94 g. of red oil which gave a further crop of crystals by chilling. These were bulked with the first batch and recrystallized from 800 ml. of isopropyl alcohol giving white flakes, m. p. 88.0–88.7°. They were shown to be 2-nitro-1,4-di-*t*-butylbenzene (II).

Anal. Calcd. for $C_{14}H_{21}O_2N$: C, 71.5; H, 9.0. Found: C, 71.1; H, 9.1.

The residual oil was fractionated under reduced pressure. It was mainly 4-nitro-*t*-butylbenzene (III) (b. p. 144 (10 mm.); n^{30}_D 1.5230) and a little (II).

Oxidation of (II) (2.5 g., 48 ml. of 50% nitric acid, 180°, ten hours) gave a green solution which yielded 0.74 g. (32%) of 2-nitroterephthalic acid, when evaporated to dryness. Its neut. equiv. was 107.3 (calcd. 105.6). The m. p. of its dimethyl ester[10] was 71.5–72.5°. Oxidation of (III) (4 g.), 48 ml. of 50% nitric acid, 180°, ten hours) gave 2.2 g. (57%) of 4-nitrobenzoic acid, m. p. 235–237°. The m. p. of its methyl ester was 94.6–95.3° and was not depressed by admixture with authentic methyl 4-nitrobenzoate.

2-Amino-1,4-di-*t*-butylbenzene (IV).—The nitro compound (II) (300 g.) dissolved in 500 ml. of isopropyl alcohol was reduced by hydrogen in the autoclave over a nickel on kieselguhr catalyst at 100°. The initial hydrogen pressure (at 30°) was 1250 lb./sq. in. Reduction

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[13a] Mann, Montonna and Larian, *Ind. Eng. Chem.*, **28**, 598 (1936).

[13b] Newton, This Journal, **65**, 2434 (1943).

[14] Kharasch and Flenner, *ibid.*, **54**, 674 (1932); Gleave, Hughes and Ingold, *J. Chem. Soc.*, 238 (1935).

was continued for four hours after the pressure ceased to fall. The cooled product was crystalline. An additional 200 ml. of isopropyl alcohol was added to enable the catalyst to be filtered from the hot solution. White needles formed on cooling. They melted at 104.5–104.8° and became faintly pink on exposure.

Anal. Calcd. for $C_{14}H_{23}H$: C, 81.9; H, 11.3. Found: C, 81.8; H, 11.3.

The hydrochloride was prepared by shaking a carbon tetrachloride solution of the amine with 35% hydrochloric acid and allowing to stand for eight hours. A white solid almost insoluble in water separated at the interface. Its neut. equiv. (in 40% isopropyl alcohol) was 241.6 (calcd. 241.7).

2-Acetylamino-1,4-di-*t*-butylbenzene gave white flakes from 75% acetic acid, m. p. 155.6–156.4°.

Anal. Calcd. for $C_{16}H_{25}ON$: C, 77.7; H, 10.2. Found: C, 77.8; H, 10.3.

2-Benzoylamino-1,4-di-*t*-butylbenzene gave white felted needles from 96% isopropyl alcohol, m. p. 202.3–203.0°.

Anal. Calcd. for $C_{21}H_{27}ON$: C, 81.5; H, 8.8. Found: C, 81.7; H, 8.7.

Reduction of (III) gave 4-amino-*t*-butylbenzene as an oil with a typical odor. The acetyl derivative[10] melted at 174.0–175.0° and the benzoyl derivative[10] at 142.3–142.9°. The m. ps. were not depressed when the compound was admixed with the corresponding authentic derivatives.

2,5-Di-*t*-butylphenol.—The amine (IV) (80 g.) was dissolved in 600 ml. of glacial acetic acid and 100 ml. of water. It was cooled to 10° and 50 ml. of 98% sulfuric acid was added. This solution was diazotized with rapid stirring at −2° by the addition of a solution containing 30 g. of sodium nitrite in 60 ml. of water. The final milky solution was decomposed by pouring into 1000 ml. of 20% sulfuric acid, boiling under reflux. The orange-brown oil was extracted three times with petroleum ether, then ten times with 100-ml. portions of 15% sodium hydroxide at 70°. (Solubility was very low.) The caustic extract was reacidified, steam-distilled, and the distillate extracted twice with petroleum ether. Evaporation left 39.2 g. (48.5%) of a pale yellow oil which crystallized on cooling. Recrystallization from 120 ml. of petroleum ether and 20 ml. of benzene gave 31.6 g. of pale yellow solid, m. p. 141.1–142.2°.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.5; H, 10.8. Found: C, 81.5; H, 10.9.

Dinitration: 2,6-(V), 2,5-(VI), 2,3-(VII)-Dinitro-1,4-di-*t*-butylbenzene, 2-Nitro-1,4-di-*t*-butylbenzene (II), and 4-Nitro-*t*-butylbenzene (III).—Well-powdered 1,4-di-*t*-butylbenzene (100 g.) was added in the course of forty-five minutes to 300 ml. of 96% nitric acid (13.6 equivs.) vigorously stirred at 15–30°. The temperature was raised to 60° and stirring continued for five hours. On pouring into ice and water, a yellowish oily solid formed. Prolonged filtration and washing with petroleum ether gave white needles, m. p. 191.4–192.4°, after three crystallizations from isopropyl alcohol. It was shown to be (V). The filtrate contained an orange oil. This was combined with the oil from two other batches (total hydrocarbon used was 330 g.) and with some oil from the mother liquors after crystallization of (V). Fractionation at 100 mm. pressure showed this oil to be a mixture of all the above nitro compounds. By chilling in Dry Ice, (II) and a mixture consisting of (V) and (VI) were removed from the appropriate fractions. The compound (VI) was isolated by fractional crystallization from isopropyl alcohol. It formed white flakes, m. p. 138.7–139.7°. In admixture with 3,5-dinitro-1-isopropyl-2-*t*-butylbenzene (m. p. 143.1–143.7°) it melted at 102–109°. The mixed m. p. with 4,6-dinitro-1-isopropyl-3-*t*-butylbenzene (m. p. 165.4–166.3°) was 123–150°. The constitution of (VI) was not definitely confirmed.

Anal. Calcd. for $C_{14}H_{20}O_4N_2$: C, 60.0; H, 7.2. Found: C, 60.1; H, 7.2.

Refractionation of the residual oil gave two fractions. One (b. p., 148° (10 mm.); n^{30}_D 1.5237) was shown to be 4-nitro-*t*-butylbenzene (III) (acetylamine, m. p. and mixed m. p. 174–175°; benzoylamine, m. p. and m. m. p. 142–143°). The second fraction (b. p. 190° (10 mm.), n^{30}_D 1.5331) was probably (VII).

Anal. Calcd. for $C_{14}H_{20}O_4N_2$: C, 60.0; H, 7.2. Found: C, 59.9; H, 7.1.

The orange-colored oil (VII) was characterized by reduction (tin and hydrochloric acid) to an oily amine which gave a benzoyl derivative, m. p. 211.6–212.9°, as yellow flakes from petroleum ether containing a little benzene.

Yields of product from this nitration reaction were: (V) 183 g., 53.5%; (VI) 29 g., 8.4%; (VII) 29 g., 8.4%; (II) 30 g., 10.5%; (III) 42 g., 19.3 mole per cent.

Oxidation of (V) (5.5 g., 54 ml. of 50% nitric acid; 180°; six hours) gave 0.6 g. (10%) of 2,6-dinitroterephthalic acid. The melting point of the ethyl ester was 194.7–195.8°. The literature value[11] is 197°.

Nitration of 1,4-di-*t*-butylbenzene (60 g.) with 90 g. (5.4 equivs.) of 96% nitric acid and 90 ml. of 98% sulfuric acid at 30° for four days with stirring, and finally at 50° for one hour gave 42 g. of (V) (47.5%) and an orange oil, mainly (III), but probably containing some (VI), (VII) and (II).

Nitration of 30 g. of 2-nitro-1,4-di-*t*-butylbenzene (II) with 45 g. (5.5 equivs.) of 96% nitric acid was performed at 35–40° during the twenty-four minutes necessary to add the powdered solid. The temperature was then raised to 60° and stirring continued for three hours. On pouring into ice and water a yellow granular solid separated. It was washed, dried and crystallized from isopropyl alcohol, giving white odorless crystals of 2,6-dinitro-1,4-di-*t*-butylbenzene (35 g., 98.2%) m. p. 190.9–191.8° after two crystallizations from isopropyl alcohol. A small amount (0.5 ml.) of orange-colored oil was also formed. It was not 4-nitro-*t*-butylbenzene since after reduction it gave a benzoylamine, m. p. 200.2–203.6°.

Five grams of (II) were refluxed with 100 ml. of benzene and 5 g. of aluminum chloride for twenty-four hours and then allowed to stand for four days. The solution was decanted from the solid aluminum chloride, washed and evaporated. The yield of unchanged (II) was 4.7 g. (94%), m. p. and mixed m. p. 87.9–88.7°.

2,6-Diamino-1,4-di-*t*-butylbenzene.—The dinitro compound (V) (20 g.) dissolved in 250 ml. of isopropyl alcohol was reduced over nickel on kieselguhr at 100° and 1200 lb./sq. in. initial hydrogen pressure. After filtering the hot solution and cooling, a pale yellowish brown solid (15.1 g., 97%), m. p. 171.0–172.0°, was obtained.

Anal. Calcd. for $C_{14}H_{24}N_2$: C, 76.3; H, 11.0. Found: C, 76.3; H, 10.9.

The dihydrochloride separated when 2.2 g. of amine in 25 ml. of benzene was shaken with 25 ml. of 35% hydrochloric acid. The neut. equiv. was 147.8 (calcd. 146.7).

Diacetyl Derivative.—A white amorphous looking solid from glacial acetic acid, m. p. (uncor.) 368–370°.

Anal. Calcd. for $C_{18}H_{28}O_2N_2$: C, 71.0; H, 9.3. Found: C, 71.0; H, 9.4.

Bromination. 2-Bromo-1,4-di-*t*-butylbenzene, 4-Bromo-*t*-butylbenzene.—To a solution of 200 g. of 1,4-di-*t*-butylbenzene in 400 ml. of carbon tetrachloride was added 2 g. of iodine. While stirring at 30°, 30 ml. of bromine solution (55 ml. in 200 ml. carbon tetrachloride) were run in gradually. There was no indication of reaction although the total stirring time was sixteen hours at 30° and six hours at 45°. About 99% of the hydrocarbon was recovered unchanged.

A bromine solution (100 ml. in 400 ml. of carbon tetrachloride) was added with stirring to a solution of 360 g. of 1,4-di-*t*-butylbenzene in 500 ml. of carbon tetrachloride, containing 25 g. of iron filings. Ready evolution of hydrogen bromide occurred. After standing for forty-eight hours the product was poured into water and washed with

10% sodium hydroxide solution and water. The carbon tetrachloride was removed and the residue (414 g.) was stirred with 10 g. of solid caustic soda at 95° for four hours to remove side chain bromo compounds. (Otherwise much evolution of hydrogen bromide occurred during subsequent fractionation.) Fractionation at 10 mm. pressure in a 6-ft. column of 1″ diam. packed with 5 mm. glass balls separated two bromohydrocarbon fractions (VIII) and (IX), and some *t*-butylbenzene, in addition to unreacted 1,4-di-*t*-butylbenzene. The lower boiling bromo derivative (VIII) (b. p. 103° (10 mm.); f. p. 14°; $n^{30}\text{D}$ 1.5268; $d^{30}{}_4$ 1.2028) was 4-bromo-*t*-butylbenzene.

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.3; H, 6.2; Br, 37.5. Found: C, 56.5; H, 6.3; Br, 37.3. Bromine was estimated by the Volhard method after treatment with sodium in isopropyl alcohol.

The higher-boiling bromohydrocarbon fraction was a mixture boiling over several degrees. It was refractionated. The first fraction gave mainly 1,4-di-*t*-butylbenzene by dehalogenation with sodium and isopropyl alcohol. It was therefore 2-bromo-1,4-di-*t*-butylbenzene. The second fraction was a mixture of this with some unidentified material having the same analysis and which gave a liquid hydrocarbon after debromination.

Anal. Calcd. for $C_{14}H_{21}Br$: C, 62.5; H, 7.8; Br, 29.7. Found: C, 61.4; H, 7.6; Br, 31.0.

Chlorosulfonation. *t*-Butylbenzene-4-sulfonyl Chloride (X), 1-Isopropyl-3-*t*-butylbenzene-6-sulfonyl Chloride (XI).—A solution of 360 g. of 1,4-di-*t*-butylbenzene in 1200 ml. of carbon tetrachloride was stirred at 22–25° for two hours while adding 560 ml. (2.2 equivs.) of chlorosulfonic acid. After washing with iced water and removal of the carbon tetrachloride, 303 g. of a dark gray oily solid was left. Two recrystallizations from 100 ml. of petroleum ether gave white prisms (X), m. p. 79.9–81.2°, and a dark oil. In admixture with authentic *t*-butylbenzene-4-sulfonyl chloride (m. p. 81.0–82.0°) the m. p. was 80.5–81.9°.

Anal. Calcd. for $C_{10}H_{13}O_2SCl$: C, 51.6; H, 5.6; Cl, 15.2. Found: C, 51.8; H, 5.7; Cl (by hydrolysis), 15.2.

The sulfonic acid sodium salt was prepared by hydrolysis of (X) and recrystallized till free from inorganic salts. It was analyzed for sodium (by ashing with sulfuric acid) and for water of crystallization.

Anal. Calcd. for $C_{10}H_{13}O_3SNa$: Na, 9.73. Found: Na, 9.64. Calcd. for $C_{10}H_{13}O_3SNa \cdot 1.5\ H_2O$: H_2O, 10.3. Found: H_2O, 10.4.

Sulfonamide gave white needles from boiling water, m. p. 139.1–139.6°, and mixed m. p. with authentic *t*-butylbenzene-4-sulfonamide (m. p. 139.1–139.5°), 139.1–139.6°.

Sulfonanilide gave white flakes from 60% isopropyl alcohol, m. p. 131.9–133.0°, and mixed m. p. with authentic *t*-butylbenzene-4-sulfonanilide (m. p. 132.8–133.4°), 132.4–133.3°.

The oily filtrate from (X) was shown to be a mixture of a sulfone (insoluble in boiling 10% sodium hydroxide) with two sulfonyl chlorides (X) and (XI). It was hydrolyzed to the corresponding sulfonic acids and the sodium salts were fractionally crystallized, and then reconverted to the sulfonyl chlorides by phosphorus pentachloride. The sulfonamide from the first crop melted at 158.2–158.9° and in admixture with authentic[1] 1-isopropyl-3-*t*-butylbenzene-6-sulfonamide (m. p. 158.8–159.1°) at 158.2–159.0°. The second crop of sodium salt was a mixture. The sulfonamides prepared from it crystallized as an eutectic, m. p. 106.0–108.2°. A synthetic mixture of these two sulfonamides melted at 107.2–108.5° and the mixed m. p. of this with the second crop sulfonamides was 105.1–107.0°. The sulfonamide derived from (XI) was separated from this mixture by fractional solution in 10% sodium hydroxide followed by reprecipitation with hydrochloric acid. The melting point was 151.8–158.7°. The sulfonanilides were separated in the same manner. In this case it was the sulfonanilide from (X) which was obtained in pure form, m. p. 131.9–133.0°, and mixed m. p. with authentic *t*-butylbenzene-4-sulfonanilide (m. p. 132.8–133.4°) 132.0–132.9°. The mixed m. p. with 1-isopropyl-3-*t*-butylbenzene-6-sulfonanilide (m. p. 136.9–137.5°) was 102–106°.

The total recovered yield from the reaction was 58%, made up as follows: (X) 228 g. (88.4%); (XI) 30 g. (9.8%); sulfone 6.2 g. (1.8%).

The Jacobsen Reaction.—Finely powdered 1,4-di-*t*-butylbenzene (600 g.) was added to 1000 ml. of 98% sulfuric acid while stirring vigorously at 82°. The temperature of the homogeneous solution rose momentarily to 98°. It was rapidly cooled to 80° and then allowed to stand without stirring while cooling for two hours. After five minutes, separation of an upper layer was observed. This oil layer (86 ml.) was washed with 10% sodium hydroxide and water. Its properties were: $n^{30}\text{D}$ 1.4841, $d^{30}{}_4$ 0.8540. It was mainly 1-isopropyl-3-*t*-butylbenzene[1] (sulfonamide, m. p. and m. m. p. 157–158°; dinitro derivative, m. p. and mixed m. p. 163–164°). The acid layer was diluted with ice and hydrolyzed by steam-distillation at 145–150° yielding (with difficulty) 63 ml. of oil having the following properties: $n^{30}\text{D}$ 1.4902, $d^{30}{}_4$ 0.8653. The hydrolysis was stopped at 160° when the distillate was entirely *t*-butylbenzene. *t*-Butylbenzene composed 70% of the recovered oil. The remainder boiled mainly at 238–240° but was not identified. With a large excess of 96% nitric acid in the cold it gave a nitro derivative, m. p. 268–270°.

Aluminum Chloride Rearrangements: *t*-Butylbenzene.—The pure hydrocarbon (172 g., 1.28 moles) was stirred with 50 g. (0.4 mole) of aluminum chloride at 45° for three hours. It then stood for forty-eight hours at room temperature (26–30°). The pasty aluminum chloride layer was separated and the oil layer washed and fractionated through 12″ of Stedman packing. It gave 19 g. of benzene, 16 g. of 1,4-di-*t*-butylbenzene and 20 g. of 1-isopropyl-3-*t*-butylbenzene in addition to 59 g. of unchanged *t*-butylbenzene, a little *t*-amylbenzene and some other material not actually identified.

1,4-Di-*t*-butylbenzene.—The recrystallized solid (1100 g., 5.8 moles) was dissolved in 750 ml. of carbon bisulfide. Finely powdered aluminum chloride (175 g., 1.4 moles) was added and isobutene (12.8 moles) was passed into the well-stirred mixture at 20–30°, during the course of twenty hours. Evaporation of the carbon disulfide and fractionation of the residue gave the following per cent. yields: (a) benzene, 9.3; (b) *t*-butylbenzene, 3.6; (c) *t*-amyl- and hexylbenzenes, 1.4; (d) 1-isopropyl-3-*t*-butylbenzene, 31.4; (e) 1,4-di-*t*-butylbenzene, 27.1; (f) *t*-octylbenzenes and higher boiling material 21.9; loss (mainly benzene), 5.2.

A similar treatment without the addition of isobutene gave the same fractions in the following yields: (a) 31.9, (b) 23.4, (c) 4.0, (d) 11.4, (e) 10.3, (f) 19.0.

Summary

1,4-Di-*t*-butylbenzene has been oxidized to terephthalic acid and its behavior toward electrophilic reagents has been studied. The factors influencing the ready replacement of one of the *t*-butyl groups are discussed. New nitro, amino and bromo derivatives are described. Rearrangement in the presence of sulfuric acid leads to 1-isopropyl-3-*t*-butylbenzene.

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