141. *The Action of Aluminium Chloride on Some Phenol Homologues.*

By G. Baddeley.

The interconversions of *p*- and *m*-cresols have been studied quantitatively, and a probable mechanism suggested. All the xylenols have been found to give ultimately *m*-5-xylenol, and this is explained. Hemimellithenol isomerises quantitatively to *iso*-ψ-cumenol. The three ethylphenols undergo internuclear alkyl-group migration with the formation of some phenol and 3 : 5-diethylphenol.

The interconversion of *p*- and *m*-xylenes is related to that of *p*- and *m*-cresols. The respective significances of intra- and inter-molecular migration in the action of aluminium chloride on the homologues of phenol and benzene are related and accounted for. Intermolecular migration is shown to be associated with a high nuclear electron availability, and *p*-cresol has been demethylated by toluene in the presence of aluminium chloride. A mechanism is deduced for the Scholl reaction.

Molecular proportions of phenol and aluminium chloride furnish phenoxyaluminium chloride, which can be distilled under atmospheric pressure. *p*-Cresol yields a similarly stable derivative which remains unchanged after several hours at 200°. In the presence of more than one molecular proportion of aluminium chloride, however, even at 125°, partial conversion of *p*- into *m*-cresol occurs.

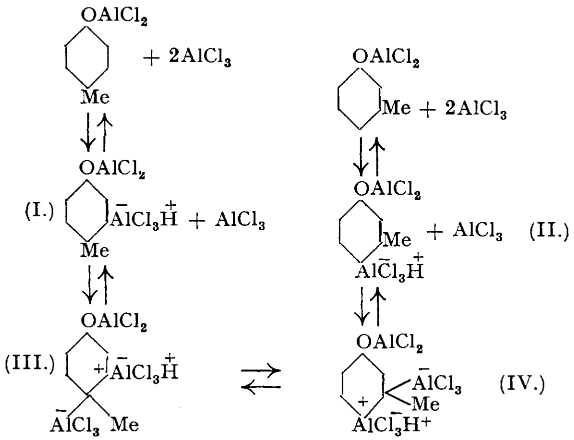
Kinetic study of this change showed it to be reversible and unimolecular in respect of *p*-tolyloxyaluminium chloride, but bimolecular in respect of the further aluminium chloride employed; the reagent is not used up in the course of the reaction, and the unimolecular velocity constant, at a given temperature, is proportional to the square of the amount of reagent present.

Unimolecular velocity constants for the interconversions p- $\underset{k_2}{\overset{k_1}{\rightleftarrows}}$ m-*cresol at* 135° *with various amounts of aluminium chloride.*

$AlCl_3$, mols.	1·00	1·20	1·26	1·40	1·53	1·60
Excess $AlCl_3$	0	0·20	0·26	0·40	0·53	0·60
$k_1 + k_2$	0	0·053	0·094	0·25	0·42	0·51
1·44 (Excess $AlCl_3$)^2	0	0·058	0·097	0·23	0·41	0·52

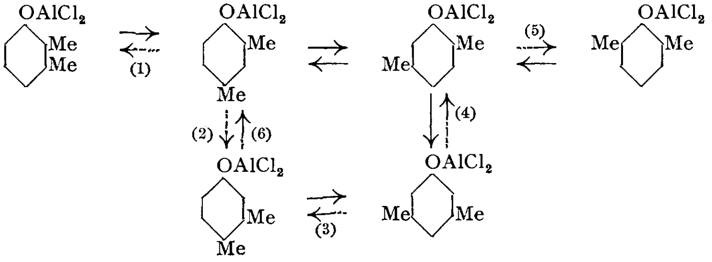
The composition of the equilibrium mixture both at 125° and at 135° was approximately in the ratio 61 *m* : 39 *p*, so the heat of isomerisation is small. The range of temperature suitable for kinetic measurements is limited by the supervention of intermolecular reaction (see below), but from these results an activation energy of 22·5 kg.-cals. may be derived. In explanation of these results, the annexed scheme is proposed.

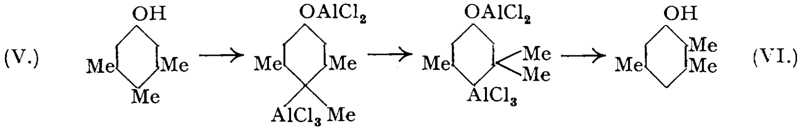
The oxyaluminochloride group has a strongly negative inductive effect, so the methyl group determines the site of attack of the tolyloxyaluminium chloride by electrophilic reagents, as in (I) and (II). Experimental confirmation of this deduction will be supplied later from the results of the alkylation and bromination of *p*- and *m*-cresols in the presence of excess of aluminium chloride. Atomic models, however, show that steric conditions in (I) and (II) determine a displacement of either the methyl or the aluminium chloride group from the plane of the nucleus (cf. Baddeley, *Nature*, 1939, **144**, 444; 1942, **150**, 178), giving rise to polarisations which permit attachment of a further molecule of aluminium chloride to the carbon atom carrying the methyl group (Hampson and Ingham, J., 1939, 981). The interconversion of the resulting products (III) and (IV) is of the Wagner–Meerwein type.



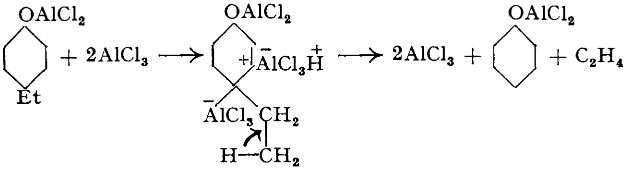
The strongly negative inductive effect of the oxyaluminochloride group is especially effective in the *o*-position, so that *o*-cresol is not isomerised under the conditions already discussed. Intranuclear migration of a methyl group in the *o*-position does, however, occur with the xylenols, and *m*-2-xylenol yields the *m*-5-isomeride. The lower mobility of the methyl group in the *o*-position, however, is illustrated by the conversion of *m*-4-xylenol into the *p*- and the *o*-3-isomeride, and of the latter into the *p*-isomeride.

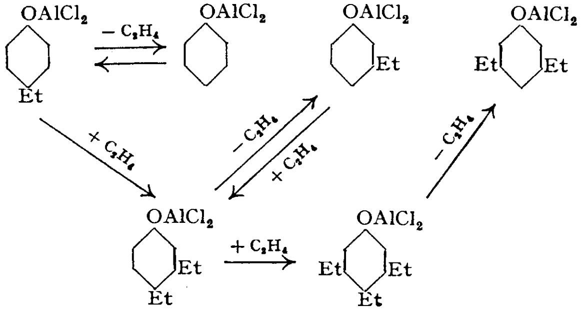
The behaviour of the xylenols towards aluminium chloride, whereby they all yield the *m*-5-isomeride, further illustrates the cogency of these considerations. Thus transformations (1), (2), and (3) are hindered, as indicated by the discontinuous arrows, by difficulty of the requisite attachment of aluminium chloride, whilst (4), (5), and (6) would require such attachment in an *o*-position to the oxyaluminochloride group. The changes which actually occur can be achieved at lower temperatures than in the cases of the cresols. Similarly, hemimellithenol (V) is converted even more readily at 100° into *iso*-ψ-cumenol (VI), and the application of the above considerations is again exemplified. As a consequence of displacement of the 4-methyl group from the plane of the nucleus by those in the 3- and the 5-position, attachment of aluminium chloride causes a migration of the alkyl group comparable with that observed with oxyacetophenone derivatives (compare this vol., p. 273).



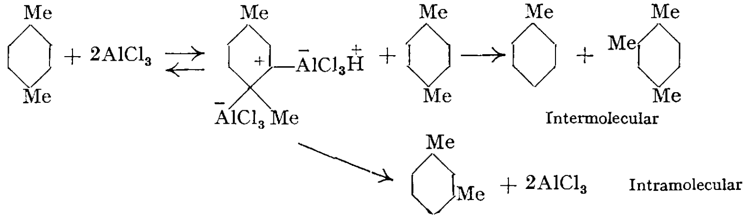


At 170° the three cresols undergo some intermolecular change leading to phenol and *m*-5-xylenol: $2C_6H_4Me{\cdot}OH \rightarrow C_6H_5{\cdot}OH + C_6H_3Me_2{\cdot}OH$. This type of reaction predominates when the three ethylphenols are treated with aluminium chloride even at 100°, and possibly involves intermediate formation of ethylene by a species of Hofmann reaction:





The familiar simultaneous intra- and inter-molecular changes of benzene homologues may be interpreted in the same manner as those of the phenols :



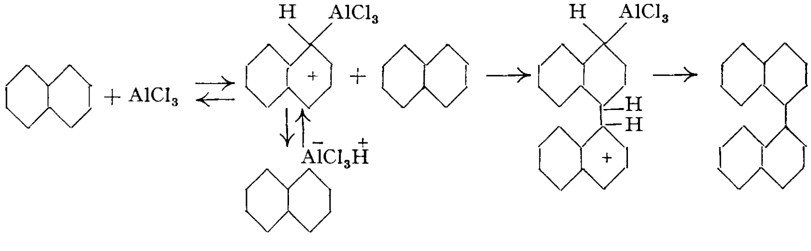
The following table shows the relative significance of intra- and inter-molecular migrations of alkyl groups in the isomerisations of some homologues of phenol and benzene :

Phenols.	Convenient temperatures for : Intramolecular migration.	Intermolecular migration.
2-Me	None	170°
3-Me; 4-Me	135°	170
Xylenols	120	150
3 : 4 : 5-Me$_3$	100	?
2-Et; 3-Et; 4-Et	?	100
Benzene		
All homologues	100	100

The readiness of the intermolecular increases more readily on descending the table than does that of the intramolecular migrations; only above the broken line can the separate occurrence of intramolecular isomerisations be procured.

The sequence benzene homologues, xylenols, cresols, phenol is one of decreasing electron availability (nucleophilic character) in the presence of excess of aluminium chloride. The obvious connection between a high electron availability of the nucleus and a ready intermolecular migration suggests that a molecule in a suitable condition to undergo a Wagner–Meerwein rearrangement can also suffer a Hofmann degradation in the presence of an aromatic nucleus of sufficient electron availability. Phenol homologues should thus isomerise less readily in the presence of a benzene homologue, since this is preferentially attacked by the aluminium chloride. Further, if the reagent is still able to attack the phenol nucleus and so produce a mobile methyl group, this should undergo nucleophilic attack by the benzene homologue. This possibility has been realised : *p*-cresol is partly demethylated when heated at 135° with toluene and an excess of aluminium chloride, although in the absence of toluene it suffers no demethylation at this temperature. The xylene primarily formed is, of course, converted into a mixture of hydrocarbons as usual. It should be further noted that under these conditions no detectable quantity of *m*-cresol is formed.

These researches originated from a suggestion that the Scholl dehydrogenation reaction was direct radical formation (Kenner, *J. Soc. Chem. Ind.*, 1933, **42**, 470). Later, the possibility of its being an ordinary case of substitution was pointed out (Baddeley and Kenner, J., **1935**, 307), and this is in accord with the above considerations :



EXPERIMENTAL.

Phenol and Aluminium Chloride.—After phenol (19 g.) and aluminium chloride (29 g., 1 mol.) had been warmed together until hydrogen chloride evolution ceased, the residue melted at 175—180° and distilled at 210°/15 mm. (Found : Cl, 37·0. Calc. for $C_6H_5{\cdot}OAlCl_2$: Cl, 37·2%). After crystallisation from carbon disulphide it melted at 183° and was thus identical with the product of the same composition prepared by Perrier (*Bull. Soc. chim.*, 1896, **15**, 1181). It suffered slight decomposition when distilled at 310°/760 mm., yielded phenol on treatment with water, and hydrogen chloride when treated with a second and a third molecular proportion of phenol.

Isomerisation of p-*Cresol.*—A mixture of *p*-cresol (32 g.) and aluminium chloride (84 g.) was gradually heated to 130°. It first melted and then set to a solid mass, with liberation of hydrogen chloride. After 0·5 hour at 130°, the mixture had become a homogeneous, pale yellow oil which slowly darkened on prolonged heating. After 2 hours, the molten mixture was cooled to 60° and poured on ice. The product was distilled with steam, the distillate extracted with ether, the extract dried over calcium chloride, the ether removed, and the residue distilled; b. p. 106°/15 mm.

(25 g.). The product did not solidify when seeded with *p*-cresol at — 10°. The benzoate, recrystallised from ethyl alcohol, was identified as that of *m*-cresol (benzoate, m. p. and mixed m. p. 54°).

As a preliminary to a kinetic study of the change, the quantitative analysis of mixtures of the two cresols by the bromination method was examined, and the following procedure adopted : 5 c.c. of a solution of the mixture in 50% aqueous acetic acid (15 g./l.) was diluted with a further 15 c.c. of the 50% acid. Carbon tetrachloride (1 c.c.), N-potassium bromate–bromide solution (5 c.c.), and 5N-hydrochloric acid (5 c.c.) were then successively added, and the mixture well shaken for 1 minute. After addition of potassium iodide (0·5 g.), free iodine was titrated with 0·2N-thiosulphate solution. The following is typical of the experiments carried out on this basis; k is calculated from $k = (1/t) \log_e (T_0 - T_\infty)/(T_t - T_\infty)$, where t is the time in hours and T is the titre, the subscripts having the conventional significance.

p-Cresol (36 g.) and aluminium chloride (56 g.; 1·25 mols.) were shaken together at approx. 130° for 40 mins., and the clear solution then placed in a thermostat at 135°.

t, hrs.	Wt. of sample, g.	50% HOAc, c.c.	T, c.c.	10^3k.
0	1·812	45·6	8·20	—
0·5	1·789	44·7	8·02	87
1·5	1·751	43·8	7·65	93
2·0	1·966	49·2	7·47	95
5·5	1·879	47·0	6·50	94
8·0	1·889	47·2	5·97	95
10·6	1·760	44·0	5·56	93
14·2	1·771	44·3	5·07	96
19·4	1·854	46·4	4·67	95
34·0	2·520	63·0	4·15	98
∞	—	—	4·00	—
				Mean 94

Equilibrium mixture. (i) The mixture of cresols was recovered after 34 hours at 135°, and 4·500 g. were made up to 250 c.c. with 50% aqueous acetic acid; 5 c.c. of this solution required 4·34 c.c. of bromate-bromide solution, whereas a similar solution made from pure *m*-cresol required 5·03 c.c. The mixture contained 58·9% of *m*- and 41·1% of *p*-cresol. Therefore the composition of the equilibrium mixture is 60·7% of *m*- and 39·3% of *p*-cresol.

(ii) *p*-Cresol (36 g.) was shaken with aluminium chloride (90 g.) at 135° for 15 mins., and the clear solution decanted from undissolved aluminium chloride. The velocity constant at 135° was 0·76 and the equilibrium mixture contained 60·8% of *m*- and 39·2% of *p*-cresol, so the composition is independent of the proportion of aluminium chloride.

(iii) A mixture of *m*-cresol (36 g.) and aluminium chloride (68 g.) gave $k_{135°} = 0·42$ and an equilibrium mixture of 61·0% of *m*- and 39·0% of *p*-cresol, *i.e.*, the same as above.

Energy of Activation of the Isomerisation.—A homogeneous mixture of *p*-cresol (72 g.) and aluminium chloride (136 g.) was divided between two flasks, and the velocity constants determined at 125° and at 135° : $k_{125°} = 0·21$; $k_{135°} = 0·42$; hence $E = 22·5$ kg.-cals. The values of T_∞ for the two experiments were identical.

Mixtures of *p*-cresol (8·09 g.) and 12·0, 14·0, and 16·0 g. of aluminium chloride gave respectively $k_{135°} = 0·053, 0·251$, and 0·506.

o-*Cresol and Excess of Aluminium Chloride.*—(*a*) *o*-Cresol (32 g.) and aluminium chloride (84 g., 2 mols.) were heated together at 130° for 3 hours, but pure *o*-cresol was recovered almost quantitatively. (*b*) *o*-Cresol (11 g.) and aluminium chloride (30 g.) were heated together at 170° for 5 hours, and the product poured on ice and distilled with steam. There was considerable non-volatile material. The distillate was extracted with ether, and the extract dried over calcium chloride and distilled : (i) b. p. 180—200° (1·5 g.), identified as phenol by its *p*-nitrobenzoate; (ii) b. p. 200—210° (2·5 g.), contained some phenol; (iii) b. p. 210—215° (1·5 g.), identified as *m*-5-xylenol by its *p*-nitrobenzoate.

Both *m*- and *p*-cresol gave small amounts of phenol, etc., under these conditions.

Reactions of Xylenols with Aluminium Chloride.—m-2-*Xylenol.* This xylenol (12 g.) and aluminium chloride (30 g., 2 mols.) were heated together at 130—135° for 4·5 hours, and the product worked up in the usual manner; b. p. 212° (10 g.). The solid (*m*-5-xylenol) recrystallised from petroleum (b. p. 60—80°) in stout needles, m. p. 64°; *p*-nitrobenzoate, m. p. and mixed m. p. 109°.

m-4-*Xylenol.* This xylenol (25 g.) and aluminium chloride (60 g., 2 mols.) were heated together at 115—120° for 2 hours. After the usual procedure, the product was fractionally distilled under 15 mm. : (i) B. p. 106° (15 g.), identified as original xylenol by *p*-nitrobenzoate. (ii) B. p. 110° (6 g.); preparation of the *p*-nitrobenzoate showed this fraction to contain both *m*-4- and *p*-xylenol. [The *p*-nitrobenzoate of the latter is more soluble in petroleum (b. p. 60—80°) than is that of the former.] (iii) B. p. 112—115° (3 g.); the *p*-nitrobenzoate after three crystallisations gave the pure derivative of *o*-3-xylenol, m. p. and mixed m. p. 104·5°.

m-4-Xylenol (20 g.) and aluminium chloride (50 g.) were heated together at 130—135° for 4·5 hours. After the usual procedure, the final product was distilled; b. p. 212° (16 g.). The semi-solid was recrystallised from petroleum (b. p. 60—80°) and identified as *m*-5-xylenol (m. p. and mixed m. p. 64°).

p-*Xylenol.* Under the conditions of the above experiment, *p*-xylenol (12 g.) and aluminium chloride (30 g.) gave a product, b. p. 212° (10 g.), identified as *m*-5-xylenol.

o-4-*Xylenol.* Under the above conditions, the xylenol (12 g.) and aluminium chloride (30 g.) produced fairly pure *m*-5-xylenol.

o-3-*Xylenol.* This xylenol (19 g.) and aluminium chloride (44 g.) were heated together at 120—125° for 4 hours. The final product obtained by the usual procedure was fractionated under 20 mm. : (i) B. p. 106—112° (10 g.), recrystallised from petroleum (b. p. 60—80°), was identified as *p*-xylenol, m. p. and mixed m. p. 74° (confirmed by means of the *p*-nitrobenzoate). (ii) B. p. 112—122° (4 g.), recrystallised from petroleum (b. p. 60—80°) and identified as *m*-5-xylenol. (iii) B. p. 130—300° (5 g.), a coloured oil not identified.

Reactions of Other Phenols with Aluminium Chloride.—*Hemimellithenol.* This phenol (1 g.) and aluminium chloride (3 g.) were heated together at 100° for 10 hours and then poured on ice. The solid obtained, m. p. 95° after recrystallisation, did not depress the m. p. of *iso*-*ψ*-cumenol, m. p. 95°.

4-*Ethylphenol.* This phenol (18 g.) and aluminium chloride (50 g.) were heated together at 120° for 4 hours. The final product, obtained in the usual way, was fractionally distilled : (i) b. p. 190—208° (4 g.), almost pure phenol; (ii) b. p. 208—218° (4 g.), a mixture containing some phenol; (iii) b. p. 218—228° (4 g.), did not give a solid *p*-nitrobenzoate and was not identified; (iv) b. p. 228—238° (4 g.) and (v) b. p. 238—240° (2 g.) were recrystallised from petroleum (b. p. 60—80°) and identified as 3 : 5-diethylphenol, m. p. and mixed m. p. 77°.

3-*Ethylphenol.* This phenol (4 g.) and aluminium chloride (10 g.) were heated together at 125° for 2 hours; the subsequent procedure was as usual : (i) b. p. 85°/20 mm. (1 g.), phenol; (ii) b. p. 110—115°/20 mm. (1·5 g.), did not give a solid *p*-nitrobenzoate and was not identified; (iii) b. p. 130—135°/20 mm. (1 g.), identified as 3 : 5-diethylphenol.

2-, 3-, and 4-*Ethylphenols at* 100°. Under conditions as for 4-ethylphenol, but at 100°, the products were the same as those from that phenol.

3-*Methyl*-4-*ethylphenol.* This phenol (5 g.) and aluminium chloride (10 g.) were heated together at 100° for 18 hours, and poured on ice, affording 3-methyl-5-ethylphenol.

Interaction of p-*Cresol and Toluene in the Presence of Aluminium Chloride.*—A mixture of *p*-cresol (43 g.), toluene (37 g.), and aluminium chloride (108 g.) was heated at 135° for 5 hours. Considerable decomposition occurred. The product was poured on ice, and extracted with ether. The extract was washed with sodium hydroxide, and the alkali-soluble product consisted of approximately equal parts of phenol and *p*-cresol (10 g. of each were obtained by fractional distillation and identified by their m. p. and mixed m. p. and also by the m. p. and mixed m. p. of their *p*-nitrobenzoates).

The author is indebted to Professor J. Kenner, F.R.S., for his interest in the work described in this and the preceding paper.

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[*Received, June 8th,* 1942.]