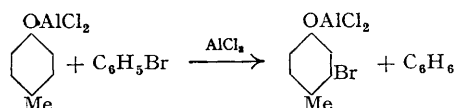


140. The Action of Aluminium Chloride on Some Aromatic Bromo-compounds.

By G. BADDELEY and J. PLANT.

Bromine atoms are shown to migrate to the nuclear positions of greatest electron density as indicated by nuclear alkylation.

BROMOBENZENE is a brominating agent in the presence of aluminium chloride, some *p*-dibromobenzene being formed; with *p*-tolylaluminium chloride (from *p*-cresol), it affords benzene and 2-bromo-*p*-cresol:



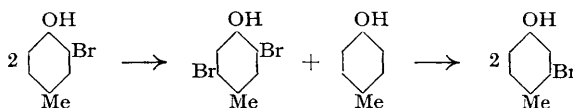
The combined reagents acting upon phenol produce considerable alkali-insoluble products but no bromophenol.

The three bromophenols give *p*-bromophenol (*ca.* 70%), phenol (*ca.* 17%), and higher-boiling products; the isomerisation of *o*-bromophenol is readier than that of the *m*-isomer. *p*-Bromophenol with *p*-cresol (1 mol.) and excess of aluminium chloride produce a mixture of approximately equal amounts of both reactants, phenol, and 2-bromo-*p*-cresol.

The products of the action of aluminium chloride (2 mols.) on 3-bromo-*p*-cresol are shown in the following table:

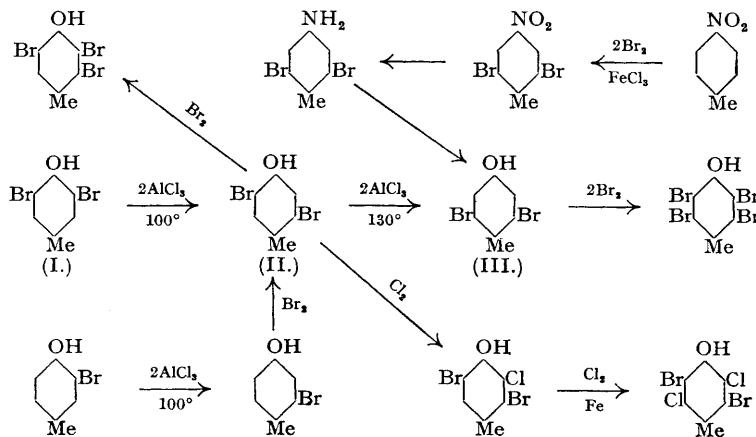
Temp.	Time (hrs.).	Products, %.			
		3-Bromo- <i>p</i> -cresol.	2-Bromo- <i>p</i> -cresol.	2 : 6-Dibromo- <i>p</i> -cresol.	<i>p</i> -Cresol.
100°	20	33	60	3	3
127	1	—	67	6	8
115	0.75	—	45	—	—

The 2-bromo-*p*-cresol is formed, no doubt, in the following steps:



The more rapid isomerisation of 2-bromo- to 3-bromo-4-ethylphenol is probably due to the induced nucleophilic condition of the 3-position of 4-ethylphenol being greater than that of the corresponding 2-position of *p*-cresol.

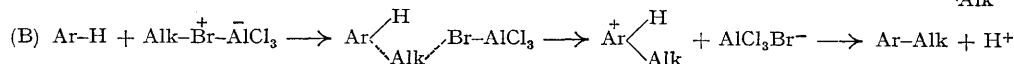
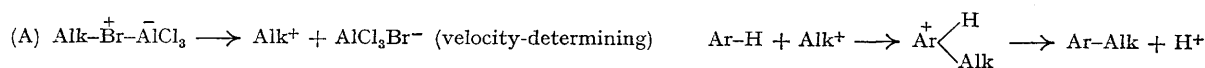
At 100° 3 : 5-dibromo-*p*-cresol (I) isomerises to the 2 : 5-dibromo-derivative (II), and at 130° this in turn is converted into the 2 : 6-dibromo-compound (III). The products are identified as shown in the following scheme:



2 : 6-Dibromo-4-ethylphenol isomerises to the 3 : 5-dibromo-compound at 120°.

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These brominations by aromatic bromo-compounds are in marked contrast with the alkylations by alkyl bromides in the presence of aluminium chloride. Whether the latter reactions involve a uni- or a bi-molecular mechanism, (A) or (B) respectively, the complex $\text{Ar}-\overset{+}{\text{Br}}-\bar{\text{AlCl}}_3$ is unlikely to behave in a similar manner since



(i) nuclear-attached halogen is firmly held and, in consequence, the unimolecular reaction is unlikely; and (ii) the induced electrophilic properties of the aromatic nucleus are distributed and so offer little encouragement for the bimolecular reaction. Apparently the electrophilic properties of the bromine atoms exceed those induced at any one position in the nucleus. The bromine atoms tend to move to the positions of greatest electron density and show little tendency to pile up in a few nuclei (as is the case with alkylation), since bromine atoms (especially in the presence of aluminium chloride) lower the electron density of the aromatic nuclei to which they are attached.

The positions taken up by the bromine atoms are those which are preferentially alkylated. For instance, alkylation of phenol occurs first in the *p*-position, and *o*- and *m*-bromophenols produce the *p*-isomeride; further, alkylation and bromination of a phenol homologue are both directed by the alkyl group and not the oxygen atom. This difference from the acylation of a phenol nucleus is readily explained by the difference in the vigour of the electrophilic attack, only the acylation being capable of developing the electromeric effect of the phenolic oxygen atom to a degree at which it can supersede the directing power of alkyl groups.

2-Chlorophenol and 3:5-dichloro-*p*-cresol are not isomerised by aluminium chloride. Chloro-2-bromophenol produces the 3-bromo-derivative, thus indicating that the directing power of the chlorine atom can compete successfully with that of the oxygen atom.

EXPERIMENTAL.

Reactions with Aluminium Chloride.—Bromobenzene. Pure bromobenzene (26 g.) and the chloride (25 g., 1 mol.) were heated together at 100° for 1·5 hours. Decomposition with ice produced bromobenzene (13 g.) and *p*-dibromobenzene (2 g.; m. p. and mixed m. p. 89°).

Bromobenzene and p-cresol. A mixture of *p*-cresol (22 g., 1 mol.), bromobenzene (31 g., 1 mol.), and the chloride (80 g., 2 mols.) was heated at 100° for 2 hours. After decomposition with ice and separation of a red precipitate, there were obtained (i) an alkali-insoluble fraction containing benzene (1 g.), bromobenzene (1 g.), and higher-boiling products (30 g.), and (ii) an alkali-soluble fraction containing *p*-cresol (11·5 g.) and 2-bromo-*p*-cresol (2 g.).

A mixture of phenol (16 g.), bromobenzene (26 g.), and reagent (70 g.), treated as above, afforded (i) an alkali-insoluble fraction, of which only 2 g. were distillable (b. p. 160—180°/25 mm.), and (ii) 6 g. of phenol.

2-Bromophenol. A mixture of the phenol (15 g.) and reagent (25 g., 2 mols.) was heated at 130° for 1 hour. Phenol (1·5 g.), 4-bromophenol (10·5 g.; benzoate, m. p. and mixed m. p. 102°), and a higher-boiling fraction (1 g.) were obtained.

3-Bromophenol. Under precisely the same conditions as for 2-bromophenol, this afforded phenol (1 g.), bromophenol (10 g.; crystallisation of the benzoate from alcohol gave first plates and then needles which were identified as the benzoates of 4-bromo- and of 3-bromophenol respectively), and a higher-boiling fraction (2 g.).

4-Bromophenol. Under the above conditions, phenol (1 g.), 4-bromophenol (10·5 g.), and a higher-boiling fraction (2 g.) were obtained.

4-Bromophenol and p-cresol. A mixture of 4-bromophenol (34·5 g., 1 mol.), *p*-cresol (21·6 g., 1 mol.), and aluminium chloride (112 g., 4 mols.) was heated at 130° for 3·5 hours and subsequently decomposed with ice. Phenol (12 g.), *p*-cresol (11 g.), 4-bromophenol (11 g.), 2-bromo-*p*-cresol (15 g.), and higher-boiling fractions (4 g.) were obtained.

3-Bromo-p-cresol. (i) A mixture of the cresol (45 g.) and reagent (65 g., 2 mols.) was heated at 127° for 1 hour. *p*-Cresol (2 g.), 2-bromo-*p*-cresol (31 g.; m. p. and mixed m. p. 55°), and 2:6-dibromo-*p*-cresol (4 g.; m. p. and mixed m. p. 109°) were obtained. (ii) From 143 g. and 190 g. respectively of the same substances, heated at 100° for 17 hours, there were obtained 2, 86, and 7 g., respectively, of the same products, together with 47 g. of unchanged 3-bromo-*p*-cresol.

Preparation of 2-Bromo- and 2:6-Dibromo-p-cresol.—Dr. Short kindly provided a sample of 2-bromo-*p*-toluidine, which was converted into 2-bromo-*p*-cresol (m. p. 55°) and its benzoate (m. p. 76°). 2:6-Dibromo-*p*-toluidine (Neville and Winther, *Ber.*, 1880, 13, 973) was converted into 2:6-dibromo-*p*-cresol, m. p. 109° (Found: Br, 59·9. $\text{C}_7\text{H}_6\text{OBr}_2$ requires Br, 60·1%).

2-Bromo-4-ethylphenol.—Bromine (32 g.) in glacial acetic acid (10 c.c.) was gradually added (2 hours) to a vigorously stirred solution of 4-ethylphenol (25 g.) in the same solvent (50 c.c.) cooled by tap water. The mixture was then heated on the steam-bath for 0·25 hour, and distilled. 2-Bromo-4-ethylphenol (33 g.; b. p. 116—120°/20 mm.) was obtained; its *p*-nitrobenzoate crystallised from light petroleum (b. p. 60—80°) in colourless radiating needles, m. p. 57° (Found: N, 4·2; Br, 22·3. $\text{C}_{15}\text{H}_{13}\text{O}_4\text{NBr}$ requires N, 4·0; Br, 22·8%).

Reaction with aluminium chloride. A mixture of the phenol (17 g.) and reagent (26 g., 2 mols.), heated at 100° for 1·25 hours, afforded 4-ethylphenol (1 g.), 2-bromo-4-ethylphenol (5 g.), and 3-bromo-4-ethylphenol (9 g.; *p*-nitrobenzoate, m. p. and mixed m. p. 108°).

3-Bromo-4-ethylphenol.—3-Bromoanisole (51 g.; prepared from 3-bromonitrobenzene) was mixed with acetyl chloride (23 c.c.) in carbon disulphide (150 c.c.), and aluminium chloride (75 g.) gradually added. 3-Bromoanisole (15 g.) and 2-bromo-4-methoxyacetophenone (39 g.; b. p. 148—156°/15 mm.) were obtained. This ketone gave a semicarbazone, m. p. 198° (Found: N, 14·8. $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_3\text{Br}$ requires N, 14·7%), and some 3-bromophenol on demethylation with hydrobromic acid (*d* 1·5) in glacial acetic acid. Clemmensen reduction of the ketone (38 g.) gave 3-bromo-4-ethylphenol (24 g.; b. p. 123—124°/15 mm.), 10 g. of which, on being refluxed with hydrobromic acid (*d* 1·5; 22 c.c.) and glacial acetic acid (70 c.c.) for 3 hours, afforded 3-bromo-4-ethylphenol (7 g.), of which the *p*-nitrobenzoate had m. p. 108° (Found: N, 4·2; Br, 22·65. $\text{C}_{15}\text{H}_{13}\text{O}_4\text{NBr}$ requires N, 4·0; Br, 22·8%) after recrystallisation from light petroleum (b. p. 60—80°).

3 : 5-Dibromo-*p*-cresol and Aluminium Chloride.—(i) A mixture of the phenol (12 g.) and reagent (12 g., 2 mols.), when heated at 130° for 1 hour, gave 2 : 6-dibromo-*p*-cresol (10 g.), which recrystallised from light petroleum (b. p. 60–80°) in long, fine needles, m. p. and mixed m. p. 109°; on treatment with excess of bromine in acetic acid, this afforded 2 : 3 : 5 : 6-tetrabromo-*p*-cresol, m. p. and mixed m. p. 199°. (ii) When 50 and 55 g., respectively, of the reagents were heated at 100° for 24 hours, they yielded 2 : 5-dibromo-*p*-cresol (28 g.), which crystallised from light petroleum (b. p. 60–80°) in needles, m. p. 61° (Found : Br, 60.2. $C_7H_6OBr_2$ requires Br, 60.1%), 2 : 6-dibromo-*p*-cresol (12 g.), and a residue (10 g.). The former cresol and excess of bromine in acetic acid gave 2 : 3 : 5-tribromo-*p*-cresol, m. p. 101° (Found : Br, 69.5. Calc. for $C_7H_5OBr_3$: Br, 69.5%) (Zincke and Wiederhold, *Annalen*, 1901, **320**, 205, give m. p. 102°).

Bromine (46 g.) was gradually added (0.75 hour) to a solution of 3-bromo-*p*-cresol (54 g.) in glacial acetic acid (70 c.c.). Fractional distillation gave 2 : 5-dibromo- (61 g.; m. p. 61°) and 2 : 3 : 5-tribromo-*p*-cresol (10 g.; m. p. 101°). Chlorine was bubbled through a solution of the former (20 g.) in carbon tetrachloride (10 c.c.) for 2 hours and 3-chloro-2 : 5-dibromo-*p*-cresol (25 g.; m. p. 95° after recrystallisation from alcohol) (Found : Cl, 11.8; Br, 53.8. $C_7H_5OClBr_2$ requires Cl, 11.8; Br, 53.3%) was obtained. This substance (10 g.) was dissolved in carbon tetrachloride (30 c.c.), and iron powder (2 g.) added. Chlorine was bubbled through the mixture at 70–80° for 40 mins., and 3 : 6-dichloro-2 : 5-dibromo-*p*-cresol (11 g.) was obtained, m. p. 177–178° (Zincke and Buff, *Annalen*, 1905, **341**, 340, give m. p. 175–176°). This substance on analysis (Viebock, *Ber.*, 1932, **65**, 586) produced halogen acids equivalent to 6.10 c.c. of N/40-sulphuric acid (Calc. for $C_7H_4OCl_2Br_2$: 6.07 c.c.).

A mixture of 3 : 6-dibromo-*p*-cresol (15 g.) and aluminium chloride (20 g.) produced the 2 : 6-dibromo-derivative (14 g.) after 1 hour at 130°.

2 : 6-Dibromo-4-ethylphenol. Bromine (3.75 c.c.) in glacial acetic acid (5 c.c.) was gradually added to a cooled solution of 2-bromo-4-ethylphenol (14.5 g.) in glacial acetic acid (20 c.c.) and gave 2 : 6-dibromo-4-ethylphenol (14 g.); its *p*-nitrobenzoate crystallised from light petroleum (b. p. 60–80°) in needles, m. p. 93° (Found : N, 3.4; Br, 37.0. $C_{15}H_{11}O_4NBr_2$ requires N, 3.3; Br, 37.3%).

Reaction with aluminium chloride. A mixture of this phenol (5 g.) and the reagent (5 g.), when heated at 120° for 1.5 hours, gave the unchanged phenol (2 g.) and 3 : 5-dibromo-4-ethylphenol (2 g.), which crystallised from light petroleum (b. p. 60–80°) in clusters of radiating needles, m. p. 116–117° (Found : Br, 57.1. $C_8H_8OBr_2$ requires Br, 57.1%). Excess of bromine in glacial acetic acid gave 2 : 3 : 5 : 6-tetrabromo-4-ethylphenol, m. p. 106° (Fittig and Kiesow, *Annalen*, 1870, **156**, 255, give m. p. 105–106°).

Chloro-2-bromophenol and Aluminium Chloride.—A mixture of the phenol (14 g.) and the chloride (21 g., 2 mols.) was heated at 125° for 2.5 hours, affording unchanged phenol (4 g.) and 4-chloro-3-bromophenol (4 g.), which crystallised from light petroleum (b. p. 60–80°) in needles, m. p. 65°. This substance was also prepared from 4-chloro-3-bromoaniline.

COLLEGE OF TECHNOLOGY, MANCHESTER.

[Received, June 8th, 1942.]