CCVI.—*The Friedel-Crafts' Reaction. Part III. Migration of Alkyl Groups in the Benzene Nucleus.*

By MAURICE COPISAROW.

THE chemical metabolism brought about by the action of aluminium chloride on alkylated hydrocarbons of the aromatic series results in profound molecular rearrangements.

The scission of alkyl groups in the benzene series by means of aluminium chloride was first recorded by Gustavson (*Bull. Soc. chim.*, 1878, [ii], **30**, 22), and by Friedel and Crafts (T., 1882, **41**, 116).

Further work by Friedel and Crafts (T., 1885, **48**, 674), Anschutz and Immendorf (*Ber.*, 1885, **18**, 657), and Heise and Tohl (*Annalen*, 1892, **270**, 168) indicated that the action of aluminium chloride results in a general migration of alkyl and, to a smaller extent, of phenyl groups, with the formation of isomerides, higher and lower alkyl derivatives of benzene, and members of the diphenyl group.

In the light of the investigations of Friedel and Crafts (*Compt. rend.*, 1885, **100**, 692), Hamer (*Proc. Camb. Phil. Soc.*, 1911, **16**, 65), Schröeter (*Brennstoff Chem.*, 1920, **1**, 39), Zanetti and Kindal (*J. Ind. Eng. Chem.*, 1921, **13**, 208, 358), and Copisarow (this vol., p. 442) the action of aluminium chloride appears to extend beyond

the migration of groups and results in pyrogenic-like fission of the benzene nucleus with the formation of members of the naphthalene, anthracene, and probably phenanthrene series. The action of ferric chloride on alkyl derivatives of benzene results, not only in migration, but also in chlorination (Thomas, *Compt. rend.*, 1898, **126**, 1213).

In the course of the present investigation the following facts were established :

(1) The action of aluminium chloride on methylated benzene represents qualitatively a reversible reaction in so far as the migration of the alkyl groups is concerned, and, therefore, in this respect it lends itself to the same treatment as is applied in the migration of the halogen atoms (Copisarow, *loc. cit.*).

(2) The fission of the benzene nucleus is facilitated by high temperatures, concentration of aluminium chloride, extent of alkylation of the hydrocarbon, and extension of the period of reaction beyond the maximum required for the migration.

The optimum conditions for the migration were attained by modifying the conditions of reaction in the light of these observations, and also the observations made by Jacobson (*Ber.*, 1885, **18**, 338) and by Anschutz and Immendorf (*Annalen*, 1886, **235**, 177) on the influence of hydrogen chloride.

The increased migration is clearly illustrated by comparison of the 22·9 and 23·7 per cent. yields of toluene from xylene obtained in the present case with that of 12·5 per cent., the maximum found by Fischer and Niggemann (*Ber.*, 1916, **49**, 1475).

The rôle of hydrogen chloride in the reaction consists in its action on the double compound formed by the hydrocarbons with aluminium chloride. Its effect may be expressed by the equations :

$$(1)\ C_6H_5\cdot CH_3 + Al_2Cl_6 = C_6H_5\cdot Al_2Cl_5 + CH_3Cl.$$
$$(2)\ C_6H_5\cdot CH_3 + CH_3Cl = C_6H_4(CH_3)_2 + HCl.$$
$$(3)\ C_6H_5\cdot Al_2Cl_5 + HCl = C_6H_6 + Al_2Cl_6.$$

The influence of nitrogen is merely mechanical, whilst the chemical effect of hydrogen is probably due to its action on the methyl chloride formed in the course of the reaction.

The duration of heating was regulated in the experiments carried out in distillation apparatus by the rate of distillation of the products of low b. p.

The limitations of the progress of migration must be attributed to the deteriorating effect of the fission products upon the active surface of the aluminium chloride, rather than to the formation of the fission products as such.

EXPERIMENTAL.

[With CYRIL NORMAN HUGH LONG.]

The Action of Aluminium Chloride on Toluene.

Series I.—Mixtures of toluene (5 parts) and finely powdered aluminium chloride (1 part) were heated on the steam-bath for eight hours under reflux, in one case in presence of a current of nitrogen and in the other of hydrogen chloride at the approximate rate of 3 bubbles per second.

The mixtures gradually darkened with the formation of a deep-red double compound of aluminium chloride with the hydrocarbons present. The reaction mixtures were subsequently treated with ice and a little hydrochloric acid and distilled in a current of steam. The oily layer of the distillate was removed, dried over sodium sulphate, and fractionally distilled, the following fractions being collected: (*a*) up to 100°, (*b*) 100—125°, (*c*) 125—155°, and (*d*) above 155°. On carefully refractionating and comparing these distillates with known mixtures of benzene, toluene, and xylene fractionated in the same apparatus, the following results were obtained:

	Yield per cent. of the theoretical.	
	In nitrogen.	In hydrogen chloride.
Benzene	8·0	11·5
Toluene	90·5	60·0
Xylene (b. p. 136—143°)	7·0	5·3

The calculation of yields was based on the equation:

$$2C_6H_5\cdot CH_3 = C_6H_6 + C_6H_4(CH_3)_2.$$

The fractions of high b. p. consist mainly of polyalkylbenzenes, whilst the small quantities of dark tarry residues left after distillation with steam represent the bulk of the products of fission.

In view of the work of Friedel and Crafts (*loc. cit.*), Anschutz and Immendorf (*loc. cit.*), and Copisarow (*loc. cit.*) no effort was made either to separate the polyalkylbenzenes, constituting the fraction of high b. p., or to isolate the complex mixture of hydrocarbons of the tarry residue.

Series II.—Mixtures of toluene and aluminium chloride, in proportions as above, contained in distillation flasks, were heated in presence of currents of nitrogen, hydrogen, and hydrogen chloride, the feature of these experiments being the removal of the products of low b. p., immediately they were formed, from the reaction media.

The temperature, duration of reaction, and method of working up were similar to those employed in series I.

The following results were obtained :

	Yield per cent.		
	In nitrogen.	In hydrogen.	In hydrogen chloride.
Benzene (before and after working up)	14·2	20·8	25·9
Toluene	63·0	77·0	57·8
Xylenes	5·7	8·0	6·5

The fractions of high b. p. and the tarry residue, especially the former, were very small in the experiment carried out in presence of hydrogen.

Series III.—A mixture of toluene (100 parts) and aluminium chloride (3 parts), contained in a distillation flask, was heated in presence of a current of hydrogen chloride, the experimental conditions being identical to those adopted in series II.

The following results were obtained :

Benzene	22·0	per cent. of the theoretical
Toluene	74·2	,, ,, ,,
Xylenes	17·8	,, ,, ,,

The quantity of other products was small.

The Action of Aluminium Chloride on Commercial Xylene.

The xylene employed in the subsequent experiments was prepared by washing crude commercial xylene with a little (6 per cent.) cold concentrated sulphuric acid, with sodium hydroxide, and with water, then drying over sodium sulphate and fractionally distilling, the fraction boiling at 136—143° being utilised.

Series I.—Mixtures of purified commercial xylene (5 parts) with finely powdered aluminium chloride (1 part), contained in a distillation flask, were heated for eight hours in presence of a current of hydrogen chloride.

Experiments were carried out at 100° and 120°. The features of the reaction were similar to those of toluene.

The product of reaction, after treatment with ice and hydrochloric acid, was deep green and showed distinct fluorescence.

The following results were obtained on fractionation of the distillate in a manner identical to that adopted in the previous experiments.

	Yield per cent.	
	At 100°.	At 120°.
Benzene (before and after steam distillation)	7·7	4·1
Toluene ,, ,, ,, ,,	23·7	16·3
Xylenes (b. p. 136—143°)	45·8	37·0

calculated on the basis of the equations :

$$2C_6H_4(CH_3)_2 = C_6H_5{\cdot}CH_3 + C_6H_3(CH_3)_3 \text{ and}$$
$$2C_6H_4(CH_3)_2 = C_6H_6 + C_6H_2(CH_3)_4$$

although some of the benzene formed may have been due to the action of aluminium chloride on the hydrocarbons produced during the reaction. The residue left after steam-distillation was a viscous, dark-green tar.

Series II.—A mixture of xylene (100 parts) and aluminium chloride (3 parts) was heated at 120° under conditions identical to those of series I.

The product of reaction was pale green, and when subjected to distillation with steam, left but a small tarry residue. The following results were obtained on fractionating the distillate :

Benzene	3·8	per cent.	of the	theoretical
Toluene	22·9	,,	,,	,,
Xylenes	50·4	,,	,,	,,

The complexity and relative quantities of the fractions of high b. p. and residues may be seen from the table given below, 212 grams (2 gram-mols.) of xylene being employed in each experiment.

	Series I.		Series II.
Fraction.	At 100°.	At 120°.	At 120°.
143—162°	10·4 grams	9·8 grams	30·4 grams
162—185°	42·0 ,,	16·3 ,,	35·4 ,,
185—195°	4·8 ,,	4 ,,	2·6 ,,
195—270°	5·2 ,,	4 ,,	3 ,,
Residue (tar)	20 ,,	78 ,,	4 ,,

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