

CCCLXXX.—*Orientation in the Addition of Halogens and Hydrogen Halides to Simple Ethylene Derivatives. Part I. Some Additions with Iodine Monochloride.*

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THE term orientation, as applied in connexion with additions to conjugated unsaturated systems, is usually employed merely in relation to the constitutions of the products of addition, but the theoretical consideration of the subject emphasises the importance of another circumstance associated with addition reactions which essentially involves the idea of orientation, namely, the location in the system of the point of initial attack. In additions with halogens and with hydrogen information as to this does not emerge automatically from a knowledge of the constitutions of addition products; yet there are a number of theoretical questions which could be answered were such data available. The case of halogen additions is the more readily amenable to practical treatment, and accordingly experiments have been instituted with the object of determining, for unsymmetrical addition products, such as the 1 : 2-dibromide of butadiene and the 3 : 4-dibromide of sorbic acid, which is the point of commencement of addition and which the point of its completion. Two methods of attaining this end are being explored, namely, the appropriate applications of the competition method of Francis and others, and the use of unsymmetrical halogens such as iodine monochloride. As to the first, it is known that the eventual position of the successfully competing anion marks the point of completion of the corresponding addition reaction. With regard to the second, however, it seemed desirable to confirm, by observations on the addition of iodine monochloride to simple ethylene derivatives, the theoretical inference that the location of the iodine atom indicates

the point of initiation of addition. For this reason our work on the addition of iodine monochloride to conjugated unsaturated compounds was preceded by a study of its action on some ethylene derivatives of simple constitution.

Although iodine monochloride is a commonly used reagent for unsaturated compounds, few observations on its direction of addition have been recorded. Michael (*J. pr. Chem.*, 1899, **60**, 450) showed that its addition to propylene leads to a mixture, of which $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_2\text{I}$ was found to be the main constituent, although no quantitative method of analysis was used. Ingle (*J. Soc. Chem. Ind.*, 1902, **21**, 591), judging from the colour of the silver halide precipitate given by the products of the action of Wijs's and Hubl's solutions on unpurified styrene, concluded that choride ion was more rapidly liberated than iodide ion, and that therefore the addition product was essentially $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CH}_2\text{I}$. Erlenmeyer (*Annalen*, 1896, **289**, 270) showed conclusively that $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CHI}\cdot\text{CO}_2\text{H}$ is a principal product of the action of iodine monochloride on cinnamic acid. All this is consistent with the theory of the initiation of reaction by the iodine end of the halogen molecule, and the following results, details of which will be found in the experimental section, supply definite confirmation. (1) The addition product of iodine monochloride, in solution (mol. fraction 0.05) in dilute hydrochloric acid at the ordinary temperature, and propylene contains 69% of $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_2\text{I}$ and 31% of $\text{CH}_3\cdot\text{CHI}\cdot\text{CH}_2\text{Cl}$. (2) The addition product formed from pure styrene contains at least 95% of $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CH}_2\text{I}$. (3) Crotonic acid yields at least 92% of $\text{CH}_3\cdot\text{CHCl}\cdot\text{CHI}\cdot\text{CO}_2\text{H}$. (4) Ethylenesulphonic acid yields at least 90% of $\text{CH}_2\text{Cl}\cdot\text{CHI}\cdot\text{SO}_3\text{H}$.

EXPERIMENTAL.

Addition of Iodine Monochloride to Propylene.—Propylidene chloride, prepared from propaldehyde by Reboul's method (*Ann. Chim. Phys.*, 1898, **14**, 458), b. p. 85—87°, was treated at 100° in closed tubes with excess of alcoholic potassium hydroxide, and the product was slowly distilled. The issuing gas was washed with water, ammoniacal silver nitrate, and dilute sulphuric acid, and dried with fused calcium chloride and phosphoric oxide, all these reagents being kept at 40° throughout the distillation. The dried α -chloro- Δ^a -propylene was collected in a tube cooled in liquid air, and again distilled, b. p. 35°, through the same train of purifying agents.

*iso*Propylidene chloride, prepared from acetone by Friedel's method (*Annalen*, 1859, **112**, 236; 1865, **134**, 263), b. p. 69—71°, was treated with alcoholic potassium hydroxide as in the preceding

preparation, and the β -chloro- Δ^{α} -propylene, b. p. 23° , was similarly isolated and purified.

Well-washed propylene, prepared from isopropyl alcohol by Newth's method (J., 1901, **79**, 917), was conducted through a solution of freshly distilled and frozen iodine monochloride (mol. fraction 0.05) in dilute hydrochloric acid. The oily addition product was washed with cold dilute sodium hydroxide solution and water, dried by fused calcium chloride, and completely distilled under reduced pressure (compare Simpson, *Annalen*, 1862, **127**, 372). The product was treated at 0° with an excess of ethyl-alcoholic potassium hydroxide, and, after completion of the reaction, the temperature of the solution was raised. Towards the end of the ensuing distillation of the chloropropylenes their removal was assisted by the passage of air through the alcoholic solution, and the whole apparatus was finally swept out with air. The gases were treated at 40° with the washing and drying agents mentioned in the first paragraph, and the chloropropylenes were collected at the temperature of liquid air, and then completely redistilled through the same purifying and drying train to ensure freedom from traces of allylene. Several samples prepared in this way were kept in sealed tubes until required for analysis.

The refractometric analyses were carried out with a Pulfrich instrument, and all the specimens were examined on the same day and with the same setting on the circle, differences of refractive index being read directly on the drum. The temperature throughout was 11.5° and the wave-length that of the green line of the mercury arc. The observed indices were: α -chloro- Δ^{α} -propylene 1.41353; β -chloro- Δ^{α} -propylene 1.40317; mixtures from propylene, 1.40673, 1.40617, 1.40637, 1.40651 (mean, 1.40644). The corresponding percentages of β -chloro- Δ^{α} -propylene are: 65.6%, 71.0%, 69.1%, 67.8% respectively (mean, 68.6%).

The heterogeneity of this addition precludes comparison with the reaction of propylene with hydriodic acid (compare Part II).

Addition of Iodine Monochloride to Styrene.—Freshly distilled styrene was treated with the theoretical quantity of a solution of iodine monochloride in concentrated hydrochloric acid, in the presence of methylene chloride, and the product was extracted with this solvent. A portion of the solution was warmed at 50° with aqueous-alcoholic potassium iodide solution in order to estimate the yield of addition product by titration of the liberated iodine, whilst another portion was shaken with warm aqueous alcohol containing a little sulphuric acid in order partly to liberate halide ion, which was analysed in the form of the corresponding silver salts. In the following table the yields of addition product are calculated on the

styrene used, but the yields of halide liberated by hydrolysis are based on the addition product formed :

Sample No.	Yield of addn. prod.	Yield of halides.	Mols. %	AgCl in halides.
1	96.5	65.2		94.3
2	97.5	76.4		94.9
2	97.5	81.9		95.0
1	96.5	96.9		91.6
3	96.7	102.8		87.9

These figures show that with diminishing halide-liberation the proportion of chloride contained in the halides rises asymptotically to 94.7%. Assuming that the rates of separation of β -halogens are negligible in comparison with the rates of separation of α -halogens, this implies the presence of 94.7% of the α -chloro- β -iodo-isomeride in the mixed addition compounds. If, however, the speeds of liberation of β -halogens are not negligible, the proportion of α -chloro- β -iodocompound necessary to give the observed figures must be higher. Thus the figure recorded is a minimum value for the proportion of this isomeride in the addition product of iodine monochloride to styrene.

Addition of Iodine Monochloride to Crotonic Acid.—Crotonic acid, m. p. 72°, prepared by Delépine and Bonnet's method (*Compt. rend.*, 1909, **149**, 39) was treated with the theoretical quantity of iodine monochloride in chloroform. The solvent was removed in a vacuum and the residue was crystallised from ligroin, from which β -chloro- α -iodobutyric acid separated in prisms, m. p. 64° (Found : C, 19.2; H, 2.7. $C_4H_6O_2ClI$ requires C, 19.3; H, 2.4%).

The chloro-iodo-acid was heated for 2 hours on the steam-bath with a three-fold excess of 4*N*-ethyl-alcoholic potassium hydroxide. The product, on being poured into water, acidified, and extracted with ether, yielded nearly pure crotonic acid (m. p. and mixed m. p.), which was crystallised from ligroin.

The chloro-iodo-acid was dropped slowly into boiling pyridine, and the solution, after being cooled, was poured into water, acidified, and extracted with ether. The product, after crystallisation from water to remove crotonic acid, a considerable quantity of which was always produced, yielded α -iodocrotonic acid as colourless needles, m. p. 113° (Found : C, 22.4; H, 2.6. $C_4H_5O_2I$ requires C, 22.6; H, 2.3%).

A preparation of α -chloro- β -iodobutyric acid led to the isolation of 87.6% in the pure condition. The combined residues were well mixed and the chloro-iodo-acids were estimated in a sample by decomposition with hot aqueous potassium hydroxide and potassium iodide and subsequent neutralisation and titration with thiosulphate. The residues were thus shown to account for a further 8.7% of chloro-iodo-acids, and on treatment with pyridine they yielded

α -iodocrotonic acid in quantity sufficient to prove the presence of at least 0.8% of β -chloro- α -iodo-acid, calculated on the weight of crotonic acid employed in the preparation. These figures lead to 91.8% as a minimum for the proportion of β -chloro- α -iodo-acid in the addition product of iodine monochloride and crotonic acid.

Addition of Iodine Monochloride to Ethylenesulphonic Acid.—The acid prepared by Köhler's method (*Amer. Chem. J.*, 1898, **20**, 680) was treated in the cold for several days with the theoretical quantity of iodine monochloride in hydrochloric acid. The product was diluted, the halogen acids precipitated by treatment with lead carbonate, and the lead removed as sulphide. The acid solution thus obtained was neutralised with potassium carbonate and evaporated to dryness. The residue was almost completely soluble in alcohol, and *potassium α -iodoethylenesulphonate* crystallised therefrom in long needles (yield, 90%) (Found : C, 8.8; H, 1.1; S, 11.7; I, 46.4; K, 14.1. $C_2H_2O_3ISK$ requires C, 8.8; H, 0.8; S, 11.8; I, 46.7; K, 14.4%). The residues from the crystallisation of this salt contained chlorine as well as iodine; hence the presence of potassium α -chloroethylenesulphonate is not excluded. Köhler (*loc. cit.*; *Amer. Chem. J.*, 1899, **21**, 349) has shown that the action of bromine water on ethylenesulphonic acid under conditions comparable with those described above leads to α -bromoethylenesulphonic acid, the $\alpha\beta$ -dibromoethanesulphonic acid originally formed being too unstable to permit of its isolation from the aqueous solution.

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[Received, September 9th, 1931.]
