sulfuric acid with stirring, the temperature of the sulfuric acid mixture being maintained at 15°. After the addition was complete, stirring was continued for 16 hours at room temperature. This mixture was poured into an equal volume of water (cracked ice).

In the case of *m*-xylene and *m*-diethylbenzene this diluted medium was extracted several times with *n*-pentane. The sulfuric acid layer was then subjected to steam distillation yielding the desired hydrocarbon.

In the case of *m*-ethyl-*n*-butylbenzene and *m*-*n*-butyl-*t*-butylbenzene the original sulfonation mixture (containing sulfuric acid of sp. gr. 1.84) was diluted with an equal volume of water. The red oil which formed on top of the sulfuric acid layer was separated and diluted with about ten times its volume of water. This solution was extracted several times with *n*-pentane. The sulfonic acid was rendered insoluble by addition of concentrated sulfuric acid to the water and the organic layer was then subjected to steam distillation yielding the desired hydrocarbon.

When the sulfuric acid medium (sp. gr. 1.84) containing sulfonated *m*-di-*n*-butylbenzene was diluted 1 to 1 with water and extracted with low boiling petroleum ether, the sulfonic acid was found in the petroleum ether layer. On evaporation of the petroleum ether the acid was obtained as a red oil which upon crystallization from 30–60° petroleum ether gave pinkish white crystals which melted at 58–61°. This solid was soluble in ether, benzene, hot cyclohexane, in addition to water and alcohol. Clarification with carbon and recrystallization from 60–80° petroleum ether gave white crystals which melted at 62–64°.

Anal. Calcd. for $C_{14}H_{22}SO_3 \cdot H_2O$: C, 58.29; H, 8.38. Found: C, 58,19; H, 8.51.

After steam distillation the benzenoid hydrocarbons in every case were obtained by extraction of the steam distillate with ether, drying and distillation. The yields, physical properties and analytical data for these hydrocarbons can be found in Table I.

m-Xylene, *m*-diethylbenzene, *m*-ethyl-*n*-butylbenzene and *m*-di-*n*-butylbenzene were all oxidized with alkaline permanganate to isophthalic acid. The white solids obtained on oxidation melted above 300°. A mixed melting point determination with an authentic sample of isophthalic acid in every case melted above 300°. The di-(*p*-bromophenacyl) ester derivative of this acid was prepared in every case. These derivatives melted at 185° and gave no depression in a mixed melting point determination with the derivative prepared from an authentic sample of isophthalic acid.

2,4,6-Trinitro-*m*-xylene was prepared from our *m*-xylene sample. It melted at 182° and showed no depression in a mixed melting point determination with the 2,4,6-trinitro-derivative prepared from an authentic sample of *m*-xylene.

Preparation of *m*-*t*-Butylbenzoic Acid.—*m*-*n*-Butyl-*t*-butylbenzene (2.0 g.) was placed in 100 ml. of water in a three-neck 300-ml. flask with stirrer and reflux condenser attached. Potassium permanganate (4.0 g.) was added over a 24-hour period. The manganese dioxide was filtered and the excess potassium permanganate destroyed and then acidified with concentrated hydrochloric acid. White needles formed which on recrystallization from aqueous alcohol melted at 127° in agreement with earlier reports.[3]

Isolation of 1-Ethyl-3-*n*-butylcyclohexane.—The pentane layer which had been used to extract the solution containing sulfonated *m*-ethyl-*n*-butylbenzene was dried and then subjected to fractional distillation. After removal of the pentane a colorless liquid, 17 g. (from 82 g. of diene) was isolated, b.p. 98° (17 mm.). Redistillation of this material yielded 1-ethyl-3-*n*-butylcyclohexane, $n^{25}D$ 1.4442.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.63; H, 14.37. Found: C, 85.71; H, 14.43.

---

[3] K. T. Serijan, H. F. Hipsher and L. C. Gibbons, THIS JOURNAL, **71**, 1873 (1949).

COLLEGE PARK, MARYLAND RECEIVED MAY 12, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

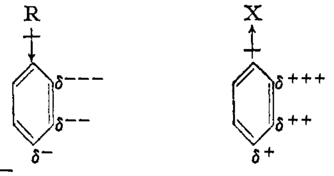
Distribution of Isomers in the Mononitration of *t*-Butylbenzene; Properties of the Pure Mononitro-*t*-butylbenzenes

BY K. LEROI NELSON[1] AND HERBERT C. BROWN

Nitration of *t*-butylbenzene with mixed acid yields *o*-, *m*- and *p*-nitro-*t*-butylbenzene in proportions of 15.8:11.5:72.7, respectively. The ortho/meta ratio is 1.37 as compared with 13.3 for toluene. The para/meta ratio is 6.32 as compared with 8.45 for toluene. The marked decrease in ortho substitution is attributed to the steric effect of the bulky *t*-butyl group. The individual mononitro-*t*-butylbenzenes have been carefully purified and their physical properties determined.

Discussion

Orientation in the substitution of benzene derivatives has been the subject of a wide variety of investigations from which a number of simplifying principles have emerged. Current theory has concerned itself primarily with the importance of electrical factors in controlling substitution. Thus, attempts have been made to correlate the observed ortho/para ratios in aromatic substitution with these electrical factors. According to this interpretation, inductive effects will activate the various ring positions in an inverse proportion to the distance from the substituent.[2]



However, it has not been possible to account for the observed ortho/para ratios in aromatic substitution in terms of the electrical factor alone. Certain anomalies in these ratios were attributed by LeFevre and his co-workers to steric hindrance by large substituent groups.[3] In this way the probability of ortho substitution would be dependent upon both the steric requirements and the electrical characteristics of the substituent groups. In support of his proposal LeFevre pointed out that electrophilic substitution of 1-methyl-4-isopropylbenzene occurs preponderantly at the 2-position.[3] However, it was pointed out that the results do not necessarily support the proposed interpretation in terms of steric effects. Consideration of hyperconjugation possibilities suggests that the position ortho to the methyl group should be more suscep-

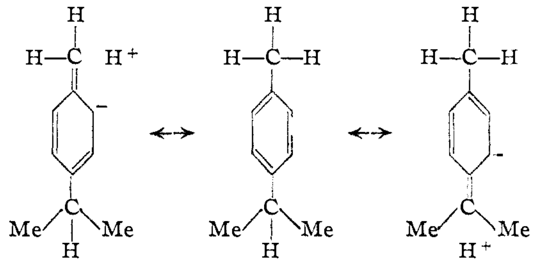
---

[1] A. E. C. Fellow at Purdue University, 1950–1951.

[2] A. Lapworth and R. Robinson, *Mem. Proc. Manchester Lit. & Phil. Soc.*, **72**, 43 (1927).

[3] (a) R. J. W. LeFevre, *J. Chem. Soc.*, 977, 980 (1933); 1501 (1934); (b) S. N. Ganguly and R. J. W. LeFevre, *ibid.*, 848, 852 (1934). For more recent discussion of steric effects as a factor in ortho substitution, see P. B. D. de la Mare and P. W. Robertson, *ibid.*, 279 (1943); E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949); M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949), and P. B. D. de la Mare. *ibid.*, 2871 (1949).

tible to electrophilic attack than the position ortho to the isopropyl group.[4]



(3 forms) (1 form)

There are a number of qualitative observations in the literature which can be quoted to support the importance of the steric factor in ortho substitution. However, it would be desirable to have quantitative data available on at least one clear-cut case which is free from the ambiguity of interpretation cited above for the substitution of 1-methyl-4-isopropylbenzene. A comparison of the orientation in toluene and *t*-butylbenzene would appear to be a suitable case of this kind. The two groups, methyl and *t*-butyl do not differ markedly in their electrical effects. Any large differences in these effects should be reflected in a change in the para/meta ratios. The steric requirements of the two alkyl groups are quite different. If there were no important differences in the para/meta ratios for the two cases, any large difference in the ortho/meta ratios would lend strong support to the importance of the steric requirements of the substituent on ortho substitution.

The nitration of toluene has been intensively studied and quantitative data are available for the relative quantities of ortho, meta and para isomers formed in the reaction. Unfortunately, similar data for *t*-butylbenzene are not available.

The nitration of *t*-butylbenzene was previously studied by Craig.[5] His fractionation equipment did not permit a complete analysis of his product and it is impossible from his results to estimate the quantities of the individual isomers that were present. By distillation he obtained three main fractions. He assumed that the first consisted of 90% ortho, the second a 50–50 mixture of ortho and para, and the third 90% para. He stated that although the meta isomer could have been present in small amounts, he found no evidence of its presence.

By the action of mixed acid on *t*-butylbenzene,[5] a 96% yield of mononitro-*t*-butylbenzenes was obtained. Careful fractionation of the product through efficient columns under reduced pressure permitted separation of the product into three fractions, b.p. 115.5, 128 and 135° at 10 mm. These fractions were established as *o*-, *m*- and *p*-nitro-*t*-butylbenzenes, respectively. *m*-Nitro-*t*-butylbenzene has been obtained previously[6] only by indirect synthesis—prior to the present study it has not been identified in the nitration of *t*-butylbenzene. However, the identity of the product was definitely established by catalytic reduction to *m*-*t*-butylaniline and preparation of the acetyl derivative, m.p. 101–102°.

The individual isomers were carefully purified and their physical properties determined. The purity of each compound was established as better than 99.5 mole per cent. from cryoscopic data. The physical properties are summarized in Table I.

Table I

Physical Properties of the Mononitro-*t*-butylbenzenes

	ortho	meta	para
B.p., °C., at 10 mm.	115.5[a]	128.0[b]	135.0[c]
M.p., °C.[d]	−2.56 ± 0.11	0.40 ± 0.09	28.41 ± 0.07
n^{20}_D	1.5171	1.5273	1.5337[e]
$\Delta H_f°$, cal./mole[f]	2340 ± 470	3080 ± 620	2820 ± 560
Purity, mole %[d]	99.68 ± 0.03	99.67 ± 0.03	99.84 ± 0.02

[a] Previously reported: 114–115° at 10 mm. [J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 2334, (1928)], 118° at 12 mm. [C. C. Price and D. C. Lincoln, This Journal, **72**, 2807 (1950)], and 143–145° at 45 mm. [ref. 5]. [b] Previously reported: 250–252° at 704 mm. [ref. 6]. [c] Previously reported: 125–130° at 10 mm. [S. and M., ref. *a*] and 155–158° at 30 mm. [ref. 5]. [d] From freezing curve data. [e] Supercooled liquid. [f] By comparative estimation.

The relative yields of isomers are listed in Table II together with data reported by Jones and Russell[7] for the nitration of toluene with mixed acid.

Table II

Distribution of Isomers Formed in the Mononitration of Toluene and *t*-Butylbenzene at 30°

	Mononitro derivative (%)		
	ortho	meta	para
Toluene	58.45	4.40	37.15
t-Butylbenzene	15.8	11.5	72.7

The mixed acid utilized by Jones and Russell (5.35% HNO_3, 1.75% HNO_2, 71.4% H_2SO_4 and 21.5% H_2O) differed from that employed in the present study (22.3% HNO_3, 65.6% H_2SO_4 and 12.1% H_2O). However, there is considerable evidence that the distribution of isomers in the nitration of toluene is not altered significantly by changes in the composition of the nitrating acid.[7,8] A comparison of the distribution of isomers in the two cases is therefore permissible.

The ratios of isomers formed in the mononitration of toluene and *t*-butylbenzene are given in Table III.

Table III

Isomer Ratios for the Mononitration of Toluene and *t*-Butylbenzene

	Isomer ratios		
	o/*p*	*o*/*m*	*p*/*m*
Toluene	1.57	13.3	8.45
t-Butylbenzene	0.217	1.37	6.32

As discussed previously, the ortho/para ratio is ambiguous in that it does not distinguish between steric and electrical factors. Since the meta position is not affected by resonance factors, it stands unique among the three positions of substitution. Therefore it seems more reasonable that this position should serve as the basis for correlations of

---

(4) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935); A. E. Remick, "Electronic Interpretation of Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., N. Y., 1949, p. 367.

(5) D. Craig, This Journal, **57**, 195 (1935).

(6) C. Gelzer, *Ber.*, **21**, 2941 (1888).

(7) W. W. Jones and M. Russell, *J. Chem. Soc.*, 921 (1947).

(8) A. F. Holleman, *et al.*, *Rec. trav. chim.*, **33**, 1 (1914); C. K. Ingold, *et al.*, *J. Chem. Soc.*, 1959 (1931).

isomer distribution. The ortho/meta ratio should exhibit the effects of both steric and electrical factors, while the para/meta ratio should reflect solely the effects of the electrical influences.

There is a tenfold reduction in the rate of substitution in the ortho position relative to the meta position of *t*-butylbenzene as compared to toluene. On the other hand, the ratio of para to meta substitution is not greatly different in the two cases.

The fact that the ratio of para to meta substitution in the two hydrocarbons does not differ greatly supports the conclusion that there is no unusual electrical effect of the *t*-butyl group which strongly activates the para position at the expense of the ortho. The marked decrease in substitution in the ortho position is more plausibly attributed to the large steric requirements of the *t*-butyl group. The results, therefore, offer clear-cut evidence of the importance of steric factors in influencing substitution in the ortho position.

Experimental Part

Nitration.[5]—A mixture of 178.0 g. (1.95 moles) of nitric acid (Baker, C.P., sp. gr. 1.42) and 383 g. of sulfuric acid (Baker and Adamson, C.P., sp. gr. 1.84) was added over a period of four hours to 261.7 g. (1.95 moles) of *t*-butylbenzene (Phillips, Pure Grade, $n^{20}D$ 1.4925) with vigorous stirring while the temperature was maintained between 25 and 30°. The reaction mixture was stirred an additional two hours at this temperature range followed by one hour at 40°. The mixture was poured over 1 kg. of cracked ice.

The oily layer was separated and the aqueous layer and reaction vessel washed with three small portions of benzene. The washings were combined with the oil and washed with 5% sodium bicarbonate solution followed by distilled water. The washed benzene and oil solution was dried over anhydrous sodium sulfate.

Separation of Isomers.—The volatile components were removed by simple distillation and the remaining oil rectified with a Todd Precise Fractionation Assembly (12 × 900 mm. column packed with $^1/_8$″ glass helices). The pressure was held constant at 10.0 mm. When the system attained equilibrium the take-off rate was adjusted at approximately 2 g. per hour (Table IV).

The intermediate fractions (4–8 Table IV) were rerectified with a miniature Podbielniak column (8 mm. × 24″ Heligrid Hastelloy packing) in order to isolate pure *m*-nitro-*t*-butylbenzene.

The homogeneity of fractions 2-a and 3-a definitely established the presence of a third component in the nitration product with b.p. 128.0° and $n^{20}D$ 1.5273.

Anal. Calcd. for $C_{10}H_{13}NO_2$: N, 7.77. Found: N, 7.92, 7.98.

Identification of the Meta Isomer.—A 2.1-g. (0.012 mole) sample of the material which was presumed to be *m*-nitro-*t*-butylbenzene (dissolved in 25 ml. of ethanol) was catalytically reduced to the corrresponding amine with PtO_2 and hydrogen at an initial gage pressure of 34 lb. The pressure became constant after shaking for ten minutes. The pressure was released, the solution filtered, and the solvent removed by simple distillation.

TABLE IV

FRACTIONATION DATA FOR DETERMINATION OF ISOMER RATIOS

Fraction	B.p. (10 mm.), °C.	Weight, g.	$n^{20}D$	Z	Isomer distribution,[a] g. ortho	meta	para
1	88–110.5	3.7	1.5173	23.9	3.7		
2	110.5–115.5	1.7	1.5171	23.9	1.7		
3	115.5	42.8	1.5171	23.9	42.8		
4	115.5–120.0	4.6	1.5185	24.1	4.3	0.3	
5	120.0–126.0	2.3	1.5248	25.8	0.6	1.7	
6	126.0–127.5	2.1	1.5263	26.2	0.2	1.9	
7	127.5–128.5	6.9	1.5277	26.3		6.5	0.4
8	128.5–130.0	8.2	1.5287	26.8		6.4	1.8
9	130.0–133.0	14.3	1.5300	27.1		8.3	6.0
10	133.0	9.4	1.5301	27.1		5.3	4.1
11	133.0–135.0	38.6	1.5332	28.1		8.4	30.2
12	135.0	7.5	1.5337	28.1			7.5
13	135.0	8.0	1.5337	28.1			8.0
14	135.0	109.7	1.5337	28.1			109.7
15	135.0	77.3	1.5339	28.1			77.3
16	Residue	*ca.* 2	....	..			
					53.3	38.8	245.0

[a] Estimated from the accurate refractive indices of the pure components.

TABLE V

DISTILLATION OF INTERMEDIATE FRACTIONS

Fraction	B.p. (10 mm.), °C.	Weight, g.	$n^{20}D$	Z
1-a	115.0–128.0	5.9	1.5244	25.6
2-a	128.0	5.2	1.5273	26.2
3-a	128.0	6.0	1.5273	26.2
4-a	128.0–130.0	2.0	1.5281	26.3
5-a	Residue	5.0	1.5326	27.7

The acetyl derivative was prepared from the crude amine. Approximately 1 g. of the amine was dissolved in a dilute hydrochloric acid solution (0.5 ml. of hydrochloric acid, sp. gr. 1.19, dissolved in 15 ml. of water) and filtered cold with Norite. To this solution was added 0.7 ml. of acetic anhydride followed by a solution of 0.7 g. of sodium acetate dissolved in 3 ml. of water. The mixture was stirred, cooled and then filtered. The solid product was recrystallized from 200 ml. of boiling water (solution clarified with a few ml. of ethanol). White leaflets were obtained. The melting point, 101–102°, agreed with previously reported values[9] for N-acetyl-*m*-*t*-butylaniline and establishes the identity of the third nitration product as the meta isomer.

Cryoscopic Investigation.—Freezing curves were prepared for a best sample of each component using a 10-junction copper–constantan thermel and a silvered permanently evacuated Dewar-type freezing tube. The data were analyzed geometrically by adaptations of the method of Rossini.[10]

LAFAYETTE, INDIANA RECEIVED MAY 14, 1951

---

[9] Previously found for N-acetyl-*m*-*t*-butylaniline: m.p. 101° (Ref. 6) and 99° (J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 2334 (1928)).

[10] F. D. Rossini, *et al.*, *J. Research Natl. Bur. Standards*, **26**, 591 (1941); *ibid.*, **35**, 355 (1945).