205. *Hydrogen Chloride–Aluminium Chloride as an Agent of Isomerisation.*

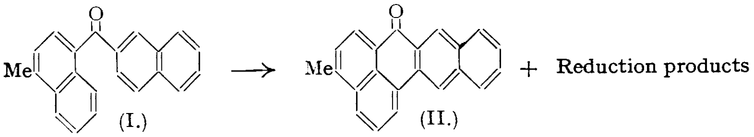
By G. Baddeley.

Hydrogen chloride catalyses the Scholl reaction and the intramolecular migration of alkyl groups in phenol homologues, aromatic ketones, and aromatic hydroxy-ketones, in the presence of aluminium chloride. These reactions do not occur, or occur at greatly reduced rates, when a stream of dry oxygen or nitrogen is passed through the reaction mixtures. The significance of these results is discussed.

Many reactions effected by aluminium chloride and other Friedel–Crafts reagents do not occur in the absence of hydrogen chloride or traces of water—for instance, the polymerisation of olefins in the presence of aluminium chloride (Thomas and Carmody, *J. Amer. Chem. Soc.*, 1933, **55**, 3854; Ipatieff and Grosse, *ibid.*, 1936, **58**, 915; Waterman and Leendertse, *J. Inst. Petr. Tech.*, 1938, **24**, 16). Polymerisation of *iso*butene by boron fluoride requires the presence of moisture or, in general, a substance YH capable of forming a strong acid BF_3,YH (A. G. Evans and Polanyi, *J.*, 1947, 252). Other Friedel–Crafts catalysts are subject to the same limitation (Plesch, Polanyi, and Skinner, *J.*, 1947, 257). Reactions of olefins with *iso*paraffins and aromatic hydrocarbons (Ipatieff and Grosse, *J. Amer. Chem. Soc.*, 1935, **57**, 1616; *J. Org. Chem.*, 1937, **1**, 559), isomerisation of paraffins and *cyclo*paraffins (Thomas, " Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold, 1941; Leighton and Heldman, *J. Amer. Chem. Soc.*, 1943, **65**, 2276; Heldman, *ibid.*, 1944, **66**, 1786), and decomposition of paraffins into higher- and lower-boiling hydrocarbons (Ipatieff and Grosse, *Ind. Eng. Chem.*, 1934, **26**, 461) are other reactions effected by aluminium chloride in the presence of hydrogen chloride.

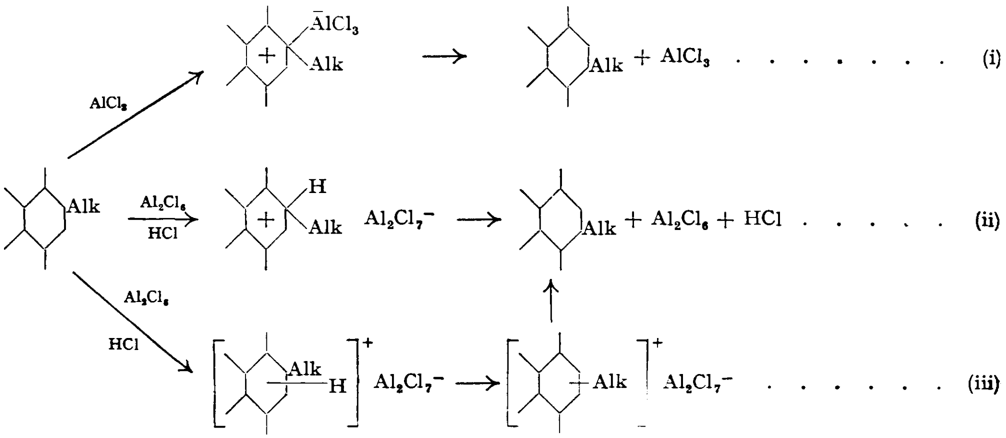
Reversible intramolecular migration of methyl groups in phenol homologues (*J.*, **1943**, 527), and irreversible intramolecular migration of methyl and ethyl groups in aromatic ketones (*J.*, **1944**, 232) and in aromatic hydroxy-ketones (*J.*, **1943**, 273), were caused by aluminium chloride in the presence of hydrogen chloride normally generated when the reactants were brought together in such a manner as to provide homogeneous reaction mixtures. To show whether hydrogen chloride promotes these reactions it is necessary to displace it from the reaction mixtures and to observe whether the rates of isomerisation are adversely affected.

4-Methyl-1 : 2′-dinaphthyl ketone (I), in solution in chlorobenzene, is readily converted (70% yield) at room temperature into 4-methyl-9′ : 10′-benz*meso*benzanthrone (II) by the addition of more than a molecular proportion of aluminium chloride (cf. Buckley, *J.*, **1945**, 561, 564). This can be considered as a disproportionation; when dry oxygen was passed through the reaction mixture in an attempt to improve the yield of (II), hydrogen chloride was swept from the mixture, and reaction did not occur; a stream of dry nitrogen had the same effect and in each case the reaction commenced when hydrogen chloride was introduced. The more conventional Scholl reaction, in which, for example, 1-benzoylnaphthalene is converted in 70% yield into benzanthrone by fusion with more than two molecular proportions of aluminium chloride at *ca.* 125°, also requires the presence of hydrogen chloride and did not occur when dry oxygen or nitrogen was passed through the molten mixture; addition of sodium chloride and consequent formation of $NaAlCl_4$ did not promote the reaction. These observations, a full account of which will be submitted in a later paper, indicated not only that the presence of hydrogen chloride is essential for the occurrence of the Scholl reaction, but also that a stream of dry nitrogen or oxygen can effectively remove hydrogen chloride from liquid mixtures containing aluminium chloride.



An expeditious and decisive method was now available for demonstrating whether the presence of hydrogen chloride is also necessary in the intramolecular migration of alkyl groups in the benzene derivatives indicated above. As a result of the earlier work on the kinetics of these reactions, homogeneous reaction mixtures of low viscosity were obtained at temperatures well below those required for isomerisation; almost all the hydrogen chloride was swept out with dry nitrogen, and the reaction mixtures were then kept at temperatures adequate for isomerisation. For example, after hydrogen chloride had been removed from a mixture of *p*-cresol and aluminium chloride at 85°, isomerisation did not occur at 135°. Under comparable conditions, but in the presence of hydrogen chloride, the 2 : 3 equilibrium mixture of *p*- and *m*-cresol was obtained. The isomerisation of acetophenone homologues is accompanied by some decomposition and consequent evolution of hydrogen chloride : a stream of dry nitrogen markedly increased the rate of decomposition of 2 : 4-dimethylacetophenone, and hydrogen chloride could not be rigorously excluded at 135°, the temperature of isomerisation. The continuous removal of hydrogen chloride had, however, an adverse effect on the rate of isomerisation. Aromatic *o*-hydroxy-ketones are more resistant to decomposition and 6-hydroxy-2 : 4-dimethylpropiophenone, which can be quantitatively converted into 6-hydroxy-3 : 4-dimethylpropiophenone, did not isomerise after hydrogen chloride had been removed. As all these isomerisations require the presence of hydrogen chloride, it is necessary to state that the reaction mixtures employed in the earlier kinetic studies were in an atmosphere of hydrogen chloride at atmospheric pressure.

So far it has not been possible to demonstrate that hydrogen halide promotes the isomerisation of *p*-xylene in the presence of aluminium halide, as aluminium halide does not combine with the hydrocarbon in the absence of a third component such as hydrogen halide. Norris *et al.* (*J. Amer. Chem. Soc.*, 1939, **61**, 1163, 2131; 1940, **62**, 1298, 1428) have prepared ternary complexes by passing hydrogen halide into a mixture of aromatic hydrocarbon and aluminium halide and, although they appear to have converted these into binary complexes by elimination of hydrogen halide under reduced pressures, Mr. Voss has found in this laboratory that a stream of dry nitrogen does not wholly remove the hydrogen bromide from its ternary complexes with aluminium bromide and *m*- or *p*-xylene. Aluminium and hydrogen halides do not interact and their combined action on aromatic hydrocarbons, which at low temperatures exhibit weak basic properties towards hydrogen chloride (Brown and Brady, *ibid.*, 1949, **71**, 3573), can be represented by: $ArH + HX + Al_2X_6 \longrightarrow ArH_2^+ + Al_2X_7^-$. This is in accord with the hydrogen exchange observed when deuterium chloride is passed into a mixture of benzene and aluminium chloride (Kenner, Polanyi, and Szego, *Nature*, 1935, **135**, 267), and when applied to the migration of alkyl groups in benzene derivatives leads to mechanism (ii) or (iii) instead of (i) which was previously proposed.



As previously emphasised (Baddeley, *loc. cit.*), the essential feature of all these isomerisations is the formation of a carbonium ion, followed by a rearrangement of the Wagner and Meerwein type:

and subsequently the isomerisation of paraffins and *cyclo*paraffins has been shown to involve intramolecular rearrangement of carbonium ions. Traces of alkyl or *cyclo*alkyl halide in the presence of aluminium halide or of olefin in the presence of both aluminium and hydrogen halides (Pines *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 153; 1948, **70**, 1742) or of sulphuric acid (Burwell and Gordon, *ibid.*, 1948, **70**, 3128) provide carbonium ions (R^+) which initiate chain reactions resulting in isomerisation:

$$\begin{aligned} R^+ + AlkH &\longrightarrow RH + Alk^+ \\ Alk^+ &\rightleftharpoons Alk_I^+ \\ Alk_I^+ + AlkH &\rightleftharpoons Alk_IH + Alk^+ \end{aligned}$$

This mechanism is in accord with the rapid conversion of *tert.*-butyl bromide and *iso*pentane into *iso*butane and *tert.*-amyl bromide in the presence of aluminium bromide (Bartlett, Condon, and Schneider, *ibid.*, 1944, **66**, 1531), and with the observation (Ipatieff, *ibid.*, 1949, **71**, 749) that benzene, by combining with alkyl cations, inhibits the isomerisation of methyl*cyclo*pentane by the combined action of *sec.*-butyl bromide and aluminium bromide. Aluminium and hydrogen bromides do not combine in *n*-butane or *n*-hexane (Fontana and Herold, *ibid.*, 1948, **70**, 2281) and it is not surprising therefore that hydrogen halide does not promote the interconversion of *cyclo*hexane and methyl*cyclo*pentane in the presence of aluminium halide (Stevenson and Beeck, *ibid.*, 1948, **70**, 2890).

EXPERIMENTAL.

A mixture of *p*-cresol (64 g.) and freshly sublimed aluminium chloride (180 g.) was kept at 120—125° (oil-bath) for 15 minutes and subsequently at 90° for 30 minutes. The clear pale brown liquid was decanted from undissolved chloride into two vessels which were placed in a thermostat at 90°. One was fitted with a drying ($CaCl_2$) tube and the other (*A*) with a sintered-glass gas distributor through which dry (P_2O_5) nitrogen at the temperature of the thermostat was passed at a rate of 30 c.c. per minute. The escaping gases were passed through a large plug of glass wool to remove aluminium chloride, a drying ($CaCl_2$) tube, and a bubbler containing water. After several hours, the gases escaping in the following hour neutralised 1·0 c.c. of N/10-sodium hydroxide. The reaction mixtures were then kept at 135° for 9 hours. The amount of hydrogen chloride in the escaping gases remained small. The mixtures were decomposed with ice and dilute hydrochloric acid, and the cresol isolated. That obtained from the mixture (*A*) was nearly pure *p*-cresol (m. p. 31°; mixed m. p. 33°); the other did not solidify at 0° and contained *m*- (60%) and *p*-cresol (40%) (bromate analysis, *loc. cit.*).

A mixture of 2 : 4-dimethylacetophenone (50 g.) and aluminium chloride (100 g.) was heated at 100° for 15 minutes and the homogeneous solution decanted into two vessels. Subsequent procedure was as above. At 135° the mixture (*B*), from which considerable quantities of hydrogen chloride were continuously removed by nitrogen, became much darker than the other. The latter, on decomposition with ice and dilute hydrochloric acid, provided 3 : 4-dimethylacetophenone (semicarbazone, m. p. and mixed m. p. 235°) which contained very little initial ketone (separated by the greater solubility of its semicarbazone in ethanol). The product from (*B*) contained a considerable amount of tar, and the steam-volatile material was a mixture of approximately equal amounts of 2 : 4- and 3 : 4-dimethylacetophenone.

The procedure with 6-hydroxy-2 : 4-dimethylpropiophenone was similar. The reaction mixture was obtained from *m*-5-xylenyl propionate (55 g.), aluminium chloride (126 g.), and sodium chloride (12 g.). Samples which were removed after 5 hours at 85° gave pure 6-hydroxy-2 : 4-dimethylpropiophenone. The nitrogen emitted in an hour now contained an amount of hydrogen chloride which neutralised 0·5 c.c. of N/10-sodium hydroxide, which was increased to 15 c.c. when the temperature was raised to 140°, the reaction mixture becoming much darker than when hydrogen chloride was not removed. These mixtures provided 6-hydroxy-2 : 4- (m. p. and mixed m. p. 75°) and 6-hydroxy-3 : 4-dimethylpropiophenone (m. p. and mixed m. p. 60°) respectively. The former was separated from tar by distillation with steam.

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