CCLVI.—*The Addition of Halogens to Unsaturated Acids and Esters. Part I. The Addition of Equimolecular Mixtures of Bromine and Chlorine to Cinnamic Acid and its Derivatives in Non-hydroxylic Solvents.*

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THERE is no direct physicochemical evidence for the existence of a chloride of bromine BrCl, either in the liquid or the solid state (compare Karsten, *Z. anorg. Chem.*, 1907, **53**, 365; Lebeau, *Compt. rend.*, 1906, **163**, 589), but many cases are on record showing that a mixture of bromine and chlorine, dissolved in a suitable solvent, behaves towards ethylenic compounds as though at least some bromine chloride, capable of reacting as a molecule of such, were present. For instance, the addition of the mixed halogens in hydrochloric acid solution to several ethylenic hydrocarbons has been accomplished, the addition products being termed "chlorobromides" (Simpson, *Bull. Soc. chim.*, 1879, **31**, 409; J. W. James, J., 1883, **43**, 37; Delépine and Ville, *Compt. rend.*, 1920, **170**, 1390). Further, the last-named authors obtained indications that an equimolecular mixture of dry bromine and chlorine at 0° is much more reactive towards ethylene than either of its constituents separately. By employing a chloroform solution of the mixed halogens, Walden (*Ber.*, 1897, **30**, 2883) achieved their simultaneous addition to maleic anhydride, the product being chlorobromosuccinic anhydride.

By allowing a solution of the mixed halogens in hydrochloric acid to react with cinnamic acid, Erlenmeyer (*Annalen*, 1896, **289**, 259) obtained, along with ω-bromostyrene and phenyl bromohydracrylic acid, about a 50% yield of an acid which he proved to be β-chloro-α-bromo-β-phenylpropionic acid. This was only one of four possible addition products, *viz.*, the two pairs of externally compensated stereoisomerides corresponding to the formulæ

$C_6H_5\cdot CHCl\cdot CHBr\cdot CO_2H$ (I) and $C_6H_5\cdot CHBr\cdot CHCl\cdot CO_2H$ (II).

The structural isomerides having these formulæ and melting at 182° (I) and 184·5° (II), respectively, have already been described (Glaser, *Annalen*, 1868, **147**, 78; Erlenmeyer, *ibid.*, 1896, **289**, 259).

In the present paper, the addition of equimolecular mixtures of bromine and chlorine, dissolved in carbon tetrachloride or chloroform, to cinnamic acid and some of its derivatives is described. The products of the addition to cinnamic acid have been found to be two acids, both possessing the structure $C_6H_5\cdot CHCl\cdot CHBr\cdot CO_2H$, melting at 182° and 75°, analogous to the cinnamic acid dihalides (higher-melting) and *allo*-dihalides (lower-melting), respectively, and therefore stereoisomeric. The structure of these acids has been established by an examination of their behaviour when treated with two equivalents of methyl-alcoholic potash. This treatment caused elimination of a mixture of hydrogen chloride and bromide from both acids—no detectable substitution of methoxyl for halogen occurring—and the consequent production of the corresponding monohalogenocinnamic acids. The acid melting at 182° evolved 39% by weight of the available hydrogen bromide, and 61% by weight of the available hydrogen chloride, the products of this elimination being a mixture of acids from which α-bromo-, α-bromo*allo*-, and β-chloro*allo*-cinnamic acids were isolated and identified. The isomeric acid melting at 75° evolved 15% of hydrogen bromide and 84% of hydrogen chloride, the only product isolated being α-bromocinnamic acid. These results demonstrate that the acids are stereoisomerides having the structure $C_6H_5\cdot CHCl\cdot CHBr\cdot CO_2H$. Further evidence in favour of such a structure is afforded by the fact that a specially prepared specimen of α-chloro-β-bromo-β-phenylpropionic acid proved to be isomeric and not identical with the higher-melting (182°) of these acids, in that it evolved hydrogen bromide only, to the extent of 95% by weight of the available hydrogen bromide, when similarly treated.

These results are in conformity with those obtained from the cinnamic acid dihalides. It is well known that α-hydrogen and β-halogen split off from these acids in preference to the alternative, and also that hydrogen bromide is evolved from the dibromide more readily than hydrogen chloride from the dichloride. The ultimate result in the case of the various chlorobromo-β-phenylpropionic acids would be due to a combination of these two factors. The nature of the products of elimination harmonises with the conclusion that the configurations of the higher- and lower-melting addition products of "bromine chloride" to cinnamic acid are analogous to those of the cinnamic acid dihalides (higher-melting) and *allo*-dihalides (lower-melting), respectively.

Regarding the relative positions in the molecule taken up by the component atoms of " bromine chloride " when this combines with cinnamic acid, the general rule relating to the addition of diatomic molecules is obeyed, the more negative (*i.e.*, the chlorine) atom attaching itself to the β-carbon atom.

That the rate of addition of " bromine chloride " to cinnamic acid is considerably more rapid than is the case with either of the pure halogens has been shown by a series of kinetic experiments similar in method to those described by Williams and James (this vol., 344). In this case the reaction is bimolecular in type and there is no inhibition period. Corresponding experiments have been carried out with certain substituted cinnamic acids and esters, and in every case examined " bromine chloride " has proved much more reactive than bromine alone, the reaction generally being of the bimolecular type.

Modern theory regarding the interpretation of addition reactions (see Lowry, J., 1923, **123**, 832; Norrish, *ibid.*, p. 2008) postulates a process of unsymmetrical activation, of both the unsaturated molecule and the addendum, which precedes or accompanies such reactions. The cinnamic acid and bromine molecules in this activated state may be represented thus: $C_6H_5\cdot\overset{+}{C}H{=}\overset{-}{C}H\cdot CO_2H$ and $\overset{+}{Br}{-}\overset{-}{Br}$, the bromine molecule breaking up, not into two neutral atoms, but into two ions. Since the rate of addition of bromine to cinnamic acid and its derivatives is generally slow, the ionisation in solution of the former probably occurs to a limited extent.

Experimental evidence points to the conclusion that if a compound of bromine and chlorine—" bromine chloride "—does exist, it must undergo dissociation in solution to such an extent that it escapes physicochemical methods of detection. If—and there is no evidence to the contrary—this dissociation is ionic in nature, then the molecules in solution undergo almost complete disruption into the ions Br^+ and Cl^-, which, being in the activated state, combine rapidly with cinnamic acid. The final interaction between these ions and the activated cinnamic acid molecule would amount merely to a neutralisation of oppositely charged ions, the chlorine ion becoming neutralised by, and uniting with, the β-carbon atom; a similar reaction occurring between the bromine ion and the α-carbon atom.

EXPERIMENTAL.

A finely divided suspension of cinnamic acid in carbon tetrachloride was mixed with one molecular proportion of a solution in the same solvent of an equimolecular mixture of bromine and chlorine. Complete addition had occurred after exposure to dull light for 4 days. The white powdery product, after filtration and crystallisation from chloroform–carbon tetrachloride, melted at 182° as described by Erlenmeyer (*loc. cit.*) (Found: Br, 30·9; Cl, 13·5. Calc. for $C_9H_8O_2ClBr$: Br, 30·3; Cl, 13·5%).

The filtrate after removal of this product yielded on evaporation a thick, colourless oil which solidified in a vacuum. After crystallisation from light petroleum the substance consisted of small colourless prisms, m. p. 75°. Analysis and the reactions described below indicate that it is stereoisomeric with the substance melting at 182° and is therefore the lower-melting (*allo-*) *β-chloro-α-bromo-β-phenylpropionic acid*, $C_6H_5{\cdot}CHCl{\cdot}CHBr{\cdot}CO_2H$ (Found: Br, 30·9; Cl, 13·2. $C_9H_8O_2ClBr$ requires Br, 30·3; Cl, 13·5%).

In a series of experiments carried out under the conditions described, the proportion of the higher- to the lower-melting product was approximately 1 : 3.

The isomeric α-chloro-β-bromo-β-phenylpropionic acid was prepared by converting cinnamic acid into its chlorohydrin (compare Read and Andrews, J., 1921, **119**, 1774), and replacing the hydroxyl group by bromine by means of concentrated hydrobromic acid (Glaser, *Annalen*, 1868, **147**, 78). The distinction between this acid, m. p. 184·5°, and the acid described above, m. p. 182°, has been established by Erlenmeyer (*loc. cit.*).

The action of methyl-alcoholic potash on these three acids has been investigated, under conditions which would extract one equivalent only of hydrogen halide. About 0·5 g. of each acid was warmed with exactly 2 equivalents of alkali on a water-bath, the alcohol being subsequently evaporated. The residues were dissolved in water and acidified with dilute nitric acid, the precipitated organic acids were filtered off and washed, and the filtrate was analysed for chloride and bromide. The results indicated that the following proportions of hydrogen chloride and hydrogen bromide were extracted:

Acid, m. p.	% HCl extracted.	% HBr extracted.
182°	61	39
75	84	15
184·5	0	95

The products of these reactions were isolated in experiments conducted on a larger scale.

Acid, m. p. 182°. The acid (7 g.) was dissolved in methyl alcohol and treated with methyl-alcoholic potash (2 equivs.). The solvent was evaporated, the residue taken up with water, and a slight excess of 10% barium chloride solution added (compare Sudborough and

Thompson, J., 1903, **83**, 673; Sudborough and James, J., 1906, **89**, 107). After 3 hours, the sparingly soluble barium salt was removed and this and the filtrate were treated separately with dilute acid. The sparingly soluble salt yielded 1·3 g. of acid which on recrystallisation from benzene had melting point 131° and proved to be α-bromocinnamic acid. The filtrate gave 3·5 g. of acid of low melting point from which by fractional crystallisation from chloroform and light petroleum were isolated (1) α-bromo*allo*cinnamic acid, m. p. 120°, and (2) β-chloro*allo*cinnamic acid, m. p. 131—132°.

Acid, m. p. 75°. 5 G. were treated as above and yielded 3·5 g. of α-bromocinnamic acid (m. p. 131°) as the only recognisable product.

The results of kinetic experiments are summarised in the tables. Table I gives the values for the bimolecular velocity coefficient $k=1/t\,.\,x/a(a-x)$, based upon time (t) in hours and concentrations (a and x) in g.-mols. per litre for "bromine chloride," and for comparison Table II gives results for bromine alone under similar conditions.

The substances examined were (1) † cinnamic acid, (2) † α-methylcinnamic acid, (3) † methyl *o*-methoxycinnamate, (4) † methyl *o*-methoxy*iso*cinnamate, (5) * α-bromo-*o*-methoxycinnamic acid, (6) * *m*-methoxycinnamic acid, and (7) † methyl *m*-methoxycinnamate.

Temperature 0°.

	TABLE I.		TABLE II.	
Substance.	Limits of k.	Mean k.	Limits of k.	Mean k.
1	113—96·3	104	0·173—0·041	0·146
2	2·83—2·07	2·51	0·013—0·011	0·012
3	2730—2032	2382	13·3 (0·117)—5·47 (9·27)	—
4	5682—4412	5009	44·9 (0·200)—18·9 (8·29)	—
5	124 (0·038)—59·2 (2·51)	—	0·158—0·123	0·137
6	4166 (0·016)—922 (0·292)	—	79·2 (0·030)—3·97 (61·5)	—
7	243—182	199	1·24—0·717	1·09

The figures in parenthesis denote the time (in hours) at which the value of k is that which precedes them. In such cases the reaction is not bimolecular and k varies with t.

The value of the velocity coefficient for the addition of chlorine to cinnamic acid under similar conditions was found to be 0·209.

Summary.

An equimolecular mixture of bromine and chlorine, dissolved in carbon tetrachloride, has been found to react additively with cinnamic acid as bromine chloride, were such a compound existent, the

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* Indicates reactions in chloroform as solvent.

† Indicates reactions in carbon tetrachloride as solvent.

product of addition being the two stereoisomeric β-chloro-α-bromo-β-phenylpropionic acids.

Such a " bromine chloride " solution has been shown kinetically to react at a far more rapid rate with cinnamic acid and some of its derivatives than bromine solution itself. These phenomena appear to be readily explicable along the lines of modern polarity theories.

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