XII.—*Derivatives of Tolybenzene.*

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IN a former paper (this Journal, Trans., 1885, 47—586) we described one monobromotolybenzene and two dibromophenylbenzoic acids, but were unable to separate the dibromotolybenzenes from which these latter were derived. The present paper gives an account of the preparation of another monobromotolybenzene, the separation of the dibromo-compounds, and the formation of new oxidation-products from these.

I. *Monobromo-1,4-Tolybenzene.*

α -Bromotolybenzene, $C_6H_5 \cdot C_6H_3Br \cdot CH_3 = [1 : 2 \text{ or } 3 : 4]$.—To prepare this compound, 15.5 grams of toylbenzene were dissolved in carbon bisulphide, and 14.8 grams of bromine slowly added to the

mixture. After the chemical action had ceased, the flask containing the mixture was gradually heated for two hours with a reflux condenser. The carbon bisulphide was next distilled off, the residue in the flask treated with excess of caustic soda to remove the hydrobromic acid, then well washed with water, and finally extracted with boiling alcohol. From this, a mass of crystals, A, separated on cooling, and on evaporating the mother-liquor a yellowish oil, B, was obtained. When purified by further crystallisation, the portion A melted at 127—129°, and in other respects exhibited properties exactly similar to those of the monobromotolylbenzene previously described. On oxidation with either excess or deficit of chromic and glacial acetic acid, it gave monobromoterephthalic acid (m. p. 304—306° corr.), as proved by its general properties and by analysis. No intermediate product of oxidation could be obtained. The formation of monobromoterephthalic acid as a final product of oxidation proves that the monobromotolylbenzene must have the constitution $C_6H_5 \cdot C_6H_3BrMe = [1:2 \text{ or } 3:4]$. The monobromoterephthalic acid obtained as above described sublimed very easily on heating in an open tube, yielding a sublimate which melts at 243—245°. This is probably the anhydride, though the quantity of material at our disposal was not sufficient for an analysis.

β-Bromotolylbenzene, $C_6H_4Br \cdot C_6H_4Me = [1':4':1:4]$.—The yellow oil B was freed from alcohol and moisture first by heating it for some time to nearly 100°, and afterwards by exposing it for about three weeks over strong sulphuric acid. When cooled to a low temperature, the oil solidified to a yellow crystalline mass, which melted at 27—30°, and on analysis gave the following results:—

	Calculated.	Found.
$C_{13}H_{11}Br$	32.38	32.03 per cent. Br.

This compound is therefore an isomeride of the crystalline monobromotolylbenzene previously described, and differs from it chiefly in having a much lower melting point, and in being more soluble in alcohol. On oxidation with a deficit of chromic and glacial acetic acids, a product was obtained which was only partly soluble in ammonia. The soluble part after purification melted at 193—194°, and was easily soluble in cold ether, though but sparingly soluble in alcohol and benzene. It gave the following result on analysis, proving it to be a monobromophenylbenzoic acid:—

	Calculated.	Found.
$C_{13}H_9BrO_2$	28.88	28.38 per cent. Br.

On treating another portion of the oil with a large excess of the same oxidising agents, a pure white compound was obtained, readily

soluble in ammonia and melting at 247—249°. The residue, insoluble in ammonia in the former oxidation, was also treated with excess of oxidising agents, when the product was found to be easily soluble in ammonia, and melting at 248—249°. On analysis, both these products gave the same result, which, with the melting point, proves the compound to be 1,4 bromobenzoic acid, $C_6H_4Br \cdot COOH$. The monobromotolylbenzene, melting at 27—30°, therefore on oxidation gives first a monobromophenylbenzoic acid, $C_6H_4Br \cdot C_6H_4 \cdot COOH = [1' : 4' : 1 : 4]$, and finally monobromobenzoic acid, $[C_6H_4Br \cdot COOH = 1 : 4]$.

II. Dibromotolylbenzenes, $C_{13}H_{10}Br_2$.

α-Dibromotolylbenzene, $C_6H_4Br \cdot C_6H_3Br \cdot CH_3 = [1' : 4' : 1 : 2 \text{ or } 3 : 4]$.—35.6 grams of bromine were slowly added to 18.7 grams of tolylbenzene dissolved in carbon bisulphide, and the chemical action moderated by keeping the flask in cold water. After allowing the contents to remain together for about 12 hours, the flask was gently heated with a reflux condenser for two hours, and the carbon bisulphide distilled off. The residue was well washed with caustic soda, and afterwards with water, and was then repeatedly boiled for a considerable time with excess of alcohol, in which only a small part A was soluble, the bulk of it remaining as an insoluble mass B. The part A, after several crystallisations from hot alcohol, was obtained in exceedingly beautiful, transparent, ferny plates, melting at 113—115°, giving on analysis results agreeing with a dibromotolylbenzene :—

	Calculated.	Found.
$C_{13}H_{10}Br_2$	49.02	48.52 per cent. Br.

A portion of this on partial oxidation gave an acid melting at 202—204°, moderately soluble in alcohol, and easily soluble in ether and benzene. Its properties, melting point, and analysis agree with those of the dibromophenylbenzoic acid described in our last paper. On oxidation with a large excess of chromic and glacial acetic acids, an acid was obtained melting at 248—249°, and corresponding in all other respects with 1,4 bromobenzoic acid. These facts prove that one of the bromine-atoms is in the benzene-group, and one in the tolyl group, and that the one in the benzene-group must be in the para-position; *α*-dibromotolylbenzene on oxidation therefore gives first dibromophenylbenzoic acid, $C_6H_4Br \cdot C_6H_3Br \cdot COOH = [1' : 4' : 1 : 2 \text{ or } 3 : 4]$, and finally bromobenzoic acid, $C_6H_4Br \cdot COOH = [1 : 4]$, and has consequently the constitution ascribed to it above.

β-Dibromotolylbenzene, $C_6H_4Br \cdot C_6H_3Br \cdot CH_3 = [1' : 4' : 1 : 3 \text{ or } 2 : 4]$.—The mass B, which was almost insoluble even in hot alcohol, was so easily soluble in benzene that definite crystals could not be obtained.

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Treatment with ether, however, yielded needle-shaped crystals, which, after purification, melted at 148—150°, and gave on analysis the following results:—

	Calculated.	Found.
$C_{13}H_{10}Br_2$	49.02	48.67 per cent. Br.

On partial oxidation, it gave an acid which melted at 231—232°, and contained the following percentage of bromine:—

	Calculated.	Found.
$C_{12}H_7Br_2 \cdot COOH$	44.94	44.77 per cent. Br.

This acid corresponds with the one described in our previous paper, and like it sublimes easily and almost completely without melting, and is therefore *β*-dibromotolylbenzoic acid,

Oxidation with a large excess of chromic and glacial acetic acids gives an acid melting at 250—251°, and in all other respects similar to parabromobenzoic acid. A residue, insoluble in ammonia, left in the previous partial oxidation, also gave parabromobenzoic acid, melting at 249—251°, when treated with excess of the oxidising agents. *β*-Dibromotolylbenzene, on oxidation, therefore gives first dibromophenylbenzoic acid, $C_6H_4Br \cdot C_6H_4Br \cdot COOH = [1' : 4' : 1 : 3 \text{ or } 2 : 4]$, and finally bromobenzoic acid, $[C_6H_4Br \cdot COOH = 1 : 4]$, and hence has the constitution ascribed above.

It thus appears that the difference in the properties and melting points of the *α*- and *β*-dibromotolylbenzenes arises from the fact that in the one the bromine in the tolyl-ring is in the ortho-position, and in the other in the meta-position, but which of these two positions is to be ascribed to the two compounds respectively we have as yet had no means of deciding.

The results above described may be expressed in the following tabular scheme:—

I. Mono-bromo-Compounds.

α-Bromotolylbenzene.
M. p. = 129°.

Bromoterephthalic acid.
M. p. = 304—306°.

No intermediate oxidation-product could be obtained.

β -Bromotolylbenzene.
M. p. = 27—30°.

Bromophenylbenzoic acid.
M. p. = 193—194°.

Bromobenzoic acid. M. p. = 247—249°.

II. Dibromo-Compounds.

α -Dibromotolylbenzene.
M. p. = 113—115°.

α -Bromophenylbromobenzoic acid.
M. p. 202—204°.

Bromobenzoic Acid. M. p. = 249—251°.

β -Dibromotolylbenzene.
M. p. = 148—150°.

β -Bromophenylbromobenzoic acid.
M. p. = 231—232°.

Bromobenzoic acid. M. p. 249—251°.

The two dibromophenylbenzoic acids referred to above and melting at 202—204° and 231—232° respectively, are isomeric with the dibromophenylbenzoic acid described by Holm (*Ber.*, **16**, 1082; and *Abstr.*, **44**, 922), and which he obtained by fusing β -dibromofluorene ketone with caustic potash. Holm's acid is consequently a derivative of 1,2 phenylbenzoic acid, whereas both our acids are derived from 1,4 phenylbenzoic acid.