CLXXI.—*The Nature of the Alternating Effect in Carbon Chains. Part XIX. The Mechanism of Certain Aromatic Migrations.*

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IN explanation of the process of halogenation, Fry, Cofman, Francis, and others have supposed that the halogen molecule ionises, the positive ion being the active agent. Whilst, however, it seems unlikely that such a decomposition, involving the exclusive appropriation of electrons by one atom, would take place without external excitation, the electron repulsion of a negative centre (*e.g.*, in an aromatic nucleus) might supply the necessary stimulus by tending to divest a halogen atom of its shared electrons during combination, leaving the other halogen atom to escape as a negative ion. Thus, the activity of a molecular chlorinating agent, X·Cl, should increase with the electron affinity of X, and similarly for bromination and iodination, which agrees with the fact that bromine chloride is a powerful brominating agent, but does not chlorinate, that iodine monochloride iodinates, and, generally, that the efficiency of halogenating agents is in the anticipated order (electron affinity sequence : $\mathrm{Cl} > \mathrm{Br} > \mathrm{I} > \mathrm{OH}$) :

$\mathrm{Cl{\cdot}Cl} > \mathrm{OH{\cdot}Cl}$	$\mathrm{Cl{\cdot}Br} > \mathrm{Br{\cdot}Br} > \mathrm{OH{\cdot}Br}$	$\mathrm{Cl{\cdot}I} > \mathrm{I{\cdot}I}$
(chlorinating agents)	(brominating agents)	(iodinating agents)

On the other hand, iodine trichloride is a chlorinating agent, but this is explicable on the theory of " singlet " linkings (Prideaux, *Chem. and Ind.*, 1923, **42**, 672; Ingold and Ingold, J., 1926, 1314; Sugden, this vol., p. 1174), since the *positively charged* iodine atom will attract electrons very strongly.

Reasoning on these lines, we deduced, for instance, that the " rearrangements " of aryl iodide dichlorides are not true internal migrations, but substitutions in one aromatic molecule of chlorine derived from another, the process being regenerative and continuous (compare Ingold and Ingold, *loc. cit.*). From this it follows that the ortho–para-migration law need not necessarily be obeyed, and that ordinary orientation rules should hold. A search of the literature revealed much that is consistent with this view [including the important observation by Brazier and McCombie that *p*-iodophenol dichloride, in which the *p*-position is blocked, yields 2-chloro-4-iodophenol (J., 1912, **101**, 968)], and nothing inconsistent with it, except the following.

o-Iodoanisole dichloride (I) was prepared by Jannasch and Hinterskirch (*Ber.*, 1898, **31**, 1710), who diagnosed the main product of its decomposition as 5-chloro-2-iodoanisole (II) (para-migration). According to the above mechanism, this would mean that iodine is more strongly *op*-orienting than methoxyl, which is contrary both to the theoretical sequence of these groups and to the order indicated by nitration experiments (Reverdin, *Ber.*, 1896, **29**, 997). The case, in fact, is one in which a meta-" migration " would be anticipated, and, actually, an independent synthesis (*vide* experimental portion) of 4-chloro-2-iodoanisole (III) has shown that this is the real structure of Jannasch and Hinterskirch's product.

(I.)

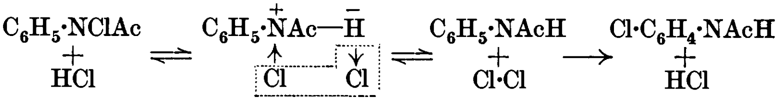
(II.)

(III.)

(IV.)

The group ·NHAc is more strongly *op*-orienting even than ·OMe (Ingold and Ingold, *loc. cit.*), and collateral evidence of the intermolecular character of these " migrations " was obtained by allowing the dichloride (IV) to decompose in the presence of acetanilide; the latter then acted as an acceptor for chlorine, the products being *p*-chloroacetanilide and chloroiodoanisole (III).

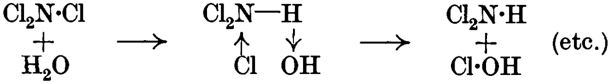
A somewhat similar transference of chlorine to a "foreign" aromatic nucleus has been established by Orton and King (J., 1911, **99**, 1185) for *N*-chloro-anilides in the presence of hydrogen chloride, which Armstrong (J., 1900, **77**, 1051) proved to be necessary for the conversion of the *N*-chloro-compounds into their *p*-chloro-isomerides. The corresponding explanation, which involves the addition of hydrogen chloride, through hydrogen, to the unshared nitrogen electrons,



$$\begin{array}{c}C_6H_5{\cdot}NClAc\\+\\HCl\end{array} \rightleftharpoons \begin{array}{c}C_6H_5{\cdot}\overset{+}{N}Ac-\overset{-}{H}\\ \uparrow \qquad \downarrow\\ \boxed{Cl \qquad Cl}\end{array} \rightleftharpoons \begin{array}{c}C_6H_5{\cdot}NAcH\\+\\Cl{\cdot}Cl\end{array} \longrightarrow \begin{array}{c}Cl{\cdot}C_6H_4{\cdot}NAcH\\+\\HCl\end{array}$$

(small concentration)

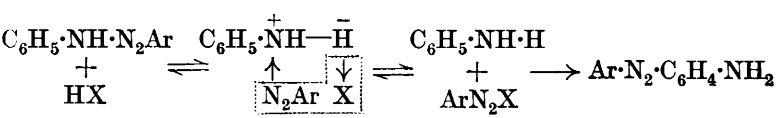
incorporates all the essential features of Orton's theory and one feature of Armstrong's (compare *Brit. Assoc. Reports*, 1910, 85), and is consistent with the equilibrium established by Orton and Jones (J., 1909, **95**, 1456) and with the available dynamical data (Blanksma, Orton). It corresponds closely with Sidgwick's explanation of the hydrolysis of halides in its application to nitrogen halides (J., 1924, **125**, 2672),



$$\begin{array}{c}Cl_2N{\cdot}Cl\\+\\H_2O\end{array} \longrightarrow \begin{array}{c}Cl_2N-H\\ \uparrow \quad \downarrow\\ Cl \quad OH\end{array} \longrightarrow \begin{array}{c}Cl_2N{\cdot}H\\+\\Cl{\cdot}OH\end{array} \quad \text{(etc.)}$$

and shows how the lability of the halogen depends on the distribution of charges in the ammonium complex.

The "rearrangement" of aromatic diazoamino-compounds may be similarly regarded, the final irreversible reaction being a diazo-coupling:



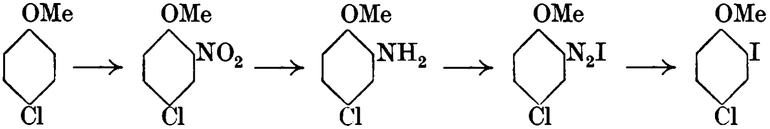
$$\begin{array}{c}C_6H_5{\cdot}NH{\cdot}N_2Ar\\+\\HX\end{array} \rightleftharpoons \begin{array}{c}C_6H_5{\cdot}\overset{+}{N}H-\overset{-}{H}\\ \uparrow \qquad \downarrow\\ \boxed{N_2Ar \quad X}\end{array} \rightleftharpoons \begin{array}{c}C_6H_5{\cdot}NH{\cdot}H\\+\\ArN_2X\end{array} \longrightarrow Ar{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2$$

(small concentration)

This scheme is also in agreement with dynamical observations (Goldschmidt), and here again the transference of the ArN_2-group to a foreign nucleus has been realised (Nietzki, *Ber.*, 1877, **10**, 662). Other aromatic migrations may differ in certain respects from the above (see p. 1249), but a circumstance common to them all may be assumed to be the withdrawal of electrons from the mobile group by the attraction of a positively charged atom (compare Orton, *Proc. Roy. Soc.*, 1903, **71**, 156).

EXPERIMENTAL.

Preparation of 4-Chloro-2-iodoanisole.—This was obtained from *p*-chlorophenol as follows :



p-Chloroanisole (b. p. 194—198° uncorr.; recorded b. p. 198—202° corr.), obtained by methylation of *p*-chlorophenol with methyl sulphate and 10% sodium hydroxide, was nitrated with cooling and constant stirring in acetic anhydride solution, 5% more than the theoretical quantity of nitric acid (*d* 1·5), previously dissolved in the same solvent, being used. Water was added, and after decomposition of the acetic anhydride the nitro-compound was collected, and washed with dilute sodium hydroxide solution to remove the colour, and with water. The yield was 93% (m. p. 96—97·5° ; recorded m. p. 97·5°). Reduction was effected by means of stannous chloride in hot hydrochloric acid, and the 4-chloro-*o*-anisidine (yield 95%, m. p. 82°) isolated by prolonged distillation in steam after addition of a large excess of concentrated sodium hydroxide solution. The base was diazotised in dilute hydrochloric acid below 5°, and the solution was treated with an excess of potassium iodide and warmed until the evolution of nitrogen ceased. The product was distilled in steam, the distillate extracted with ether, and the extract washed successively with hydrochloric acid, sodium hydroxide solution, and water. The residue obtained after drying and evaporation of the ether readily solidified, and crystallised from ligroin in large, transparent, rhomboidal plates, m. p. 48° (Found : C, 31·1 ; H, 2·1. C_7H_6OClI requires C, 31·3 ; H, 2·2%).

Chlorination of o-*Iodoanisole.*—Jannasch and Hinterskirch's *o*-iodoanisole dichloride was obtained without difficulty when a chloroform solution (50 c.c.) of *o*-iodoanisole (10 g.) was saturated with dry chlorine. A bright yellow solid separated, which was collected and washed with chloroform ; it then melted at about 63° (decomp.). Hydrogen chloride was evolved in the cold, and the main product, contaminated with a pink oil, consisted of the characteristic rhomboidal plates, m. p. 48° (Found : C, 31·3 ; H. 2·1%), identical with those described above (mixed m. p. 48°).*

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* In Beilstein's " Handbuch " (4^{te} Aufl., Bd. VI, s. 209) the oil, b. p. 273—278°, described by Jannasch and Naphtali (*Ber.*, 1898, **31**, 1715) as the product of decomposition of *o*-iodophenetole dichloride, is referred to as " 5-chloro-2-iodophenetole," evidently by analogy with Jannasch and Hinterskirch's " 5-chloro-2-iodoanisole." The revision in the orientation of the latter involves a corresponding change in the formula of its homologue.

Dichlorination of o-*Iodoanisole*.—During an attempted preparation of *o*-iodoanisole dichloride, evolution of hydrogen chloride set in, and an iodo-dichloride was obtained probably identical with that described below. This in course of time decomposed, giving a green liquid, from which, by cooling, needles, m. p. 37°, of apparently a *dichloroiodoanisole* were obtained (Found: C, 27·9; H, 2·0. $C_7H_5OCl_2I$ requires C, 27·7; H, 1·65%).

Chlorination of 4-*Chloro*-2-*iodoanisole*.—The iodo-dichloride, which was prepared by means of chloroform in the usual way, has a deeper yellow colour than that derived from *o*-iodoanisole, and melts at about 76° (decomp.). The product of its spontaneous decomposition in chloroform solution was a brown oil, from which, by cooling, crystals of the compound, m. p. 37°, and of 4-chloro-2-iodoanisole (m. p. 48°) were obtained.

Chlorination of Acetanilide by an Aryl Iodide Dichloride.—The dichloride (4 g.) of 4-chloro-2-iodoanisole and acetanilide (1·4 g.) were together dissolved in chloroform. Heat was spontaneously generated, hydrogen chloride was evolved, and the yellow colour of the iodo-dichloride quickly disappeared. The product obtained on concentration of the chloroform solution was distilled in steam, and the residue crystallised from hot water; 1·4 g. (80%) of almost pure *p*-chloroacetanilide were then obtained (m. p. 171—174°; m. p. when fully purified, 175°). The distillate, which contained a liquid and a solid besides the aqueous layer, was filtered; the solid melted at about 60° and appeared to be impure *o*-chloroacetanilide. The non-aqueous liquid, which contained a little chloroform, when separated, dried, and left in a vacuum, completely solidified, yielding nearly pure 4-chloro-2-iodoanisole (m. p. 40—45° unpurified), which was identified, after purification, by direct comparison.

Other Rearrangements.—Numerous experiments, which need not be described in detail, have been made (and are being continued) in order to ascertain whether the hydroxyl group in β-arylhydroxylamines and the arylimino-group in αβ-diarylhydrazines can be transferred to a foreign nucleus by allowing the rearrangement with acids to occur in the presence of another strongly orienting aromatic compound (arylamines and their derivatives, and phenols in solutions of different hydrogen-ion concentration have been used); and whether migrations, directed by an independent substituent, to the meta-position of the same nucleus can be realised. The results have so far been wholly negative, and although we find it difficult entirely to convince ourselves on the grounds of such observations, the conclusion seems to be that the rearrangements of arylhydroxylamines and the benzidine and semidine conversions are not intermolecular processes in the same sense as are the reactions discussed in the introduction to this paper. We are studying along similar lines the migration of nitroxyl and alkyl groups from a side chain to the aromatic nucleus.

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[*Received, April 23rd*, 1927.]