

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 69

SEPTEMBER 25, 1947

NUMBER 9

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

Alkylbenzenes from Benzene and Isobutene. I.^{1a} Preparation, Identification of Several Fractions

By D. I. LEGGE^{1b}

An investigation of the reactions of poly-*t*-butylbenzenes would be valuable from a theoretical viewpoint, particularly since the polyisopropylbenzenes have now been studied.^{1c} Apart from *t*-butylbenzene itself, only 1,4-di-*t*-butylbenzene is known, although Senkowski² prepared a solid, m. p. 129°, which he described as a tri-*t*-butylbenzene. The alkylation of benzene with isobutene, catalyzed either by aluminum chloride³ or by sulfuric acid,⁴ did not yield any new poly-*t*-butylbenzenes. Two *t*-butyl groups could be introduced into the para position of the benzene nucleus, but it was not found possible to prepare tri- or tetra-*t*-butylbenzenes. However, a considerable number of unexpected alkylbenzenes were obtained. The pure hydrocarbons were isolated by fractionation when possible. In other cases crystalline derivatives usually could be prepared in pure condition and these served to identify the alkylbenzenes.

Benzene was stirred with a small proportion of aluminum chloride at 15–22° while isobutene was passed into the mixture. The product was washed, and by a combination of fractional distillation and crystallization, was separated into the alkylbenzene fractions shown in Table I and in Figs. 1 and 2. There were also benzene and a small unsaturated fraction corresponding to isobutylene trimer. The composition of the portion boiling between 170 and 250° is shown in Table II.

The physical properties of fractions 1 and 5 were sufficient to identify them as *t*-butyl- and 1,4-di-*t*-butylbenzene, respectively, by comparison with

TABLE I

Fraction	B. p., °C.	Yield, wt. %	d_{20}^{25}	n_D^{20}	Spec. dispersion $10^4 \times (n_F - n_C)/d$
1	168.9 ^a	^c	0.8582 ^a	1.4878 ^a	159.3
2	190–191	1.4	.8589	1.4862	152.7
3	205–209	1.6	.8564	1.4868	149.7
4	221–222	15.9	.8512	1.4832	148.4
5	236.5 ^b	43.5	(77.7–78.4) ^b	...
6	240–243	6.9	.8645	1.4885	143.7
7–12	250–304	22.4	.8566	1.4856	142.7
			-.8705	-1.4929	-140.7
13	>304	8.2

^a Literature values^{3,4} for *t*-butylbenzene: b. p. 168.5°, n_D^{20} 1.4915, d_{20}^{25} 0.8660. ^b Melting point: Literature values^{3,4} for 1,4-di-*t*-butylbenzene: b. p. 236.5, m. p. 77–78°. ^c Not included in yield figures since most of this fraction was put back for further alkylation.

the literature values. Confirmatory evidence will be presented in a subsequent paper dealing with the reactions of 1,4-di-*t*-butylbenzene.

Fraction 2 was shown to be *t*-amylbenzene by the melting points of its derivatives, alone and in admixture with the corresponding derivatives of authentic *t*-amylbenzene prepared by the method of Ipatieff, Pines and Schermerling.⁵

Fraction 3 (B. p. 205–210°).—This mixture gave both benzoic acid and phthalic acid on oxidation. It was possible to isolate an amine hydrochloride and a diamine dihydrochloride of a hydrocarbon of molecular weight 176 (C₁₃H₂₀). A dinitro derivative melted at 143° and oxidized to 3,5-dinitrophthalic acid. The hydrocarbon was presumably 1-isopropyl-2-*t*-butylbenzene. Barbier⁶ gave 142° as the melting point of the dinitro derivative. A crystalline acetylamine, benzoyl-

(5) Ipatieff, Pines and Schermerling, *J. Org. Chem.*, **5**, 264 (1940).

(6) Barbier, *Helv. Chim. Acta*, **19**, 1345 (1936).

(1a) Abstract of a thesis for the degree of Ph.D. in the University of London.

(1b) Present address: Anglo Transvaal Consolidated Investment Co. Ltd., Johannesburg, South Africa.

(1c) Newton, *THIS JOURNAL*, **65**, 320 (1943).

(2) Senkowski, *Ber.*, **23**, 2413 (1890).

(3) Potts and Carpenter, *THIS JOURNAL*, **61**, 663 (1939).

(4) Ipatieff, Corson and Pines, *ibid.*, **68**, 919 (1936).

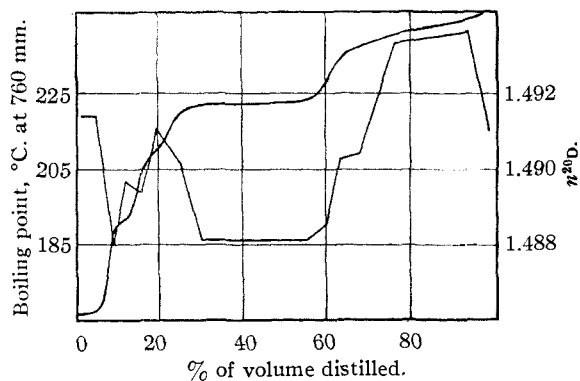


Fig. 1.

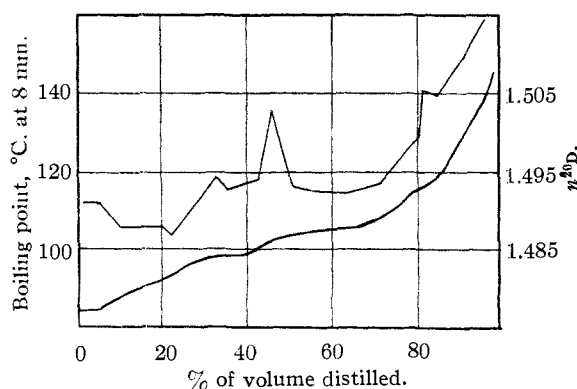


Fig. 2.

amine, phenol, diamine and sulfonamide were also prepared and their analyses agreed with derivatives of 1-isopropyl-2-*t*-butylbenzene. The yields of derivatives indicated about 15–17% of this hydrocarbon in the fraction.

From the remainder only one crystalline derivative could be isolated. It was one of the isomeric 4-benzoylamino-*t*-hexylbenzenes, m. p. 112°. The liquid nitro derivative (the filtrate from the 3,5-dinitro-1-isopropyl-2-*t*-butylbenzene), on oxidation, gave 4-nitrobenzoic acid and was therefore derived from a monoalkylbenzene. Fractional crystallization of the sulfonic acid sodium salts gave a first fraction which oxidized to 4-nitrobenzoic acid and was a mixture derived from the isomeric *t*-hexylbenzenes (by analysis for sodium). The sulfonamide was oily and could not be crystallized.

Fraction 4 (B. p. 220–221°).—This gave isophthalic acid on oxidation. The neutral equivalents of the amine and diamine hydrochlorides indicated the composition C₁₃H₂₀ for the hydrocarbon. This was confirmed by determination of sodium in the sulfonic acid sodium salt and by the hydrolyzable chlorine content of the sulfonylchloride. The dinitro derivative melted at 164° and oxidized to 4,6-dinitroisophthalic acid. A solid mononitro compound was prepared and oxidized to 4-nitroisophthalic acid, whilst a liquid isomer (10%) oxidized to 4-nitrobenzoic acid and

was evidently a *t*-heptylbenzene derivative. Several other derivatives were prepared and analyzed. Treatment with aluminum chloride in the presence of benzene gave *t*-butylbenzene as almost the only liquid product. There was no isopropylbenzene.

Fraction 6 contained a mixture of *t*-octylbenzenes and 1-*t*-amyl-2-*t*-butylbenzene, which could not be separated by fractionation. Oxidation of the mixture gave both benzoic and phthalic acids. After nitration a solid dinitro derivative was isolated and oxidized to 3,5-dinitroisophthalic acid. A liquid nitro derivative formed at the same time gave 4-nitrobenzoic acid on oxidation. The equivalent weight of the diamine dihydrochloride preparation from the solid nitro derivative indicated the formula C₁₅H₂₄ for the hydrocarbon which is presumably 1-*t*-amyl-2-*t*-butylbenzene. A crystalline benzoylamine of this hydrocarbon was isolated, and the oily phenol gave a crystalline benzoyl ester.

Chlorosulfonation of the mixture followed by hydrolysis and fractional crystallization of the mixed sulfonic acid sodium salts, gave a first fraction derived from a hydrocarbon of molecular weight 246 (C₁₈H₃₀). A crystalline sulfonyl chloride and sulfonamide were prepared from it. The parent hydrocarbon could not have been present in the original fraction, and was evidently formed by disproportionation of *t*-octylbenzenes. A crystalline amide was obtained from the 1-*t*-amyl-2-*t*-butylbenzene-sulfonic acid in the second fraction of sodium salts, but no crystalline derivative could be obtained from the remainder of this fraction.

Treatment of fraction 6 with aluminum chloride in the presence of benzene gave *t*-butylbenzene by degradation of part of the *t*-octylbenzenes originally present. The 1-*t*-amyl-2-*t*-butylbenzene was substantially unaffected, since the same yield of its dinitro derivative and sulfonamide was obtained both before and after aluminum chloride treatment.

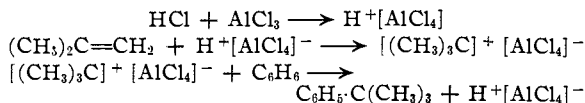
The tertiary structure is tentatively assigned to the hexyl, heptyl and octyl groups in view of, (a) the method of preparation, (b) the boiling points of the mixtures, (c) the difficulty of oxidation to the carboxyl group, (d) in the case of the octylbenzene the formation of *t*-butylbenzene by treating the hydrocarbon mixture with aluminum chloride.

Fractions 7–12.—No derivatives were prepared but each fraction was oxidized, giving terephthalic acid. By evaporation of the acid filtrates, residues were obtained from two of the fractions which gave positive fluorescein tests for phthalic acid. No tricarboxylic acid could be detected in any of the oxidation products, and apparently the main constituents of the 250–304° cut are *p*-di-*t*-alkylbenzenes. The tertiary structure is again assumed, for the reasons given in (a), (c) and (d) above.

When 96% sulfuric acid was used as the alkylation catalyst earlier reports^{4,7} that *t*-butyl- and 1,4-di-*t*-butylbenzene are the main products were confirmed. However, *t*-amylbenzene and material corresponding to fraction 4 of the aluminum chloride preparation were obtained in sufficient yield to permit definite identification by means of crystalline derivatives, while other fractions appeared to be similar to fractions 3 and 6 of the aluminum chloride preparation. Only a very small proportion of the product boiled above 250°.

Discussion

Any plausible mechanism to explain the course of this complicated reaction must take into account the fact that no isopropylbenzene is ever formed and hence no propene or propyl ion ever exists free in the solution. It is suggested that the alkylbenzenes described in this paper were formed by further reactions of *t*-butyl- and 1,4-di-*t*-butylbenzene which constitute the primary reaction products. *t*-Butylbenzene is formed in the manner now widely accepted for such alkylations, by the reaction of a positively charged *t*-butyl ion with a benzene molecule which may also be activated by the presence of aluminum chloride.⁸



Reaction with a second *t*-butyl ion gives 1,4-di-*t*-butylbenzene. Exclusive formation of the *p*-disubstituted derivative agrees with previous experience of *t*-butylbenzene substitution reactions.⁹ It is due to the strong inductive displacement of electrons caused by the *t*-butyl group¹⁰ and to the shielding effect of this group in the ortho position.

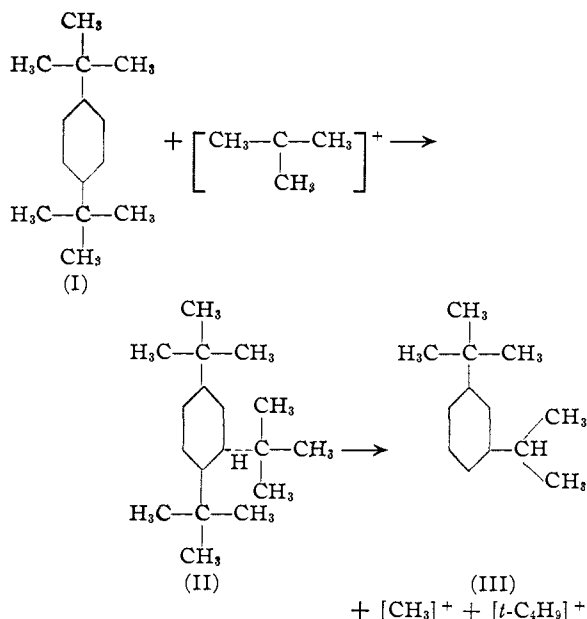
In the molecule of 1,4-di-*t*-butylbenzene (I), inductive displacements from two *t*-butyl groups set up a very high electron density in the nucleus which tends to facilitate further substitution. However attack by a *t*-butyl ion tending to form 1,3,4-tri-*t*-butylbenzene proceeds only to the transition complex stage (II), when closer approach of the entering group to form a stable linkage is prevented by steric hindrance from the adjacent *t*-butyl group. Even in the transition complex state the latter group must be strained from its normal position. The instability due to this strain is increased by electromeric displacements from the group entering the ortho position which reinforce those of the group occupying the para position. Finally the transition complex is characterized by a high electron density on the quaternary carbon atom of the attacking group, induced by the high nuclear density.

(7) Koch and Steinbrink, *Brennstoff-Chemie*, **19**, 277 (1938).

(8) Whitmore, *THIS JOURNAL*, **54**, 3274 (1932); Lure and Golovacheva, *J. Gen. Chem., U. S. S. R.*, **13**, 189 (1943) *C. A.*, **38**, 1483; Fairbrother, *Trans. Faraday Soc.*, **37**, 763 (1941); Price and Ciskowski, *THIS JOURNAL*, **60**, 2499 (1938).

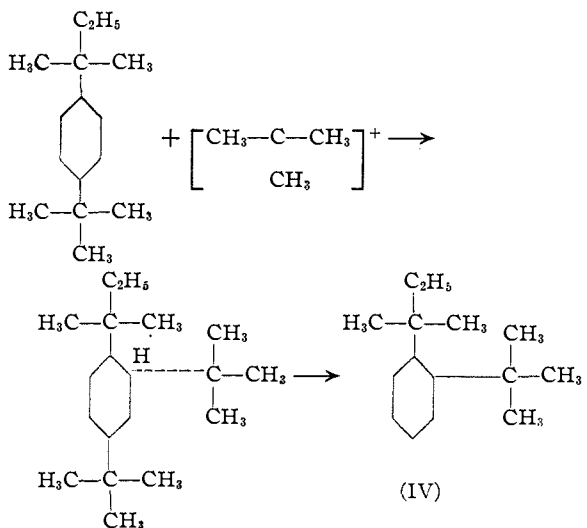
(9) Shoesmith and Mackie, *J. Chem. Soc.*, 2334 (1928).

(10) Kharasch and Flenner, *THIS JOURNAL*, **54**, 674 (1932); Gleave, Hughes and Ingold, *J. Chem. Soc.*, 238 (1935).



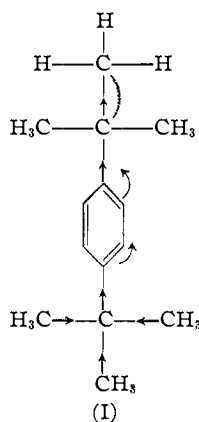
A stable molecule forms from this transition complex as a result of two processes. The proton being displaced from the nucleus by the entering *t*-butyl group forms a new attachment to the adjacent electronegative quaternary carbon atom of this group, and one of the less electrophilic methyl groups is expelled as a cation. At the same time the unstabilized group in the ortho position suffers replacement by a more electrophilic proton, the final stable product being 1-isopropyl-2-*t*-butylbenzene (III). Formation of 1-isopropyl-3-*t*-butylbenzene follows a similar sequence in which the other *t*-butyl group in (II) is replaced by proton. The considerably smaller extent of this reaction as compared to that leading to 1-isopropyl-3-*t*-butylbenzene is a measure of the relative stabilities of the para *t*-butyl groups in the complex (II).

1-*t*-Amyl-2-*t*-butylbenzene (IV) is formed in a



similar manner from 1-*t*-amyl-4-*t*-butylbenzene, which, although not identified, is very probably a constituent of the alkylate fraction boiling above 250°. In this case the different alkyl substituents cause unequal electron distribution in the nucleus. The position ortho to *t*-amyl will be the preferred center for attack since the electronic displacements caused by this group exceed those of the *t*-butyl group. The latter will be sufficiently labile to migrate, leaving a stable molecule, before the entering *t*-butyl ion can be degraded to isopropyl.

The methyl ion liberated during the formation of (III) is evidently unable to alkylate the benzene nucleus under the experimental conditions. Instead it reacts with a *t*-butyl group of 1,4-di-*t*-butylbenzene, forming 1-*t*-amyl-4-*t*-butylbenzene and liberating a proton. Reaction of additional methyl ions with this compound gives 1-*t*-hexyl-4-*t*-butylbenzene, 1-*t*-heptyl-4-*t*-butylbenzene and 1-*t*-octyl-4-*t*-butylbenzene. Although secondary and tertiary hydrogen atoms will be most easily replaced, attack is not confined to these and a mixture of isomers is formed in each case. These compounds boil above 250°. They were obtained in narrow boiling range cuts but complete isolation was impracticable. However, during the reaction they were partly dealkylated to the corresponding *t*-amyl-, *t*-hexyl-, *t*-heptyl- and *t*-octylbenzenes. These monoalkylbenzenes were in molecular quantities which decreased in the following order: *t*-octyl- > *t*-amyl- > *t*-hexyl- > *t*-heptylbenzene. It is suggested that part of the *t*-octylbenzenes was formed by a similar route in which 1,4-di-*t*-butylbenzene was alkylated by a *t*-butyl ion. Since part of this material was decomposed by aluminum chloride with formation of *t*-butylbenzene, the possibility of direct alkylation by isobutene dimer is not excluded.



This novel alkylation is readily explained by considering the conjugation of the nucleus to extend to the side chain¹¹ of 1,4-di-*t*-butylbenzene.

The inductive effect of one *t*-butyl group is transmitted to the methyl carbon atoms of the

p-*t*-butyl group (I). During part of the resonance cycle these carbons will have a fractional negative charge and be readily available points of attack for a positive carbonium ion.

Support for this proton-carbonium ion mechanism is provided by the isolation of the same products when the alkylation is catalyzed by sulfuric acid, another proton donor, instead of aluminum chloride. Elsewhere it has been shown that proton donating substances such as hydrogen fluoride¹² and ferric chloride³ are capable of catalyzing the alkylation of benzene by olefins whilst boron fluoride¹³ does not cause alkylation in the absence of proton donating promoters.

Additional evidence in support of the above mechanisms will be presented in the next paper of the series.

Experimental

Materials.—Commercial pure benzene was fractionated through a column containing 12" of 1" diam. Stedman packing¹⁴ (about ten theoretical plates). A fraction was selected which boiled at 80.5° and had the properties n_{D}^{20} 1.4943, d_4^{20} 0.8683.

Isobutene was prepared by the dehydration of pure *t*-butyl alcohol (f. p. 25°) over activated bauxite at 350°. Analysis with mercuric nitrate solution¹⁵ indicated 100% purity. A sample hydrogenated over nickel on kieselguhr was shown to be 100% isobutane by Podbielniak analysis.

Aluminum chloride was J. T. Baker Analyzed.

Preparation.—Benzene (1500 ml., 16.5 moles) was placed in a 3-liter 3-necked flask fitted with gas inlet and outlet tubes, thermometer and a mercury seal stirrer. Aluminum chloride (50 g., 0.4 mole) was added and isobutene was passed into the well-stirred mixture at 15–22°.

When a 60% volume increase had taken place, the viscous aluminum chloride layer was separated. The clear top layer was neutralized with 5% sodium hydroxide solution, washed with water and dried. The product was distilled through a 12" Hempel column and the following fractions were separated: <90°; 90–177°; 177–205°; 205–235°; 235–250°; >250°. Corresponding fractions from successive batches were mixed and refractionated separately through the Stedman packed column into 10-ml. cuts.

A considerable quantity of 1,4-di-*t*-butylbenzene was crystallized (ice, then solid carbon dioxide) from the two fractions boiling between 205–250° before they were refractionated.

The fraction <90° was benzene. Refractionation of the 90–177° fraction removed a little benzene and the remainder was pure *t*-butylbenzene (fraction (1)). The 177–205° fraction contained some *t*-butylbenzene. The remainder was mainly *t*-amylbenzene (fraction (2)) but three refractionations were necessary to obtain this substantially free from olefinic material boiling slightly below 190°. The highest boiling cuts from this fraction were combined with the lowest boiling cuts from the 205–235° fractions, and after several refractionations a product was obtained, distilling at 205–210° which could not be more completely resolved (fraction (3)). Most of the 205–235° fraction distilled at 221–222° after three refractionations (fraction (4)). 1,4-Di-*t*-butylbenzene crystallized extensively from the higher boiling cuts and residue from this fraction. As much solid as possible was filtered off and the filtrates were refractionated. It was possible

(12) Simons and Archer, *ibid.*, **60**, 986, 2952 (1938).

(13) Wunderley, Sowa and Nieuwland, *ibid.*, **55**, 1007 (1936).

(14) Bragg, *Ind. Eng. Chem.*, **33**, 279 (1941).

(15) Newton and Buckler, *Ind. Eng. Chem. Anal. Ed.*, **12**, 251 (1940).

(11) Baker and Nathan, *J. Chem. Soc.*, 1844 (1935); Hughes, Ingold and Taher, *ibid.*, 949 (1940); Mulliken, Rieke and Brown, *THIS JOURNAL*, **63**, 41 (1941).

to remove a further small quantity of solid from the residue of the second fractionation. Similarly from the lower boiling cuts of the 235–250° fraction, 1,4-di-*t*-butylbenzene could be crystallized after six refractionations. Most of the material from this fraction distilled at 240–243° and was a mixture of *t*-octylbenzenes with 1-*t*-amyl-2-*t*-butylbenzene (fraction (6)). The solid, removed at various stages, was combined and recrystallized twice from isopropyl alcohol. It gave large white crystals, m. p. 77.8–78.4°.

TABLE II
CRUDE ALKYLATE 170–250°: COMPOSITION

Frac- tion	Benzenes		Weight, %	Moles, %
	Monoalkyl	Dialkyl		
2	<i>t</i> -Amyl-		2.07	2.60
3	<i>t</i> -Hexyl-		1.86	2.13
4	<i>t</i> -Heptyl	1-Isopropyl-2- <i>t</i> -butyl-	0.45	0.47
		1-Isopropyl-3- <i>t</i> -butyl-	1.96	1.98
5		1,4-Di- <i>t</i> -butyl-	20.41	21.53
6	<i>t</i> -Octyl		63.23	61.75
		1- <i>t</i> -Amyl-2- <i>t</i> -butyl-	8.75	8.37
			1.25	1.19

Figure 1 is a demonstration graph. It was obtained by recombining the fractions from the Hempel column in the correct proportions and refractionating through the Stedman packing. Most of the *t*-butylbenzene and 1,4-di-*t*-butylbenzene were removed. Material boiling above 250° was distilled separately under reduced pressure. The distillation curve is shown in Fig. 2. Corresponding fractions from successive distillations were bulked and given one refractionation.

In another series of alkylations benzene well stirred at 20–30° reacted with isobutene in the presence of 5% of 96% sulfuric acid. The mixture became thick with solid 1,4-di-*t*-butylbenzene after a short time and isobutene no longer reacted with it. When the mixture was thinned down with a considerable quantity of carbon disulfide, the 1,4-di-*t*-butylbenzene still did not react with any more isobutene. The latter passed through the solution with but little absorption.

It was always necessary to decompose alkyl sulfates which were formed in the reaction and gave a purple color to the mixture, by autoclaving at 200° for six hours with 40% sodium hydroxide. Even so, it was necessary to fractionate the liquid product at 8–10 mm. pressure in order to avoid some decomposition.

The product contained 85% of 1,4-di-*t*-butylbenzene. Of the remainder 5% was *t*-butylbenzene, 2% *t*-amylbenzene, 4% 1-isopropyl-3-*t*-butylbenzene, and the rest was higher boiling material. These products were identified in exactly the same manner as described for the products of the aluminum chloride catalyzed reaction.

Experimental Methods: Oxidation.—All of the hydrocarbons were completely resistant to oxidation by dilute nitric acid under reflux, potassium permanganate or chromic acid. They could be oxidized at 135–180° and with 15–60% nitric acid according to the difficulty of oxidation. A flask having a ground jointed stopper through which passed a 3" length of 1-mm. capillary tubing¹⁶ and fitting inside a rotating autoclave, was used. Before heating the autoclave was filled with hydrogen at 1000 lb./sq. in. pressure. Oxidation conditions were critical and it was often difficult to obtain oxidation without nitration. In some cases the addition of vanadium pentoxide proved useful. Nitro compounds were all oxidized in a similar manner with 50% nitric acid at 180° for six hours.

Methyl and ethyl esters were prepared by refluxing the acid with an excess of the requisite alcohol in presence of dissolved hydrogen chloride for four hours.

Nitration.—A well-stirred solution of hydrocarbon, usually about 1 g. mole, in an equal volume of acetic acid and two-thirds the volume of acetic anhydride was

nitrated with slightly more than one equivalent of 96% nitric acid added dropwise at 30–40°. After standing twenty-four hours water was added, the product was taken up in petroleum ether, and washed with dilute sodium hydroxide and water. Solids were purified by crystallization and liquids by fractionation at 8–10 mm. pressure.

The dialkylbenzenes were dinitrated by stirring with 13–18 equivalents of 96% nitric acid at room temperature. Under these conditions the monoalkylbenzenes gave only liquid mononitro derivatives. In certain cases a higher temperature or addition of sulfuric acid gave better yields of the solid dinitro derivatives.

Amines.—The nitro compounds were dissolved in two parts of alcohol and reduced over nickel on kieselguhr at 100°, the initial hydrogen pressure being 1200 lb./sq. in. The product was fractionated, or recrystallized if solid. Acetic anhydride was used in preparing acetyl derivatives. Benzoyl derivatives were prepared with benzoyl chloride in pyridine.

Chlorosulfonation.—A solution of hydrocarbon (about 1 g. mole) in four to five volumes of carbon tetrachloride was stirred at room temperature while adding an 80% excess of chlorosulfonic acid. The mixture was immediately poured on shaved ice, washed and neutralized. If solid, the sulfonyl chlorides were recrystallized from petroleum ether.

Sulfonamides were prepared by treating a benzene solution of the sulfonyl chloride with 28% ammonia at room temperature for twenty-four hours. The products were crystallized from boiling water or 1% aqueous isopropyl alcohol. Sulfonanilides were prepared in the same way with a small excess of aniline instead of ammonia. They were crystallized from isopropyl alcohol with just insufficient water to cause precipitation as an oil. The solubility of these derivatives in 10% sodium hydroxide solution was very low.

All melting points given are corrected.

Fraction 2: *t*-Amylbenzene.—Oxidation (2.6 g., 60 ml. of 15% nitric acid; 135°; eight hours) gave a green solution containing a suspension of 4-nitrobenzoic acid. This was filtered off, washed with a few ml. of water and dried. It weighed 0.3 g. (10%), m. p. 238–240°. The methyl ester melted at 92.3–93.7°. In admixture with an authentic specimen (m. p. 95.8–96.2°) the m. p. was 92.0–93.8°. Evaporation of the filtrate to 10 ml. gave 1 g. (48%) of benzoic acid, m. p. and m. m. p. with an authentic specimen, 121°. The amine hydrochloride

TABLE III
FRACTION 2: *t*-AMYL BENZENE

Derivative ^a	M. p., °C.	Yield, %	Lit., m. p., °C.
4-Acetylamino-	138.5–139.5	82 ^b	141–142° 138–139 ^d
4-Benzoylamino-	108.1–108.9	92 ^b	112–113° 158 ^d
4-Hydroxy- ^b	92.3–93.3	54 ^b	95° 93 ^d
4-Sulfonylchloride	50.4–51.3	85 ^e
4-Sulfonamido-	84.7–85.2	92 ^f	83–84 ^g
4-Sulfonanilido- ⁱ	110.6–111.4	90 ^f

^a Similar derivatives were prepared from the authentic *t*-amylbenzene made by the method of Ipatieff, Pines and Schmerling, ref. 5. The melting points were identical with those of the corresponding derivatives given in Table III, and the mixed melting points showed no depression.

^b Based on amine used; yield of amine was 74% of hydrocarbon. ^c Ipatieff, Pines and Schmerling, THIS JOURNAL, 60, 1476 (1938). ^d Anschütz and Beckerhof, Ann., 327, 218 (1903). ^e On hydrocarbon. ^f On sulfonyl chloride. ^g Huntress and Autenrieth, THIS JOURNAL, 63, 3446 (1941). ^h By diazotizing the amine sulfate. ⁱ Calcd. for C₁₇H₂₁O₂NS: C, 67.3; H, 7.0. Found: C, 67.5; H, 7.0.

(from 20% hydrochloric acid) had a neut. equiv. of 200.0 (calcd. for $C_{11}H_{17}N \cdot HCl$, 199.7). The melting points of other derivatives prepared from this fraction are given in Table III.

Fraction 3: *t*-Hexylbenzenes, 1-Isopropyl-2-*t*-butylbenzene.—Oxidation (5 g., 56 ml. of 28% nitric acid, 1 g. vanadium pentoxide, 130°, six hours) gave a green solution with some pale yellow solid in suspension and some unreacted oil. Nitrated acids were reduced with tin overnight and benzoic acid (0.6 g., 15%) melting point and mixed melting point with an authentic specimen, 121°, was isolated by extraction with benzene. The unreacted oil (2.2 g.) was oxidized with 40 ml. of 50% nitric acid, (0.6 g. vanadium pentoxide, 180°, five hours). The product was treated in the same manner as above and finally ether extraction gave 0.3 g. (15%) of phthalic acid. This gave strongly positive fluorescein and phenolphthalein tests. A sample of phthalanil prepared from it melted at 199–202° (insufficient to recrystallize), and this melting point was not depressed in admixture with authentic phthalanil.

3,5-Dinitro-1-isopropyl-2-*t*-butylbenzene.—Nitration in acetic acid gave a mixture of oily mononitro derivatives. Dinitration gave an oily mixture from which a pale yellow solid crystallized. It melted at 143.1–143.7°. Barbier's dinitro-1-isopropyl-2-*t*-butylbenzene⁸ melted at 142°.

Oxidation (4 g., 48 ml. of 50% nitric acid, 180°, six hours) gave a green solution which was evaporated to 20 ml. 3,5-Dinitroisophthalic acid (0.55 g., 13%), m. p. 220–224°, crystallized on cooling. The ethyl ester (0.5 g., 95%) melted at 184.0–185.0°. Beilstein and Kurbetow¹⁷ gave 226 and 187° for the melting points of the acid and ester, respectively.

The remainder of the nitration product was an oil, evidently 4-nitro-*t*-hexylbenzenes, since oxidation gave 4-nitrobenzoic acid, melting point and mixed melting point of the methyl ester with an authentic specimen, 93.4–94.8°.

The mononitration product (acetic acid) was hydrogenated, giving a mixture of amines. A solution containing 110 g. of the amines in 200 ml. of petroleum ether was treated with dry hydrogen chloride and a precipitate (21.3 g., 17%) of 5-aminohydrochloride-1-isopropyl-2-*t*-butylbenzene was formed. The neut. equiv. was 226.8 (calcd. for $C_{13}H_{21}N \cdot HCl$, 227.8).

The dihydrochloride (dry hydrogen chloride on an iso-octane solution of the diamine) was easily hydrolyzed by water. Its neutralization equivalent was 141.0 (calcd. 139.6). From the remaining liquid portion of amine hydrochlorides a crystalline benzoyl derivative was obtained. It was 4-benzoylamino-*t*-hexylbenzene. The structure of the hexyl group is unknown. It formed white crystals m. p. 111.2–112.0°. In admixture with 4-

benzoylamino-*t*-amylbenzene (m. p. 108.0–108.9°) the m. p. was 100.0–105°.

The melting points and analyses of other derivatives of 1-isopropyl-2-*t*-butylbenzene are given in Table IV.

Fractional crystallization of the total sulfonic acid sodium salts from this fraction (by hydrolysis of the sulfonfyl chloride mixture) gave a mixture containing mainly *t*-hexylbenzene derivatives.

Anal. Calcd. for $C_{13}H_{17}O_3SNa$: Na, 8.70. Calcd. for $C_{13}H_{19}O_3SNa$, 8.26. Found: Na, 8.62.

Oxidation gave 4-nitrobenzoic acid, m. p. and mixed m. p. of the methyl ester gave 94.6–95.9°.

Reconversion to sulfonyl chlorides (phosphorus pentachloride) and then to sulfonamides gave a semi-solid mixture from which no single sulfonamide could be crystallized.

Fraction 4: 1-Isopropyl-3-*t*-butylbenzene, *t*-Heptylbenzenes.—Oxidation (7.7 g., 48 ml. of 50% nitric acid, 180°, five hours) gave a green solution with a pale yellow solid in suspension. The acid was purified and nitro derivatives were removed as described for fraction 3. Isophthalic acid (2 g., 28%) was left and gave dimethyl isophthalate, m. p. 65.1–66.1°. This melting point was not depressed when in admixture with an authentic specimen. When three times the ratio of nitric acid was used a 41% yield of 5-nitroisophthalic acid was obtained, m. p. 246.0–247.4°. The dimethyl ester melted at 121.2–121.6°. Corresponding literature values¹⁸ are 249 and 121.5°, respectively. Oxidation (2.6 g., 50 ml. of 10% nitric acid, 0.5 g. vanadium pentoxide, 150°, twelve hours) left most of the oil apparently unchanged. The dark green solution was made alkaline with solid sodium carbonate, extracted twice with benzene, filtered and re-acidified with hydrochloric acid. An oil separated and solidified on standing (0.32 g., 12%). It was recrystallized from boiling water, giving small white needles, m. p. 127.5–127.9°. The melting point of 3-*t*-butylbenzoic acid is reported¹⁹ as 127°. From the liquid, by evaporation to 25 ml. there was obtained 0.14 g. (5%) of 5-nitro-3-*t*-butylbenzoic acid, m. p. 140.0–140.4°. The literature value¹⁸ is 140°.

6-Nitro-1-isopropyl-3-*t*-butylbenzene (I).—Nitration of fraction 4 in acetic acid with 1.3 equivalents of nitric acid gave a 78% yield of (I) together with 11% of 4-nitro-*t*-heptylbenzenes and 11% of unreacted hydrocarbon.

Oxidation of (I) (5 g.) gave 2.2 g. (47%) of 4-nitroisophthalic acid m. p. 243–244.5°, which gave the dimethyl ester melting at 85.8–87.2°. Axer²⁰ reported 87–88.5°. In admixture with methyl 4-nitrobenzoate the m. p. was depressed to 62.0–71.6°. Oxidation of the liquid nitroheptylbenzenes gave 4-nitrobenzoic acid m. p. and mixed m. p. of the methyl ester, 93.9–95.6°.

The hydrochloride of 6-amino-1-isopropyl-3-*t*-butylbenzene was prepared by hydrolysis of the acetyl derivative with 10% hydrochloric acid, and directly from the amine; neut. equiv. was 228.2 (calcd. 227.8).

4,6-Dinitro-1-isopropyl-3-*t*-butylbenzene (II).—Nitration of 85 g. of fraction 4 at room temperature for six hours gave 113 g. (88%) of pale yellow oily solid. Crystallization from isopropyl alcohol gave white plates turning yellow on exposure, m. p. 154.2–156.7°. A yellow oil (9.4 g.) was also obtained (from the *t*-heptylbenzenes). By repeated recrystallization a small quantity of the mono nitro derivatives (I) was removed and the melting point was raised to 165.4–166.3°. This melting point was more readily obtained by further treatment of the once crystallized material with nitric acid, followed by another crystallization. Barbier³ gave 149° as the melting point of the dinitro derivative which he obtained from 1-isopropyl-3-*t*-butylbenzene.

Oxidation of 5 g. of (II) gave 0.6 g. (12%) of 4,6-dinitroisophthalic acid, ethyl ester m. p. 122.2–123.0°. The literature value²¹ for diethyl 4,6-dinitroisophthalate is 124°.

(18) Beyer, *J. prakt. Chem.*, [2] **25**, 490 (1894).

(19) Kelbe and Pfeiffer, *Ber.*, **19**, 1726 (1886).

(20) Axer, *Monatsh.*, **41**, 158 (1920); *C. A.*, **14**, 3409 (1920).

(21) Ruggli and Schmid, *Helv. Chim. Acta*, **18**, 247 (1935).

TABLE IV

FRACTION 3: 1-ISOPROPYL-2-*t*-BUTYLBENZENE

Derivative ^a	M. p., °C.	Analyses, %			
		Carbon		Hydrogen	
		Calcd.	Found	Calcd.	Found
5-Acetylamino ^b	123.6–123.9	77.8	77.9	9.9	10.0
5-Benzoylamino ^c	167.3–168.2	81.3	81.6	8.5	8.6
5-Sulfonamido ^d	186.6–187.5	61.6	60.9	8.3	8.3
5-Hydroxy ^e	118.7–119.9	81.2	81.3	10.5	10.3
3,5-Dinitro	143.1–143.7	58.6	59.5	6.8	6.8
3,5-Diamino ^f	130.6–131.3	75.7	75.2	10.7	10.7
3,5-Diacetylamino ^g	239.3–240.6	70.3	70.4	9.0	8.9

^a Yields of primary derivatives were 12–15% on the total hydrocarbon. The remainder consisted of non-crystallizable mixtures of *t*-hexylbenzene derivatives.

^b White flakes (50% isopropyl alcohol). ^c White interlocking needles (isopropyl alcohol). ^d Long white needles (2% isopropyl alcohol). ^e By diazotizing an acetic acid solution of the amine. Pale yellow flakes from petroleum ether. ^f Buff solid (iso-octane). ^g White flakes (50% isopropyl alcohol).

(17) Beilstein and Kurbetow, *Ann.*, **202**, 227 (1880).

TABLE V
 FRACTION 4: 1-ISOPROPYL-3-*t*-BUTYL BENZENE

Derivative ^a	M. p., °C.	Analyses, %			
		Carbon		Hydrogen	
		Calcd.	Found	Calcd.	Found
6-Nitro. ^b	50.1-51.1	70.6	70.6	8.6	8.5
6-Acetylamino. ^b	153.3-153.6	77.3	77.3	9.9	9.9
6-Benzoylamino. ^c	233.9-234.1	81.3	81.1	8.5	8.6
6-Sulfonylchloride. ^{d,i}	89.5-90.5	56.8	56.9	7.0	7.0
6-Sulfonamido. ^e	158.8-159.1 ^g	61.1	61.3	8.3	8.4
6-Sulfonanilido. ^f	136.9-137.5	68.9	68.6	7.6	7.6
4-Nitro-6-sulfonyl chloride. ^k	142.6-143.6	48.8	49.1	5.7	5.7
4-Nitro-6-sulfonamido. ^g	184.8-185.8	52.0	52.1	6.7	6.8
4-Nitro-6-sulfonanilido. ^g	184.5-185.6	60.6	60.7	6.4	6.6
4,6-Dinitro-.	165.4-166.3	58.6	58.7	6.8	6.9
4,6-Diamino. ^l	159.1-160.6	75.7	75.7	10.7	10.7
4,6-Diacetylamino. ^m	323-325 ^h	70.3	70.5	9.0	9.0

^a Yields of primary derivatives were 75-80%. The remainder consisted mainly of non-crystallizable derivatives of mixed *t*-heptylbenzenes. ^b White flakes (90% isopropyl alcohol). ^c Long white needles (isopropyl alcohol-benzene). ^d White prisms. ^e White ribbons. Repeated recrystallization of the crude sulfonamide from petroleum ether gave a product m. p. 147.7-148.8°, which probably contained some sulfone. ^f White flakes. ^g White flakes (isooctane, benzene). ^h Uncorrected. ⁱ Calcd.: Cl, 12.9. Found: Cl (by hydrolysis) 12.9. ^k Calcd.: Cl, 11.1. Found: Cl (by hydrolysis), 11.0. ^l Light brown crystals (isooctane). ^m White flakes (dilute acetic acid).

The dihydrochloride of 4,6-diamino-1-isopropyl-3-*t*-butylbenzene crystallized from 20% hydrochloric acid, as very soluble white needles. Neut. equiv. was 139.9 (calcd. 139.6).

1-Isopropyl-3-*t*-butylbenzene-6-sulfonyl Chloride (III).—By adding 480 g. (2.1 equiv.) of chlorosulfonic acid to 170 g. of fraction 4, 154 g. (67%) of (III) was obtained.

The corresponding sulfonic acid sodium salt (by hydrolysis of (III) with 10% sodium hydroxide) crystallized readily from water.

Anal. Calcd. for C₁₃H₁₉O₃SNa: Na, 8.26. Found: Na (as Na₂SO₄), 8.20. Calcd. for C₁₃H₁₉O₃SNa·5H₂O: H₂O, 24.45. Found: H₂O, 24.4.

The oily residue remaining from (III) probably contained *t*-heptylbenzene-sulfonyl chlorides since oxidation gave 4-nitrobenzoic acid.

4-Nitro-1-isopropyl-3-*t*-butylbenzene-6-sulfonyl Chloride.—Powdered (III) (8 g.) was added rapidly at 30° to 25 ml. (20 equivs.) of 96% nitric acid. A homogeneous orange solution formed. After shaking for sixty-five minutes it was poured into 2000 ml. of ice-cold water, and a white granular solid separated (8.2 g., 90%). It crystallized from petroleum ether, m. p. 142.6-143.6°.

Aluminum Chloride.—Stirring 128 g. (0.72 mole) of fraction 4 with 750 ml. of benzene and 25 g. (0.19 mole) of aluminum chloride at 45° for two hours, gave 93 g. (0.66 mole) of *t*-butylbenzene (acetylamino, m. p. and mixed m. p. 173.0-174.3°). The remainder was mainly *t*-heptylbenzenes boiling at the original temperature. No isopropylbenzene was formed.

Fraction 6: *t*-Octylbenzenes, 1-*t*-Amyl-2-*t*-butylbenzene.—Oxidation (4.2 g., 62 ml. of 28% nitric acid, 1 g. of vanadium pentoxide, 180°, nine hours) gave a green solution with some pale yellow solid in suspension and some unreacted oil. The solid dissolved when sodium carbonate was added. The solution was extracted with benzene and filtered. Nitrated acids were reduced with tin overnight (hydrochloric acid) and the resulting solution was extracted three times with benzene. Evaporation left 0.4 g. (10%) of benzoic acid. The m. p. and the m. m. p. with an authentic specimen were 121°. Oxidation (6 g., 60 ml. of 60% nitric acid, 180°, eight hours) followed by reduction and benzene extraction as above left an almost colorless solution from which 0.2 g. (4%) of phthalic acid was obtained by ether extraction. This gave phthalanil (insufficient to recrystallize) m. p. 199-202.7°, not depressed when in admixture with an authentic specimen. It gave strongly positive fluorescein and phenolphthalein tests.

5-Benzoylamino-1-*t*-amyl-2-*t*-butylbenzene.—This was the only crystalline derivative which could be isolated in

a pure condition after nitration and reduction of fraction 6. It separated (1.2 g.) as a white solid when the viscous mixed benzoyl derivatives (from 4.6 g. of amine) were triturated with petroleum ether.

3-*t*-Amyl-4-*t*-butylphenol.—By diazotizing 9 g. of the mixed amines there was obtained after caustic solution and steam distillation, 7.2 g. of brown oil which would not crystallize. Benzoyl chloride in pyridine reacted with these phenols (6 g.) to give 6.6 g. of ester from which 1.9 g. of solid eventually crystallized.

 TABLE VI
 FRACTION 6: 1-*t*-AMYL-2-*t*-BUTYL BENZENE

Derivative ^a	M. p., °C.	Analyses, %			
		Carbon		Hydrogen	
		Calcd.	Found	Calcd.	Found
5-Acetylamino. ^b	109-113
5-Benzoylamino. ^c	208.7-209.9	81.7	81.7	9.0	9.0
5-Hydroxybenzoate. ^d	117.2-117.9	81.4	81.5	8.7	8.6
5-Sulfonamido. ^e	206.6-207.6	63.6	63.3	8.9	8.9
3,5-Dinitro. ^f	201.0-202.0	61.1	61.1	7.5	7.4
3,5-Diamino. ^g	181.4-182.6 ^h	76.9	76.9	11.2	11.2
3,5-Diacetylamino-.	239.6-240.0 ⁱ	71.6	71.3	9.5	9.3

^a Yields were of the order of 12-15%, the remainder being mainly mixed derivatives of isomeric *t*-octylbenzenes which would not crystallize. ^b After standing for three weeks and trituration with petroleum ether; from isopropyl alcohol. ^c From 90% isopropyl alcohol. ^d Silvery white flakes (80% isopropyl alcohol). ^e White crystals (15% isopropyl alcohol). ^f Pale yellow flakes which turn buff color on exposure. ^g White flakes from isooctane, turning brown on keeping. ^h Decomposition. ⁱ Uncorrected.

3,5-Dinitro-1-*t*-amyl-2-*t*-butylbenzene.—After stirring fraction 6 (22 g.) with 96% nitric acid at 60°, 3.8 g. (9%) of the dinitro compound crystallized from the product, which was mainly oil. At 0° the yield was 6%. At 60°, 43 g. of hydrocarbon with 112 g. (7 equivs.) of nitric acid and 200 ml. of 98% sulfuric acid, gave 8 g. (12%) of dinitro compound.

Oxidation (4 g.) gave 0.72 g. (17%) of 3,5-dinitro-phthalic acid. The ethyl ester¹⁷ melted at 185.0-186.0°.

The remainder of the nitration product evidently consisted of 4-nitro-*t*-octylbenzenes since oxidation gave 4-nitrobenzoic acid, m. p. and mixture m. p. of the methyl ester, 95.3-95.9°.

The dihydrochloride of 3,5-diamino-1-*t*-amyl-2-*t*-butylbenzene was prepared by passing dry hydrogen chloride

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 $C_{18}H_{29}O_2S$: 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 $C_{18}H_{29}O_2NS$: 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 $C_{14}H_{21}O_2S$: Cl, 12.3. Calcd. for $C_{16}H_{23}O_2S$: 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

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

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. 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

[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 years² 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 failed³ and proof of orientation has rested mainly on the claim by Boedtker⁴ of its oxidation to 4-*t*-butylbenzoic acid by chromic oxide in acetic acid. Baur⁵ sulfonated the compound and described the product as 1,4-di-*t*-butylbenzene-2-sulfonic acid. Huntress and Autenrieth⁶ 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 Baur⁵ using hot nitrosylsulfuric acid this compound melted at 167–168° and smelt of musk. Verley³ 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 Boedtker⁷ 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-

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

(1a) Present address: Anglo Transvaal Consolidated Investment Company, Ltd., Johannesburg, South Africa.

(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).