CCCVIII.—*Alternating Reactive Positions in the Nucleus of* tert.*-Butylbenzene.*

By JOHN BALDWIN SHOESMITH and ALEXANDER MACKIE.

IT is well known that when a substituent enters the nucleus of *tert.*-butylbenzene it does so almost exclusively in the para-position, *i.e.*, as far as possible from the *tert.*-butyl group. The isolation of ortho-compounds has been reported in only two cases: Seńkowski (*Ber.*, 1890, **23**, 2414), claimed to have prepared both ortho- and para-nitro-*tert.*-butylbenzenes by direct nitration, and Kozak (*Bull. Akad. Sci. Cracow*, 1906, 407) brominated the hydrocarbon and submitted the reaction product to the action of methyl iodide and sodium, whereby he isolated two isomeric *tert.*-butyltoluenes, one of which he described as the ortho-compound. Since Malherbe (*Ber.*, 1919, **52**, 319) was unable to repeat Seńkowski's results, the evidence that reaction can take place at both ortho- and para-positions is confined to the observations of Kozak.

It has now been proved that Seńkowski isolated *o*-nitro-*tert.*-butylbenzene, and a further example has been obtained of the alternating influence of the *tert.*-butyl group in that, when treated with hydrogen iodide, the isomeric iodo-*tert.*-butylbenzenes only react if the iodine is in the *o*- or *p*-position.

o-*Nitro*-tert.*-butylbenzene.*—It was not found possible to prepare this compound by direct nitration (compare Malherbe, *loc. cit.*), but it was obtained in the following manner. *p*-Nitro-*tert.*-butylbenzene (the constitution of which was proved definitely by Malherbe) on further nitration gives a dinitro-compound, m. p. 62°, which might be 2 : 4- or 3 : 4-dinitro-*tert.*-butylbenzene, the latter possibility requiring consideration because of the inhibiting effect of the *tert.*-butyl group on substitution in the ortho-position. The dinitro-compound on reduction with ammonium hydrogen sulphide gives a nitroamino-compound, m. p. 55°, and elimination of the amino-group gives an oil, b. p. 250·5°/765 mm.; this can be converted into an amine of which the acetyl derivative has m. p. 161° and strongly depresses the m. p. of *p*-acetamido-*tert.*-butylbenzene (169°). Since the m. p. of the corresponding meta-compound, which would result in the same way from the 3 : 4-isomeride, is 99° (see p. 2338), this leaves no doubt as to the constitution of the *o*-nitro-compound and also classifies the nitroamino-compound as 2-*nitro*-4-*amino*-tert.-*butylbenzene*, and the dinitro-compound as 2 : 4-dinitro-*tert.*-butylbenzene. The above proof is necessitated by the fact that it was not found possible to obtain *o*-nitrobenzoic acid from *o*-nitro-*tert.*-butylbenzene, a point stressed by Seńkowski (*loc. cit.*), who gave the b. p. of the compound as 247—248°/738 mm. and the m. p. of the *o*-acetamido-compound as 159°.

The Reduction of the Isomeric Iodo-tert.-*butylbenzenes.*—The ease of removal of iodine from these compounds by hydrogen iodide is $o > p > m$, and the comparative ease with which the ortho-isomeride was reduced shows that iodine may be removed from a position which is almost immune from attack by the ordinary substituting reagents. This can readily be understood if the preliminary stage in the replacement of iodine by hydrogen is the attraction of a proton to a negatively polarised position such as would be expected to occur in both the ortho- and para-positions in the nucleus of *tert.*-butylbenzene. It would not be expected that the attachment of a proton in the ortho-position would be inhibited to the same extent as that of the more bulky molecules of nitrating, halogenating, and sulphonating agents; moreover, when these experiments are compared with the corresponding experiments in the toluene series (Shoesmith and Slater, J., 1924, **125**, 2278), it is found that whilst the rates of removal of iodine from *o*-iodotoluene and *o*-iodo-*tert.*-butylbenzene are similar, the quantities of ortho-compounds formed by direct substitution of the corresponding hydrocarbons are markedly different.

The Behaviour of o-*Bromo*-tert.-*butylbenzene with Magnesium.*—In a recent communication, Tschitschibabin, Elgasine, and Lengold (*Bull. Soc. chim.*, 1928, **43**, 238) have stated that when the mixture produced by the bromination of *tert.*-butylbenzene is allowed to react with magnesium, followed by ethyl orthoformate, *p*-*tert.*-butylbenzaldehyde is formed exclusively, since on oxidation only *p*-*tert.*-butylbenzoic acid could be isolated. They conclude that any *o*-bromo-*tert.*-butylbenzene present does not form a magnesium derivative. As the present authors had already found that o-*iodo*-

tert.-*butylbenzene* readily gives a Grignard reagent, this appeared remarkable, and o-*bromo*-tert.-*butylbenzene* was therefore prepared as follows: *p*-Nitro-*tert.*-butylbenzene is brominated with difficulty at 90° in presence of finely divided iron, giving a compound which must be 2-*bromo*-4-*nitro*-tert.-*butylbenzene*, since on reduction it gives an amine the *acetyl* derivative of which is different from 3-bromo-4-acetamido-*tert.*-butylbenzene (the only other possible reaction product). 2-*Bromo*-4-*amino*-tert.-*butylbenzene* on elimination of the amino-group gives *o*-bromo-*tert.*-butylbenzene which in ethereal solution reacts *vigorously* with magnesium, and from the product o-tert.-*butylbenzoic acid* may be produced in the usual manner. This acid may also be prepared from the *o*-iodo-derivative. The authors do not suggest that this is additional evidence in favour of the polarisation of the ortho-position, but merely wish to point out that the steric effect of the *tert.*-butyl group is not sufficient to inhibit a reaction involving the attack by magnesium of a halogenated ortho-position.

EXPERIMENTAL.

There is much confusion in the literature with respect to *iso*- and *tert.*-butylbenzene derivatives, and we therefore used as our starting product the authentic *tert.*-butylbenzene prepared by the method of Schramm (*Monatsh.*, 1888, **9**, 615), who proved that *iso*- or *tert.*-butyl chloride condensed with benzene in presence of aluminium chloride to give *tert.*- and not *iso*-butylbenzene. References which describe compounds as *iso*butyl when in reality they are *tert.*-butyl are marked with an asterisk.

*iso*Butyl alcohol was converted to a mixture of *iso*- and *tert.*-butyl chlorides by means of zinc chloride and phosphorus trichloride (Dehn and Davis, *J. Amer. Chem. Soc.*, 1907, **29**, 1332), but only a 32% yield could be obtained, the chief product being apparently a mixture of polymerised butylenes. The mixed chlorides were condensed with benzene as described by Schramm (*loc. cit.*); continuous stirring and efficient condensing apparatus improved the yield (27%), and *white* aluminium chloride of very good quality was found to be advantageous. The *tert.*-butylbenzene had b. p. 165—170°.

p-*Nitro*-tert.-*butylbenzene*.—Nitric acid (*d* 1·52) was gradually added to an equal weight of vigorously stirred *tert.*-butylbenzene at the ordinary temperature; when reaction was complete (2 hours), the mixture was poured into water, and the yellow oil washed with water, dried, and distilled: b. p. 125—130°/10 mm. It could not be solidified.

2 : 4-*Dinitro*-tert.-*butylbenzene*.—A mixture of nitric acid (*d* 1·51; 2 parts by weight) and concentrated sulphuric acid (3 parts) was

added during 5 hours to vigorously stirred *tert.*-butylbenzene (1 part) maintained at 60°. The nitration product was poured on ice, and the precipitated yellow oil slowly solidified. The solid was filtered off and washed with water. It crystallised from aqueous alcohol in white prisms, m. p. 61—62° (compare Malherbe, *loc. cit.*, and Baur, *Ber.*, 1894, **27**, 1610), which slowly turned yellow on exposure to light. The same compound was obtained by heating vigorously stirred *p*-nitro-*tert.*-butylbenzene with an equal weight of nitric acid (*d* 1·51) at 60° for 2—4 hours.

2-*Nitro*-4-*amino*-tert.-*butylbenzene*.—Finely divided 2 : 4-dinitro-*tert.*-butylbenzene (20 g.) was added to a mixture of ethyl alcohol (76 c.c.) and ammonia (*d* 0·880; 10 c.c.), and hydrogen sulphide passed into the mixture for one hour, the reaction flask being occasionally agitated. The mixture was then heated for a few minutes on the steam-bath, cooled, and the process repeated. To the reaction mixture an excess of water was added, and the nitro-amino-compound, precipitated as a yellow solid mixed with sulphur, was filtered, washed with water, and heated under reflux with an excess of hydrochloric acid (*d* 1·05) for 5 minutes. The solution was filtered from sulphur, the filtrate cooled until the hydrochloride commenced to crystallise out, and an excess of ammonia (*d* 0·880) was immediately added. The nitroamine separated as an oil which rapidly solidified; yield 71%. 2-*Nitro*-4-*amino*-tert.-*butylbenzene* crystallises from aqueous alcohol as yellow plates, and from light petroleum as yellow needles, m. p. 55° (Found: N 14·7. $C_{10}H_{14}O_2N_2$ requires N, 14·4%). When boiled with acetic anhydride, it gives the acetyl derivative, colourless needles, m. p. 112° from aqueous alcohol.

o-*Nitro*-tert.-*butylbenzene*.—To the amino-compound (1 part), dissolved in absolute alcohol (3 parts), concentrated sulphuric acid (3 parts) was added, and the whole cooled to 0°; the sulphate crystallised out and the amine was diazotised, the reaction mixture then being allowed slowly to attain the laboratory temperature and finally heated on the steam-bath. *o*-Nitro-*tert.*-butylbenzene was removed in a current of steam, extracted from the distillate with ether, and ultimately obtained as a yellow oil (yield 54%) with a characteristic odour, b. p. 114—115°/10 mm. or 250·5°/765 mm.

o-*Amino*-tert.-*butylbenzene*.—Fine iron filings (12 g.) were mixed with water (15 c.c.) and the mixture slowly stirred and heated whilst 1 c.c. of glacial acetic acid and 0·3 c.c. of *o*-nitro-*tert.*-butylbenzene were added; the temperature was raised to 90° and 10 g. of the *o*-nitro-compound were slowly introduced during 3 hours. After a further 2 hours' heating, the amine was distilled in steam, extracted from the distillate with ether, dissolved in dilute hydrochloric acid, separated from unchanged nitro-compound by ether extraction, and precipitated from its hydrochloric acid solution by addition of ammonia; when re-extracted with ether and purified by distillation it had b. p. 102°/10 mm.; yield 75%. The amine was found to be a colourless liquid, very volatile in steam, becoming red on exposure to air which caused separation of a small quantity of crystals, probably carbonate (compare Seńkowski, *loc. cit.*). *o*-Acetamido-*tert.*-butylbenzene was obtained from the amine in the usual way, and crystallised from benzene in prismatic needles, m. p. 161° (Seńkowski gives 159°).

o-*Iodo*-tert.-*butylbenzene*.—Dilute sulphuric acid (60 c.c.; *d* 1·12) was added to the above amino-compound (5·5 g.), the whole well stirred to ensure formation of a finely divided precipitate of amine sulphate, and the latter diazotised by a solution of sodium nitrite (5 g. in 10 c.c. of water) at −10°. The diazonium sulphate is very unstable and appeared to decompose at about −8°. Potassium iodide (15 g.) in water (25 c.c.) was then rapidly added to the *very vigorously stirred* diazo-solution, the temperature was allowed slowly to rise to 18°, and decomposition completed on the steam-bath. Excess of aqueous alkali was added to the reaction mixture to remove free iodine, and the iodo-compound distilled in a current of steam. The ethereal extract of the distillate finally yielded an oil, and that from several experiments was fractionated under reduced pressure. o-*Iodo*-tert.-*butylbenzene* is a colourless oil, b. p. 116—118°/10 mm. (Found: I, 48·3. $C_{10}H_{13}I$ requires I, 48·8%); yield 13%.

m-*Iodo*-tert.-*butylbenzene*.—This was obtained as follows: *p*-nitro-*tert.*-butylbenzene was reduced by iron and hydrochloric acid (as for the ortho-compound), the amino-derivative acetylated (m. p. of acetamido-compound, 169°; Malherbe, *loc. cit.* gives 169°), the acetyl derivative nitrated at 35—40° by acid of *d* 1·46, and the product hydrolysed by alkali to *m*-nitro-*p*-amino-*tert.*-butylbenzene; the amino-group was removed and the resulting nitro-compound reduced (as before) to *m*-amino-*tert.*-butylbenzene (an oil of b. p. 107—108°/9 mm.); acetylation then gave a product of m. p. 99° (Gelzer,* *Ber.*, 1888, **21**, 2949 gives 101°) from which the amino-compound was regenerated, and this was finally converted into the iodo-compound. m-*Iodo*-tert.-*butylbenzene* is a liquid, b. p. 106—108°/9 mm. (Found: I, 48·4. $C_{10}H_{13}I$ requires I, 48·8%).

p-Iodo-*tert.*-butylbenzene, obtained by the usual methods from the *p*-nitro-compound, distilled at 116—118°/9 mm. (compare Willgerodt and Rampacker, *Ber.*, 1901, **34**, 3669; Pahl,* *Ber.*, 1884, **17**, 1233; Boedtker, *Bull. Soc. chim.*, 1906, **35**, 832). It is noteworthy that whilst *o*-*tert.*-butylbenzenediazonium sulphate is very

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* See p. 2336.

unstable even at 0°, the *m*- and *p*-isomerides are comparatively stable, a phenomenon which is paralleled in the corresponding toluene derivatives.

o-*Bromo*-tert.-*butylbenzene*. — 2 - *Bromo*-4 - *nitro*-tert.-*butylbenzene* was prepared by heating *p*-nitro-*tert.*-butylbenzene (6 g.) with bromine (7 g.) in presence of finely divided iron (1·2 g.) in a flask fitted with a reflux condenser and calcium chloride tube, to about 90°. Evolution of hydrogen bromide was moderately brisk, and after about ½ hour, a further 7 g. of bromine were slowly added and the whole was heated for 7 hours. When cold, the product formed a semi-solid mass, and on distillation in a current of superheated steam, a yellow, oily solid slowly collected in the receiver. This was filtered off, pressed on a porous plate, and crystallised from alcohol, forming long, colourless needles, m. p. 94·5° (Found: Br, 30·6. $C_{10}H_{12}O_2NBr$ requires Br, 31·0%). This bromination is much slower than that of *p*-nitrotoluene, but if all unbrominated oil is recovered, a yield of about 88% may be obtained.

2-*Bromo*-4-*amino*-tert.-*butylbenzene*. Concentrated hydrochloric acid (1 c.c.) was added to a solution of the foregoing bromo-compound (7·5 g.) in 30 c.c. of alcohol, and the mixture heated under reflux to the boiling point, finely divided iron (5 g.) then being added in 4 equal portions. After 2 hours, reduction was complete and the alcoholic solution was filtered from iron, water added to the filtrate, and the filtrate extracted with ether. The amine hydrochloride, precipitated on the addition of hydrochloric acid to the ethereal extract, was filtered, washed with ether, and dissolved in hot dilute hydrochloric acid, the amine then being precipitated by addition of concentrated ammonia and extracted with ether. After distillation of the ether, 2-*bromo*-4-*amino*-tert.-*butylbenzene* was obtained as a pale yellow liquid, b. p. 153—155°/11 mm. (Found: Br, 35·1. $C_{10}H_{14}NBr$ requires Br, 35·1%); yield 70%. Its *hydrochloride* has m. p. 235° (decomp.), and its *acetyl* derivative crystallised from aqueous alcohol in colourless rectangular plates, m. p. 142—143°.

o-*Bromo*-tert.-*butylbenzene*. The amino-group was eliminated from 2-bromo-4-amino-*tert.*-butylbenzene as for the corresponding *o*-nitro-compound. The diazonium compound was unstable and decomposed above —2°. o-*Bromo*-tert.-*butylbenzene* is a colourless liquid, b. p. 96—98°/12 mm. (Found: Br, 38·0. $C_{10}H_{13}Br$ requires Br, 37·6%); yield 54%.

o-tert.-*Butylbenzoic Acid*.—*o*-Bromo (or *o*-iodo)-*tert.*-butylbenzene was dissolved in ether and the equivalent quantity of magnesium added. On the addition of a crystal of iodine, reaction commenced immediately and continued at the ordinary temperature until almost all the magnesium had disappeared. The flask was finally heated on the water-bath for 1 hour, after which a current of carbon dioxide was passed into the solution for approximately 15 hours. The viscous mass was disintegrated by the addition of ice, followed by dilute hydrochloric acid, the whole extracted with ether, the ethereal layer in turn extracted with sodium carbonate solution, which was acidified with dilute acid, and again extracted with ether. o-tert.-*Butylbenzoic acid* was thus obtained after crystallisation from aqueous alcohol (20%) as well-defined, hexagonal plates, m. p. 68·5° (Found: C, 73·8; H, 7·8. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%); yield 60%.

Reduction of the Isomeric Iodo-tert.-*butylbenzenes.*—A weighed quantity (w) of each of these was allowed to stand at 25° in a solution of glacial acetic acid containing 0·40 g. of hydrogen iodide per c.c., and the rate of reduction measured as previously (Shoesmith and Slater, *loc. cit.*). The results are recorded below, t being the time in days, and x the proportion changed.

	o-Isomeride (w = 0·3955 g.).	p-Isomeride (w = 0·4045 g.).
t.	x.	x.
2	61%	11%
4	76	19
14	86	35

The meta-isomeride was unaffected under these conditions. The order of reduction was unchanged even at 100° and 110°.

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EDINBURGH UNIVERSITY.

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