65. *Derivatives of* tert.*-Butylbenzene and Transmitted Polar Effects.*

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IN continuation of the previous investigation (J., 1928, 2334) m- and p-tert.*-butylbenzyl bromides* have been prepared and the lability of the halogen in them investigated. Many fruitless attempts were made to obtain *o-tert.*-butylbenzyl bromide.

The isomeric *tert.*-butylbenzoic acids were also prepared in order to trace any regularities which might appear in their dissociation constants, since this is one of the properties influenced by substituent groups.

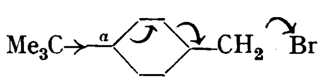
The main conclusion which has emerged is that the introduction of the *tert.*-butyl group into a benzene nucleus produces a marked difference in the reactivity of groups attached to the *m*- and *p*-positions.

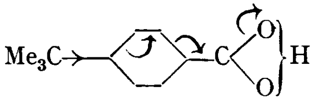
The Reduction of m- *and* p-tert.*-Butylbenzyl Bromides.*—With hydriodic acid, the rate of reduction was $m > p$, which shows that the electromeric effect of the *p-tert.*-butyl group diminishes the reactivity of the bromine atom.

The *tert.*-butyl group is electron-repelling and therefore produces an inductive effect, whose sign is taken as negative (compare Robinson, J., 1932, 1445, footnote). This $-I$

effect should cause the greatest electronic pressure to be exerted at C_α, giving rise to the electromeric changes (I).

(I.)





(II.)

This inductive effect does not explain, however, the fact that the *tert.*-butylbenzyl bromides are more easily reduced than the unsubstituted benzyl bromide. It would appear, therefore, that there is a factor at work, other than the electromeric and inductive effects, which causes an increased " positivity " of the bromine atom in the butyl derivatives.

The Hydrolysis of m- *and* p-tert.-*Butylbenzyl Bromides.*—The electromeric effect due to the *tert.*-butyl group is again apparent in the more rapid hydrolysis in aqueous alcohol of *p-tert.*-butylbenzyl bromide than of the *m*-compound, a reversal of the order of reactivity which was observed in hydriodic acid.

The rate of hydrolysis, $p > m >$ unsubstituted, indicates that there is an appreciable transmission of an influence to the *m*-position, and that at this point the effect is definitely opposite to that excited in the *p*-position. The inductive effect results in the two isomerides being more rapidly hydrolysed than the unsubstituted compound.

The Dissociation Constants of the tert.-*Butylbenzoic Acids.*—The *tert.*-butyl group produces, like the methyl group, an influence on the dissociation constant of the opposite sign from its general polar effect. This is illustrated by the fact that *o-tert.*-butylbenzoic acid ($K_o^{25°} = 3{\cdot}5 \times 10^{-4}$) is stronger than benzoic acid ($K_u^{25°} = 6{\cdot}5 \times 10^{-5}$) and *m-tert.*-butylbenzoic acid ($K_m^{25°} = 5{\cdot}2 \times 10^{-5}$) is weaker (compare Bennett and Mosses on the corresponding toluic acids; J., 1930, 2366). The abnormally high dissociation constant of *o-tert.*-butylbenzoic acid is probably due to a direct polar effect of the substituent on the carboxyl group (Lapworth and Manske, J., 1928, 2539). A comparison of the *m*- and *p*-derivatives, however, shows that the presence of the electromeric effect is also to be recognised here, since the *p*-compound (II) is the weaker acid.

EXPERIMENTAL.

m-tert.-*Butylbenzyl Bromide.*—The requisite quantity of bromine was volatilised in a current of dry air and passed into *m-tert.*-butyltoluene at its b. p. The butylbenzyl bromide formed was boiled with formic acid (100%) for 25 minutes to remove di- or tri-bromo-derivative and when cold the bromide was separated, washed in turn with water and sodium carbonate solution, and extracted with ether. The ethereal layer was shaken with sodium bisulphite solution to remove aldehyde, the solvent evaporated, the bromide dissolved in benzene, and the solution saturated with dry hydrogen bromide to convert any benzyl alcohol into bromide. After removal of the benzene, the bromide was fractionated in a vacuum (modification of the Widmer flask; *Helv. Chim. Acta*, 1924, **7**, 52). The portion, b. p. 124—126°/13 mm., had a low percentage of hydrolysable bromine, probably owing to the difficulty of converting the last trace of alcohol (formed during purification) back into the bromide. The impure butylbenzyl bromide was therefore gently heated with a slight excess of phosphorus pentabromide, the mixture kept over-night, the excess of phosphorus pentabromide removed, and the product fractionated in a vacuum, m-tert.-*butylbenzyl bromide* being obtained as a colourless non-lachrymatory liquid, b. p. 115·5°/8 mm. (Found : Br, 35·0. $C_{11}H_{15}Br$ requires Br, 35·25%).

p-tert.-*Butylbenzyl Bromide.*—A weighed quantity of bromine was slowly added to *p-tert.*-butyltoluene (b. p. 190—193°; Verley, *Bull. Soc. chim.*, 1898, **19**, 67) at 115°. The butylbenzyl bromide was purified in a manner similar to that by which the *m*-isomeride was obtained pure. The portion, b. p. 132·5—134·5°/15 mm., was cooled to — 16° and the solid obtained was crystallised from absolute alcohol at — 18°. p-tert.-*Butylbenzyl bromide* is a colourless liquid at the ordinary temperature, b. p. 132·5°/14 mm., with slight lachrymatory properties. It is hygroscopic and darkens on keeping. The solid crystallises from absolute alcohol and light petroleum at — 18° in colourless prismatic needles, m. p. 12—13° (Found : Br, 35·3%). Verley (*loc. cit.*) does not describe this compound fully and states that it cannot be distilled without decomposing. He did not obtain it crystalline.

m-tert.-*Butylbenzoic Acid.*—*m-tert.*-Butylbenzyl bromide was oxidised by potassium permanganate; the acid obtained crystallised from water in white plates, m. p. 127°. The same acid was prepared by the action of carbon dioxide on the Grignard compound formed from magnesium and *m*-bromo-*tert.*-butylbenzene. The latter method of preparation appeared necessary in order to prove the constitution of the acid obtained in the former case, since some doubt exists in the literature as to the constitution of this acid obtained by oxidation methods (compare Kelbe,* *Ber.*, 1883, **16**, 620; Effront,* *Ber.*, 1884, **17**, 2330).

p-tert.*-Butylbenzoic Acid.*—*p-tert.*-Butyltoluene or *p-tert.*-butylbenzyl bromide was heated with nitric acid (*d* 1·20) for 6 hours, *p-tert.*-butylbenzoic acid being obtained. It crystallised from alcohol in rhombic prisms (compare Bialobrzeski, *Ber.*, 1897, **30**, 1775), m. p. 165° (Verley, *loc. cit.*, p. 71, gives 164°).

Reduction of m- *and* p-tert.*-Butylbenzyl Bromides.*—10 C.c. of a standard solution of the bromide and 10 c.c. of constant-boiling hydriodic acid were placed in a graduated flask and made up to 25 c.c. with glacial acetic acid, and the contents mixed. The flask was then placed in a thermostat at 110°, and the amount of bromide reduced in a definite time estimated. The results are in Table I, where t is the time in hours and x the percentage changed.

TABLE I.

t	1½	3	6
m-Isomeride, x	58	79	97
p-Isomeride, x	48	70	93

The order of reduction was unchanged at 25° and 100°.

Reduction of benzyl bromide at 110°: x = 34, 55, and 78 for t = 1½, 3, and 6 respectively (Shoesmith, Hetherington, and Slater, J., 1924, **125**, 1316).

Isolation and Identification of the Reduction Product from p-tert.*-Butylbenzyl Bromide.*—The bromide (1·5 g.) was dissolved, in a stoppered cylinder, in 15 c.c. of a solution of hydrogen iodide in glacial acetic acid. The cylinder was placed in a thermostat at 25° for 10 days, and the product then poured into water. The solid which separated was recrystallised from dilute acetic acid, forming colourless plates, m. p. 29·5—30·5°, undepressed by p-tert.*-butylbenzyl iodide* prepared by heating the bromide under reflux in acetone solution with potassium iodide for several hours (Found: I, 46·0. $C_{11}H_{15}I$ requires I, 46·3%).

Hydrolysis of m- *and* p-tert.*-Butylbenzyl Bromides.*—A satisfactory velocity constant could not be obtained at 60°, owing to the rapidity of hydrolysis. The hydrolysis was therefore carried out at 25°. Approximately 0·5 g. of the bromide was weighed into a 100 c.c. graduated flask and 90 c.c. of absolute alcohol, followed by 10 c.c. of water, were added; the contents were well mixed and then made up to 100 c.c. with absolute alcohol. 10 C.c. were withdrawn at stated intervals, and the hydrobromic acid estimated. A satisfactory unimolecular velocity constant (k) was obtained in each case, the time being measured in hours.

TABLE II.

Compound.	$k \times 10^6$.	Mean $k \times 10^6$.
Benzyl bromide		125 †
m-tert.-Butylbenzyl bromide	190, 192, 193	192
p-tert.-Butylbenzyl bromide	334, 336, 329	333

† Shoesmith and Rubli, J., 1927, 3099.

Dissociation Constants of the Isomeric tert.*-Butylbenzoic Acids.*—These were estimated by the usual Kohlrausch conductivity method at 25°. Satisfactory results could only be obtained when the cell electrodes were small and almost 1 cm. apart. Owing to the sparing solubility of the *m*- and *p*-isomerides, saturated solutions of which had concentrations of approximately $N/2000$ and $N/3500$ respectively, and the unreliability of observations at dilutions greater than these, the dissociation constants were found at one dilution only for all three acids, namely, approximately $N/3500$. The molecular conductivity at this dilution was then calculated from the usual formula. The most satisfactory method of obtaining the conductivity at infinite dilution, μ_∞, was by application of the rule, formulated by Ostwald, that the molecular conductivity at infinite dilution is the same for acids with the same number of atoms in the molecule. The *tert.*-butylbenzoic acids have 27 atoms in their molecule, from which $\mu_\infty^{25°} \doteq 368$ (Ostwald Luther, "Physiko-Chemische Messungen," Leipzig, 1910, p. 482).

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* References which describe compounds as containing *iso*butyl when in reality they contain *tert.*-butyl are marked with an asterisk (compare Shoesmith and Mackie, *loc. cit.*).

TABLE III.

Compound.	Dissociation constant.
Benzoic acid	$6{\cdot}5 \times 10^{-5}$
o-tert.-Butylbenzoic acid †	$3{\cdot}5 \times 10^{-4}$
m-tert.-Butylbenzoic acid	$5{\cdot}2 \times 10^{-5}$
p-tert.-Butylbenzoic acid	$4{\cdot}2 \times 10^{-5}$

† J., 1928, 2339.

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