

BROMINATION OF COMPOUNDS CONTAINING TWO AROMATIC NUCLEI

Part IV. Bromination of Aryl Esters of Para-Cresotic Acid

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THE present work is the continuation of the work of Jadhav and Rangwala.¹ It has been now observed that the presence of free -OH group in the molecule facilitates the bromination and the bromine is directed to the nucleus containing it. As the more favoured position para to -OH group is already occupied by the carbphenoxy group, the reaction takes place only at higher temperature, except in the case of β -naphthyl ester when the reaction takes place at room temperature. The first bromine atom takes up the position ortho to the -OH group.

Higher bromo derivatives can only be obtained directly in the case of phenyl and *m*-cresyl esters with liquid bromine. The dibromo derivatives of *o*- and *p*-cresyl esters can be prepared by using their mono bromo derivatives and liquid bromine.

The presence of the nitro group in the phenolic nucleus facilitates the formation of the mono bromo derivatives as they are formed in a shorter time but it so completely deactivates the phenolic part of the molecule, that no dibromo derivative can be prepared (*cf.*, Jadhav and Rangwala, *loc. cit.*).

Phenyl, *o*-, *m*- and *p*-cresyl, *m*- and *p*-nitrophenyl and β -naphthyl esters are worked out.

The constitutions of these bromo compounds are proved by their hydrolysis with alkali and confirmed by mixed melting point with the condensation product of 5-bromo-*p*-cresotic acid and the respective phenol, except in the case of the dibromo derivative of the *p*-cresyl ester.

EXPERIMENTAL

Bromination of phenyl, o-, m- and p-cresyl, m- and p-nitrophenyl and β -naphthyl 3-methyl-6-hydroxy-benzoates (p-cresotate).—Preparation of mono bromo derivatives.

A mixture of the ester (4 g.) dissolved in sufficient glacial acetic acid and 20 c.c. of 20% solution of bromine in glacial acetic acid was heated on a boiling water-bath for about half an hour in the case of phenyl and cresyl esters and for only fifteen minutes in the case of nitrophenyl esters. In the case of β -naphthyl ester, the reaction was allowed to proceed overnight at room temperature. The bromo derivative separated on cooling the reaction mixture or after the requisite time. All bromo compounds crystallised from acetic acid. They are described in Table I below.

TABLE I

Name of the substance	Formula	M. P.	Analysis	
			Found %	Required %
Phenyl 3-methyl-5-bromo-6-hydroxy-benzoate	$C_{14}H_{11}O_3Br$	110–11°	Br, 26.2	Br, 26.1
<i>o</i> -Cresyl 3-methyl-5-bromo-6-hydroxy-benzoate	$C_{15}H_{13}O_3Br$	147–8°	Br, 24.5	Br, 24.9
<i>m</i> -Cresyl 3-methyl-5-bromo-6-hydroxy-benzoate	$C_{15}H_{13}O_3Br$	104–05°	Br, 24.8	Br, 24.9
<i>p</i> -Crystal 3-methyl-5-bromo-6-hydroxy-benzoate	$C_{15}H_{13}O_3Br$	105–06°	Br, 24.8	Br, 24.9
<i>m</i> -Nitrophenyl 3-methyl-5-bromo-6-benzoate	$C_{14}H_{10}O_5BrN$	169–70°	Br, 22.5	Br, 22.7
<i>p</i> -Nitrophenyl 3-methyl-5-bromo-6-hydroxy-benzoate	$C_{14}H_{10}O_5NBr$	214–15°	Br, 22.6	Br, 22.7
β -Naphthyl 3-methyl-5-bromo-6-hydroxy-benzoate	$C_{18}H_{13}O_3Br$	164–5°	Br, 22.8	Br, 22.4

4-Bromophenyl-3-methyl-5-bromo-6-hydroxy-benzoate.—Liquid bromine (4 g.) was directly added to phenyl 3-methyl-6-hydroxy-benzoate (2 g.). The reaction mixture was shaken for about half an hour and then water (about 200 c.c.) was added to it, when some more solid was obtained. Sodium bisulphite was then added to remove excess of bromine and the product was washed with water and crystallised from acetic acid, m.p. 124–5° (Found: Br, 41.4%; $C_{14}H_{10}O_3Br_2$ requires Br, 41.5%).

3-Methyl-4-bromophenyl-3-methyl-5-bromo-6-hydroxy-benzoate.—It was prepared and crystallised in the same way as its phenyl homologue, m.p. 141–2° (Found: Br, 39.6%; $C_{15}H_{12}O_3Br_2$ requires Br, 40%).

2-Methyl-4-bromo-phenyl-3-methyl-5-bromo-6-hydroxy-benzoate. — Liquid bromine (2 g.) was added to *o*-cresyl-3-methyl-5-bromo-6-hydroxy-benzoate (4 g.) and the reaction mixture was shaken for about an hour. It was then worked up and crystallised in the same way as its above isomer, m.p. 156–7° (Found: Br, 39·8%; $C_{15}H_{12}O_3Br_2$ requires Br, 40%).

4-Methyl-2-bromo-phenyl-3-methyl-5-bromo-6-hydroxy-benzoate. — Liquid bromine (5 g.) was added to *p*-cresyl-3-methyl-5-bromo-6-hydroxy-benzoate (5 g.) and the reaction mixture was shaken for about an hour and it was worked up and crystallised as its other isomers, m.p. 136–7° (Found: Br, 40%; $C_{15}H_{12}O_3Br_2$ requires Br, 40%).

Hydrolysis of the bromination products.—The monobromo derivative was boiled for about four hours with excess of 5 per cent. solution of sodium hydroxide. Carbon dioxide was then passed through the cold reaction mixture when the phenolic compound that separated was extracted with ether and the aqueous layer acidified with hydrochloric acid when the acid was precipitated. It was crystallised from acetic acid and identified as 5-bromo-*p*-cresotic-(3-methyl-5-bromo-6-hydroxy-benzoic) acid, by mixed melting point. In the case of *m*- and *p*-nitrophenyl and β -naphthyl esters, the phenols also were identified by mixed melting points.

The dibromo derivatives were boiled with excess of 8 per cent. sodium hydroxide solution for about four hours. The reaction mixture was then worked up as in the case of the monobromo products and the acid was identified as 5-bromo-*p*-cresotic (3-methyl-5-bromo-6-hydroxy-benzoic) acid. In the case of *o*- and *m*-cresyl derivatives, the phenolic component was also identified as *p*-bromo-*o*-cresol (2-methyl-4-bromo-phenol) and *p*-bromo-*m*-cresol (3-methyl-4-bromo-phenol) by mixed melting points.

*Condensation of 5-bromo-*p*-cresotic acid with phenols.*—In the case of the preparation of the monobromo derivatives the acid was condensed with the corresponding phenol whilst in the case of the dibromo compounds the acid was condensed with the necessary bromophenol in presence of phosphorous oxychloride by heating them for about half an hour at the required temperature. The reaction mixture was then diluted with water and the solid was washed with very dilute alkali and crystallised from acetic acid. They are described in Table II. Mixed melting points of these condensation products with the bromination products showed no lowering.

TABLE II

Gm. of 5-bromo- <i>p</i> -cresotic acid	Name of phenol and gm.	c.c. of POCl ₃	Temp.	Condensation product	M. P.
2	Phenol 1.5	1	120-5°	Phenyl 3-methyl-5-bromo-6-hydroxy-benzoate	110-11°
2	<i>o</i> -Cresol 1.5	1	130-5°	<i>o</i> -Cresyl-3-methyl-5-bromo-6-hydroxy-benzoate	147-8°
2	<i>m</i> -Cresol 1.5	1	120-5°	<i>m</i> -Cresyl-3-methyl-5-bromo-6-hydroxy-benzoate	104-5°
2	<i>p</i> -Cresol 1.5	1	120-5°	<i>p</i> -Cresyl-3-methyl-5-bromo-6-hydroxy-benzoate	105-6°
4	<i>m</i> -Nitrophenol 3	2.5	130-5°	<i>m</i> -Nitrophenyl 3-methyl-5-bromo-6-hydroxy-benzoate	169-70°
4	<i>p</i> -Nitrophenol 3	2.5	130-5°	<i>p</i> -Nitrophenyl 3-methyl-5-bromo-6-hydroxy-benzoate	214-5°
4	β -Naphthol 3.5	2.5	130-5°	β -Naphthyl 3-methyl-5-bromo-6-hydroxy-benzoate	164-5°
4	<i>p</i> -Bromophenol 3	2.5	120-5°	4-Bromophenyl 3-methyl-5-bromo-6-hydroxy-benzoate	124-5°
4	<i>p</i> -bromo- <i>m</i> -cresol 3.5	2.5	130-5°	4-Bromo-2-methyl-phenyl 3-methyl-5-bromo-6-hydroxy-benzoate	156-7°
4	<i>p</i> -Bromo- <i>m</i> -cresol 3	2.5	130-5°	4-Bromo-3-methyl-phenyl 3-methyl-5-bromo-6-hydroxy-benzoate	141-2°

SUMMARY

Bromination of phenyl, *o*-, *m*- and *p*-cresyl, *m*- and *p*-nitro-phenyl and β -naphthyl esters of *p*-cresotic acid is described. In the case of phenyl, *o*-, *m*- and *p*-cresyl esters mono— as well as di-bromo derivatives are obtained. Their constitutions are proved by hydrolysis and confirmed by their preparation by condensation method.

REFERENCE

- Jadhav and Rangwala .. *J. Ind. Chem. Soc.*, 1935, 12, 89-92; *Proc. Ind. Acad. Sci.*, 1935, 1, 616-19.