24. *The Modes of Addition to Conjugated Unsaturated Systems. Part VI. Addition of Halogens and Hydrogen Halides to Conjugated Unsaturated Carboxylic Acids and Esters.*

By C. K. Ingold, G. J. Pritchard, and (in part) H. G. Smith.

The classification of addition reactions according to the nature of the addendum and the structural influences affecting the unsaturated system, introduced in order to serve as a basis for an orientation theory of additions to conjugated unsaturated systems, recognises the following six categories :

Case 1. Both parts of addendum stable as anions (*e.g.*, Br_2, ICl). Structural influences (*a*) favour, (*b*) inhibit anionotropy.

Case 2. One part of addendum stable as anion, and the other as cation, the cationic component being the more reactive (*e.g.*, HBr). Structural influences (*a*) favour, (*b*) inhibit anionotropy.

Case 3. One part of addendum stable as anion, and the other as cation, the anionic component being the more reactive [*e.g.*, HCN, $CH_2(CO_2Et)_2$].

Case 4. Both parts of addendum stable as cations (*e.g.*, H_2).

Some consideration has already been given to four of these categories (cases 1*a*, 2*a*, 3, and 4) in the previous Parts of this series (J., 1928, 910; 1929, 2022; 1931, 2752, 2765), and this preliminary survey is now completed by a brief discussion of the remaining cases 1*b* and 2*b*. These cases are the most difficult of all to deal with theoretically, because opposing influences are at work which cannot in general be relatively evaluated on *a priori* grounds. The type of example considered may be represented by the addition of bromine or hydrogen bromide to a Δ^{α}-unsaturated acid or a $\Delta^{\alpha\gamma}$-di-unsaturated acid, and, in the attempted application of the general methods of the theory to determine the orientation of additions in the butadiene series, the difficulty of weighting the opposing factors arises as follows. First, in relation to the question as to where addition will be initiated, the addendum is electrophilic, and therefore demands a centre of high electron-availability; but the conjugated unsaturated system contains an electron-sink, and therefore, in so far as it functions as a conjugated system, is primarily adapted to the production of regions of low electron-availability. It will in general be true that one or more of the unsaturated units composing the conjugated systems could, if it were isolated and free to polarise independently, produce a centre of greater electron-availability than can possibly arise through the polarisation of the conjugated system as a whole. Thus, because the conjugated system can produce only polarisation of a kind contrary to that required by the reagent, the forces incidental to reaction must tend to disorganise the function of conjugation, and, should these disintegrating forces be sufficiently powerful, then a reaction may ensue, the initiation of which depends on the more or less separate action of some portion of the complete conjugated system. Whether the disorganising forces of reaction will be strong enough to bring about this result in a given example cannot, in general, be foretold theoretic-

ally. On the other hand, the theory may still have a limited application in that, if the effect is observed experimentally in one case, it may be possible to say that it should occur *a fortiori* in certain others. The second difficulty arises in the determination of the position at which reaction will be completed. The point here is that the electron-sink will reduce the tendency to electrolytic dissociation, and therefore the mobility, of the anionotropic system produced in the first stage of the addition. Therefore, the cationic charge produced in the initial stage of the reaction may become bound by the associated anion in a way which does not lead to the normal statistical electron-distribution in the free cation; and in that event the actual addition product will not be that which is thermodynamically the most stable product. Once again, it is impossible theoretically to assess the precise constitutional condition necessary to bring about this result; nevertheless, assisted by observation, the theory may have some limited application, and it is possible at once to appreciate certain general relations, such as that vicinal addition may be relatively more prevalent in the cases (1*b* and 2*b*) now considered than in the corresponding cases (1*a* and 2*a*) in which no uniquely electron-absorbing group is a component part of the unsaturated system.

Case 1b. *Addition of Halogens to Conjugated Unsaturated Carboxylic Acids and Esters.*

Since the constitution of an addition product of chlorine or bromine does not alone indicate the order of entrance of the two parts of the addendum, a complete knowledge of the course of the reaction requires also the identification of the point of initial attack. Two methods have been used in order to make this diagnosis. The first, which is employed with success in one example only in this paper, consists simply in the use of the unsymmetrical halogen, iodine chloride (Ingold and Smith, J., 1931, 2742), the location of the iodine atom after addition marking the site of initiation of halogen attack. The second method, which we have applied rather more widely, employs the competition principle established by the experiments of Terry and Eichelberger and of Francis (*J. Amer. Chem. Soc.*, 1925, **47**, 1067, 2340. Compare Ingold and Smith, J., 1931, 2755), who have shown that the cation formed in the first stage of addition of a halogen can be caused to take up a foreign anion, such as the hydroxide ion, giving a product the constitution of which directly indicates the point of initial attack.

β-*Vinylacrylic Acid.*—As Farmer and Healey (J., 1927, 1060) and Muskat, Becker, and Lowenstein (*J. Amer. Chem. Soc.*, 1930, **52**, 326, 812) have shown, vinylacrylic acid yields a γδ-dichloride and a γδ-dibromide. Employing the Terry–Eichelberger–Francis principle, we have studied the action of chlorine and bromine on vinylacrylic acid in aqueous solution. In each case the main product was a halogenohydrin, which was shown by ozonolytic degradation to be a δ-halogeno-γ-hydroxy-compound. These halogenohydrins had properties identical with those of the halogenohydrins which Muskat and Hudson (*J. Amer. Chem. Soc.*, 1931, **53**, 3179) prepared by direct addition to vinylacrylic acid of the appropriate hypohalous acids, and arbitrarily (and, we consider, incorrectly) identified as γ-halogeno-δ-hydroxy-compounds. In these results one observes the disintegrating action of halogen attack on the conjugated system, and the vicinal location of the components of the addendum. Similar conditions (δ-initiation and γδ-orientation) would be expected to obtain in all butadiene-α-monocarboxylic acids, containing neither an unsaturated δ-substituent nor a second electron-attracting α- or γ-substituent. It might also be anticipated that any by-product should be characterised by α-initiation and, probably, αβ-orientation. Our experiments on the halogenation of vinylacrylic acid left us with the impression that a by-product is formed, although we were unable to determine its nature.

Sorbic Acid.—It has been shown by Auwers and Heyna (*Annalen*, 1923, **434**, 140) that the addition of bromine in inactive solvents to sorbic acid leads mainly to the γδ-dibromide. This result is now confirmed, and it is proved in addition that the αβ-dibromide is also formed in small amount. Furthermore, it is shown that the principal product of the addition of iodine monochloride is the γ-chloro-δ-iodo-compound. These results were obtained by our collaborator, Dr. H. G. Smith, and were recorded by him, and discussed

on the lines indicated above, in a thesis presented to the University of Leeds in 1929. Continuing the investigation concerning the point of initial attack of halogens, we have treated sorbic acid with chlorine in the presence of water, and have obtained as the main product a crystalline chlorohydrin, which is proved by oxidation to be the δ-chloro-γ-hydroxy-derivative. We imagine that this may be the substance which Bloomfield and Farmer (J., 1932, 2072) obtained in an impure form by the addition of hypochlorous acid to sorbic acid, and described as possessing so strong a tendency to reversible lactonisation that it was impossible to isolate either the hydroxy-acid free from its lactone, or the lactone free from its hydroxy-acid. On the other hand, when we used Bloomfield and Farmer's reagent we had no difficulty in obtaining as the main product the pure hydroxy-chloro-acid mentioned above, and this in our experience possesses little, if any, tendency to pass spontaneously into a lactone. It also combined readily with ozone, a reagent which left Bloomfield and Farmer's product largely unattacked. Similarly, the main product of the action of bromine on sorbic acid in the presence of water was shown to be the δ-bromo-γ-hydroxy-derivative, and the same compound was formed also by the direct addition of hypobromous acid. Evidently vinylacrylic and sorbic acids are consistent in behaviour : the attack of the halogen is mainly initiated in the δ-position and completed in the γ-position. A secondary reaction is expected, which should commence at the α- and terminate at the β-position, and it is consistent with this that an αβ-dibromide has been shown to arise in the addition of bromine to sorbic acid.

Cinnamylideneacetic Acid.—It has already been indicated that the regularities illustrated in the preceding two paragraphs are not expected to apply to vinylacrylic acids containing an unsaturated substituent (*i.e.*, an electron-distributing mechanism) attached to the δ-position. Such a substituent should tend to dissipate any δ-polarisation, and thus should handicap the reagent in its attempt to bring about a favourable polarisation, contrary to the forces uniting the conjugated system. It is, therefore, noteworthy that Hinrichsen and Triepel (*Annalen*, 1904, **336**, 221) were able to show that the principal product of the addition of one molecule of bromine to methyl cinnamylideneacetate is the αβ-dibromide. Thus the secondary addition of sorbic acid becomes the primary reaction in this example.

Cinnamylidenemalonic Acid.—The preceding discussion recognises the existence of a competition between the C_α- and the C_δ-carbon atom for the electrophilic reagent ; and the αβ-addition of bromine to cinnamylideneacetic acid shows that the influence of the carboxyl group in absorbing an electron-donating C_α-polarisation, and in thus deactivating C_α, is less effective than that of the phenyl group in dissipating the C_δ-polarisation, and thus deactivating C_δ; for the α-position in cinnamylideneacetic acid is the more reactive. Obviously the introduction of a further electron-absorbing substituent into the δ-position would merely intensify this result ; on the other hand, the introduction of such an additional electron-absorbing group into the α-position might evidently invert the relative reactivities of the α- and δ-positions, and it is therefore highly significant that Hinrichsen and Triepel (*loc. cit.*) succeeded in demonstrating the γδ-addition of bromine to methyl cinnamylidenemalonate.

Muconic Acid.—Chandrasena and Ingold (J., 1922, **121**, 1307) showed that the product of the addition of one molecule of bromine to ethyl muconate was the αβ-dibromide, but the proof of this rested on the elucidation of a somewhat complicated oxidative degradation. We have now confirmed the orientation of this dibromide by a simple method based on ozonolysis. We have also prepared the addition product of ethyl muconate with iodine monochloride ; but we have not yet succeeded in orienting this derivative, for, although α-initiation is considered the most probable mode of reaction, the case is one of those in which the site of the initial attack cannot with certainty be deduced from theoretical considerations.

Case 2b. Addition of Hydrogen Halides to Conjugated Unsaturated Carboxylic Acids and Esters.

This case is simpler than the one considered in the foregoing section, because we may be sure that the hydrogen atom of the polarised addendum will form the spearhead of the reagent's attack, and will enter the system by co-ordination with the carbonyl oxygen

G

atom. In the hydrohalide finally produced this hydrogen atom will therefore be found to be attached to the α-carbon atom of the butadiene system. On the other hand, there remains a certain ambiguity concerning the point at which addition will be completed; for although, as the result of α-attack, the carboxyl group becomes separated from the anionotropic system, it is impossible to know whether the orientation of the halogen atom in this system will be determined before or after the prototropic rearrangement. Thus, in a case such as β-vinylacrylic acid all that can be stated on theoretical grounds is that it should form either an α-hydro-β-halide or an α-hydro-δ-halide. On the other hand, in an example such as cinnamylideneacetic acid the presence of a strongly electron-releasing δ-substituent eliminates any such uncertainty, and the addition product definitely should possess the constitution of an α-hydro-β-halide.
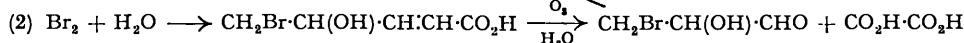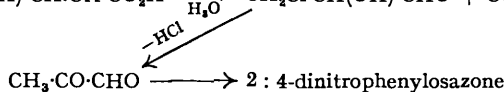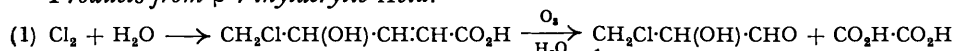
β-*Vinylacrylic and Sorbic Acids.*—These acids belong to the same theoretical category. We were unable to obtain a monohydrobromide of either, but succeeded in preparing a monohydrochloride of sorbic acid. It was proved to be the α-hydro-δ-chloride.

Cinnamylidene-acetic and -malonic Acids.—These acids also are theoretically in an identical case. The monohydrobromide of the former was prepared by Riiber (*Ber.*, 1911, **44**, 2976), who proved the residual double linking to be in the γδ-position; this is consistent with the theoretical requirement that the compound should be the α-hydro-β-bromide. Similarly Hinrichsen and Triepel (*loc. cit.*) obtained a monohydrobromide of methyl cinnamylidenemalonate, and showed it to be the theoretically required α-hydro-β-bromide.

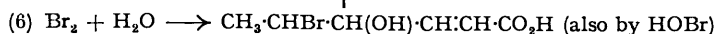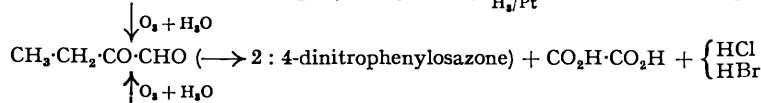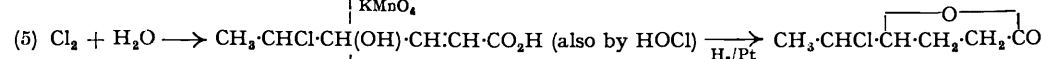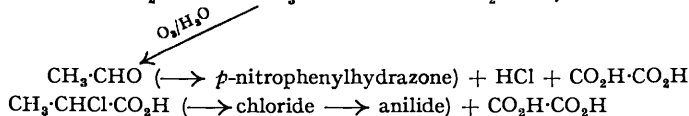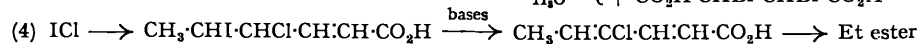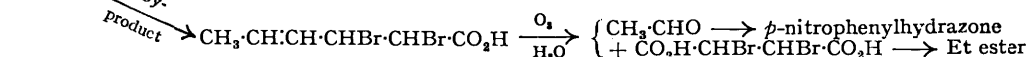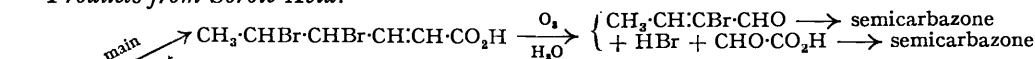*Proof of Structure of the Various Addition Products of Halogens and Halogen Acids to β-Vinylacrylic and Sorbic Acids and to Ethyl Muconate.*
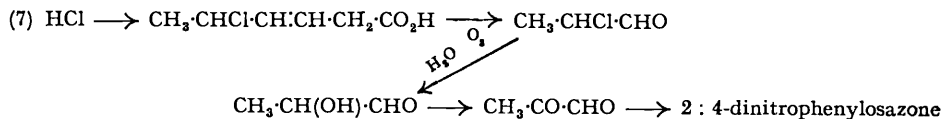
The various proofs of constitution adduced in the experimental section are summarised in the following scheme of formulæ. The structures of the main dibromide of sorbic acid, and of the dibromide of ethyl muconate, were known prior to the present work (Auwers and Heyna, *loc. cit.*; Chandrasena and Ingold, *loc. cit.*).

Products from β-Vinylacrylic Acid.

(1) $Cl_2 + H_2O \longrightarrow CH_2Cl\cdot CH(OH)\cdot CH\!:\!CH\cdot CO_2H \xrightarrow[H_2O]{O_3} CH_2Cl\cdot CH(OH)\cdot CHO + CO_2H\cdot CO_2H$

$\xrightarrow{-HCl}$

$CH_3\cdot CO\cdot CHO \longrightarrow 2:4\text{-dinitrophenylosazone}$

$\xrightarrow{-HBr}$

(2) $Br_2 + H_2O \longrightarrow CH_2Br\cdot CH(OH)\cdot CH\!:\!CH\cdot CO_2H \xrightarrow[H_2O]{O_3} CH_2Br\cdot CH(OH)\cdot CHO + CO_2H\cdot CO_2H$

Products from Sorbic Acid.

(3) Br_2
main product $\nearrow CH_3\cdot CHBr\cdot CHBr\cdot CH\!:\!CH\cdot CO_2H \xrightarrow[H_2O]{O_3} \begin{cases} CH_3\cdot CH\!:\!CBr\cdot CHO \longrightarrow \text{semicarbazone} \\ + HBr + CHO\cdot CO_2H \longrightarrow \text{semicarbazone} \end{cases}$

by-product $\searrow CH_3\cdot CH\!:\!CH\cdot CHBr\cdot CHBr\cdot CO_2H \xrightarrow[H_2O]{O_3} \begin{cases} CH_3\cdot CHO \longrightarrow p\text{-nitrophenylhydrazone} \\ + CO_2H\cdot CHBr\cdot CHBr\cdot CO_2H \longrightarrow \text{Et ester} \end{cases}$

(4) $ICl \longrightarrow CH_3\cdot CHI\cdot CHCl\cdot CH\!:\!CH\cdot CO_2H \xrightarrow{\text{bases}} CH_3\cdot CH\!:\!CCl\cdot CH\!:\!CH\cdot CO_2H \longrightarrow \text{Et ester}$

$\xrightarrow{O_3/H_2O}$

$CH_3\cdot CHO \;(\longrightarrow p\text{-nitrophenylhydrazone}) + HCl + CO_2H\cdot CO_2H$

$CH_3\cdot CHCl\cdot CO_2H \;(\longrightarrow \text{chloride} \longrightarrow \text{anilide}) + CO_2H\cdot CO_2H$

$\uparrow \text{KMnO}_4$

(5) $Cl_2 + H_2O \longrightarrow CH_3\cdot CHCl\cdot CH(OH)\cdot CH\!:\!CH\cdot CO_2H \text{ (also by HOCl)} \xrightarrow{H_2/Pt} CH_3\cdot CHCl\cdot \overset{\overline{O}}{CH\cdot CH_2\cdot CH_2\cdot CO}$

$\downarrow O_3 + H_2O$

$CH_3\cdot CH_2\cdot CO\cdot CHO \;(\longrightarrow 2:4\text{-dinitrophenylosazone}) + CO_2H\cdot CO_2H + \begin{cases} HCl \\ HBr \end{cases}$

$\uparrow O_3 + H_2O$

(6) $Br_2 + H_2O \longrightarrow CH_3\cdot CHBr\cdot CH(OH)\cdot CH\!:\!CH\cdot CO_2H \text{ (also by HOBr)}$

(7) $HCl \longrightarrow CH_3 \cdot CHCl \cdot CH\!:\!CH \cdot CH_2 \cdot CO_2H \xrightarrow[\substack{H_2O}]{O_3} CH_3 \cdot CHCl \cdot CHO$

$$CH_3 \cdot CH(OH) \cdot CHO \longrightarrow CH_3 \cdot CO \cdot CHO \longrightarrow 2 : 4\text{-dinitrophenylosazone}$$

Products from Ethyl Muconate.

(8) $Br_2 \longrightarrow CO_2Et \cdot CHBr \cdot CHBr \cdot CH\!:\!CH \cdot CO_2Et \xrightarrow[H_2O]{O_3} CO_2Et \cdot CH\!:\!CBr \cdot CHO$ ($\longrightarrow$ 2 : 4-dinitrophenyl-

osazone) $+ CO_2H \cdot CHBr \cdot CHBr \cdot CO_2H$ ($\longrightarrow$ Et ester) $+ CO_2H \cdot CO_2H + HBr$

(9) $ICl \longrightarrow CO_2Et \cdot CHI \cdot CHCl \cdot CH\!:\!CH \cdot CO_2Et$ (or, less probably, $CO_2Et \cdot CHCl \cdot CHI \cdot CH\!:\!CH \cdot CO_2Et$)

$\downarrow Na_2CO_3 \qquad\qquad \searrow O_3$

$CO_2Et \cdot CH\!:\!CH \cdot CH\!:\!CH \cdot CO_2Et \xrightarrow{H_2O} CO_2H \cdot CO_2H + I_2$, etc.
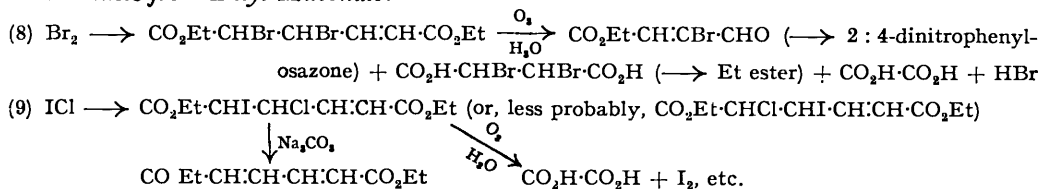
EXPERIMENTAL.

(1) *Action of Chlorine on β-Vinylacrylic Acid in the Presence of Water.*—The acid was prepared in the manner described by Burton and Ingold (J., 1929, 2028), and crystallised from ether–ligroin (1 : 3 by vol.) between the b. p. and 0°. A solution of the acid (15 g.) in water (1 l.) at 50° was treated with a solution of chlorine (10·6 g.) in water (1·5 l.). The solution was concentrated by evaporation, extracted with chloroform to remove unchanged vinylacrylic acid, saturated with sodium chloride, and extracted with ether. The *δ-chloro-γ-hydroxy-Δ^a-pentenoic acid* thus obtained was washed with ligroin and crystallised from chloroform–benzene, from which it separated in colourless needles, m. p. 73—74° (yield, after purification, 60%) (Found : Cl, 23·7. $C_5H_7O_3Cl$ requires Cl, 23·6%). By treating an ethereal solution of β-vinylacrylic acid with an aqueous solution of hypochlorous acid (2 mols.), a *dichlorodihydroxyvaleric acid* was produced, which, after crystallisation from ether, had m. p. 166° (Found : C, 29·9; H, 4·0; Cl, 34·2. $C_5H_8O_4Cl_2$ requires C, 29·6; H, 3·9; Cl, 34·9%). Muskat and Hudson (*loc. cit.*) record the m. p. of this compound as 143°. The monochlorohydrin on treatment with ozonised oxygen in ethyl acetate solution yielded a product which on decomposition with boiling water gave hydrochloric and oxalic acids and a volatile substance; this, carried by means of a stream of air into a solution of 2 : 4-dinitrophenylhydrazine in 2*N*-hydrochloric acid, gave *methylglyoxal 2 : 4-dinitrophenylosazone*, which, after crystallisation from acetic anhydride, had m. p. 299—300° (decomp.), and was identified by analysis (Found : C, 41·8; H, 2·8; N, 25·9. $C_{15}H_{12}O_8N_8$ requires C, 41·7; H, 2·8; N, 25·9%), and by comparison with a specimen prepared from a sample of methylglyoxal kindly supplied by Professor H. L. Riley.

(2) *Action of Bromine on β-Vinylacrylic Acid in the Presence of Water.*—The preparation of *δ-bromo-γ-hydroxy-Δ^a-pentenoic acid* was carried out by the method described in the case of its chlorine analogue, except that the extraction with chloroform was omitted. The yield was 70%, and the product, crystallised from benzene, had m. p. 92—93° (Found : C, 30·9; H, 3·7; Br, 40·7. $C_5H_7O_3Br$ requires C, 30·8; H, 3·6; Br, 41·0%). The same compound was obtained by the action of aqueous hypobromous acid on ethereal β-vinylacrylic acid. The ozonolysis of the addition product proceeded just as in the previous case, and in particular the methylglyoxal 2 : 4-dinitrophenylosazone was again identified by analysis (Found : C, 41·7; H, 2·8; N, 25·9%), and by direct comparison.

(3) *Addition of Bromine to Sorbic Acid* (with H. G. Smith).—The addition of bromine to sorbic acid in carbon disulphide solution proceeds as Auwers and Heyna have described, and, with this solvent, and likewise with chloroform and with hexane as solvents, the main product was the crystalline γδ-dibromide, which was formed together with a liquid by-product. The quantity of this liquid was considerable when the above-mentioned solvents were used, but was much less when the bromination was carried out with bromine in glacial acetic acid, or with quinolinium tribromide in the same solvent, the temperature in all cases being that of the room. This liquid product was examined by Farmer and Healey (J., 1927, 1060), who came to the conclusion that it contained nothing but the γδ-dibromide; we show below that it contains the αβ-dibromide also. First, concerning Auwers and Heyna's dibromide, we also ozonised it and obtained not only α-bromocrotonaldehyde, but also the complementary product, glyoxylic acid. In this experiment the compound was treated with a stream of ozonised oxygen in the presence of chloroform and water, and the two layers were separated and evaporated. The residue from the chloroform was boiled with a concentrated aqueous solution of potassium acetate, and the α-bromocrotonaldehyde was separated by distillation in steam,

and converted into its semicarbazone (Found : C, 29·2; H, 3·8. Calc. : C, 29·1; H, 3·9%). The residue from the aqueous layer yielded crystals of oxalic acid together with a syrup from which glyoxylic acid semicarbazone was prepared (Found : C, 28·2; H, 3·8. Calc. : C, 27·5; H, 3·8%). The liquid sorbic acid bromide contained a certain amount of the tetrabromide (easily isolated after ozonolytic destruction of the unsaturated substances), and it was necessary to remove this before proceeding with the search for isomeric dibromides. To this end the liquid bromide fraction was esterified by passing a stream of ethyl alcohol vapour through its solution in 5% alcoholic sulphuric acid, which was maintained for 3 hours at its boiling point, and at approximately constant volume under a short fractionating column. The alcoholic solution was poured into water, and the esters were collected in ether, washed with sodium hydrogen carbonate solution and with water, dried with sodium sulphate, and fractionated. The whole of the dibromides were contained in a fraction which was collected at 135—155°/20 mm., and boiled, for the most part, near the middle of this range (Found : C, 31·7; H, 4·1. $C_8H_{12}O_2Br_2$ requires C, 32·0; H, 4·0%). The alkaline washings from the esterification yielded on acidification, sorbic acid tetrabromide. The ethyl sorbate dibromide was ozonised as described above and, after removal of most of the chloroform, the product was oxidised with hydrogen peroxide, the volatile products were passed through *p*-nitrophenylhydrazine solution, and the *p*-nitrophenylhydrazone of acetaldehyde (Found : C, 53·9; H, 5·3; N, 23·5. Calc. : C, 53·6; H, 5·1; N, 23·5%) was thus obtained in quantity. The odour and lachrymatory effect of α-bromocrotonaldehyde were noticed. The product was separated by means of ether and aqueous sodium carbonate into a small neutral and a large acid fraction, and the latter was boiled for a short time with concentrated hydrochloric acid. The solution thus obtained was shown to contain oxalic acid, but it also yielded a crystalline acid, which, after several crystallisations from water, sublimed at 250° and consisted of pure dibromosuccinic acid (Found : C, 17·8; H, 1·6; Br, 57·8. Calc. : C, 17·4; H, 1·5; Br, 57·9%). The identity of this acid was confirmed by the preparation of its ethyl ester, m. p. 67°, which was directly compared with a specimen of known origin.

(4) *Addition of Iodine Monochloride to Sorbic Acid* (with H. G. Smith).—Sorbic acid and freshly distilled iodine monochloride were allowed to interact in glacial acetic acid at room temperature. After the greater part of the acetic acid had been removed in an evacuated desiccator over potassium hydroxide, vigorous stirring caused the formation of a thick paste of crystals. The *γ-chloro-δ-iodo-β-ethylacrylic acid* thus obtained, after crystallisation from light petroleum, had m. p. 88° (Found : C, 26·7; H, 3·1. $C_6H_8O_2ClI$ requires C, 26·2; H, 2·9%). The by-product was a liquid which has not yet been examined. We were not able to remove the elements of hydrogen iodide quantitatively from the above iodochloride, and on treatment with weak bases it invariably yielded a mixture of sorbic acid and a chlorosorbic acid, from which the latter could only be separated with difficulty by direct crystallisation. Thus the iodochloride was boiled for ½ hour with ethyl-alcoholic potassium acetate, or for a few minutes with excess of pyridine, or was left for some hours in cold pyridine solution; in all cases the mixture was poured into dilute hydrochloric acid and extracted with ether, and an acid product was obtained, m. p. 90—110°. This was esterified with ethyl alcohol by the method described in the preceding section in connexion with the purification of liquid sorbic acid dibromide. The esters on distillation split up into two distinct fractions, the first of which was ethyl sorbate, and the second, b. p. 105—110°/15 mm., was *ethyl γ-chlorosorbate*, which solidified on cooling. Crystallised from aqueous alcohol, the ester formed flattened prisms, m. p. 31—32° (Found : C, 55·0; H, 6·4. $C_8H_{11}O_2Cl$ requires C, 55·2; H, 6·3%). On boiling for 2 hours with 20% hydrochloric acid the ester gave *γ-chlorosorbic acid* (compare Riedel and Straube, *Annalen,* 1909, **367,** 51), m. p. 117° (Found : C, 49·5; H, 4·5. Calc. : C, 49·1; H, 4·8%). The constitution of the acid was confirmed by ozonolysis; the ozonide, formed in chloroform solution and decomposed by boiling with water, yielded acetaldehyde, which was identified by conversion into its *p*-nitrophenylhydrazone, and acetic, hydrochloric, and oxalic acids.

(5) *Action of Chlorine on Sorbic Acid in the Presence of Water.*—A solution of sorbic acid (10 g.) in water (2 l.) at about 85° was mixed with a solution of chlorine (7 g.) in water (1650 c.c.). After concentration, and removal of a small amount of unchanged sorbic acid which separated during this process, the product was extracted with ether and crystallised twice from chloroform. It had m. p. 97°, and the yield was about 70%, allowance being made for the recovered sorbic acid (Found : C, 43·8; H, 5·4; Cl, 21·8. $C_6H_9O_3Cl$ requires C, 43·8; H, 5·5; Cl, 21·6%). The same compound was obtained by treating an ethereal solution of sorbic acid with an aqueous solution of hypochlorous acid prepared as recommended by Bloomfield and

Farmer. The product, extracted with ether, was purified by solution in a small amount of water, and subsequent crystallisation from chloroform (m. p. and mixed m. p. 97°). This substance is shown to be δ-*chloro-γ-hydroxy-Δ^α-hexenoic acid*. An impure substance, claimed to be a mixture of this acid and its lactone, was obtained by Bloomfield and Farmer (*loc. cit.*) by the use of hypochlorous acid, but, on account of the marked difference of properties between our product and theirs, identity could not be assumed, and we have therefore placed the constitution of our compound on an independent experimental basis. This was done in the first instance by the use of ozone, a reagent which left Bloomfield and Farmer's product largely unattacked. The ozonide was formed in ethyl acetate solution, and decomposed in the usual manner by boiling with water. The volatile products were drawn from the hot solution through a solution of 2 : 4-dinitrophenylhydrazine in $2N$-hydrochloric acid, and in this way a precipitate was obtained which on crystallisation from acetic anhydride gave *ethylglyoxal 2 : 4-dinitrophenylosazone*, m. p. 247° (Found : C, 43·0; H, 3·2; N, 24·8. $C_{16}H_{14}O_8N_8$ requires C, 43·0; H, 3·1; N, 25·1%), together with its lower homologue [m. p. and mixed m. p. 294° (decomp.)] (Found : C, 41·7; H, 2·8; N, 25·7. Calc. : C, 41·7; H, 2·8; N, 25·9%). The residual aqueous solution was shown to contain hydrochloric acid and oxalic acid (m. p. and mixed m. p.). An independent proof of constitution was obtained by combining the results of an oxidation by permanganate with those of a catalytic reduction. A neutral solution of the chlorohydroxy-acid in sodium hydrogen carbonate was treated with magnesium sulphate, and a sufficient amount of 3% permanganate solution to supply 6 atoms of oxygen. Oxidation was allowed to proceed in the cold, and, after removal of the manganese oxides, the solution without concentration was extracted with a large volume of ether. The product was partly crystalline and the crystals were identified as oxalic acid. The liquid portion had b. p. 180—186° and consisted essentially of α-chloropropionic acid, the anilide, m. p. and mixed m. p. 92°, of which was obtained by successive treatment with thionyl chloride and aniline. The reason for conducting this oxidation in neutral solution was that in the absence of magnesium sulphate the alkali developed during oxidation removes chlorine from the oxidation product, as was shown by quantitative estimates of the amount of chloride ion produced. The reduction of the chloro-hydroxy-acid (30 g.) was effected in aqueous solution (300 c.c.) by means of hydrogen (4 l.) at atmospheric pressure in the presence of Adams's platinum oxide catalyst. The δ-chloro-γ-hexolactone, isolated by extraction with ether, formed an oil, b. p. 130—132°/16 mm., 243°/756 mm. (Found : C, 49·0; H, 6·2. Calc. : C, 48·5; H, 6·1%), which on being cooled set to a mass of crystals, m. p. *ca.* 10°. The lactone was slowly soluble in cold aqueous sodium hydroxide, and it slowly decolorised cold permanganate solution.

(6) *Action of Bromine on Sorbic Acid in the Presence of Water.*—A solution of sorbic acid (10 g.) in water (2 l.) at about 85° was treated with a solution of bromine (18 g.) in cold water (1 l.). The solution was concentrated, filtered from a small amount of sorbic acid, saturated with sodium chloride, and extracted with ether, and a further small amount of sorbic acid was removed from the reaction product by redissolving it in a small amount of water and re-extracting it with ether. The main product was δ-*bromo-γ-hydroxy-Δ^α-hexenoic acid*, which crystallised from chloroform in small hard prisms, m. p. 110° (Found : C, 34·6; H, 4·3; Br, 37·8. $C_6H_9O_3Br$ requires C, 34·5; H, 4·3; Br, 38·2%). An oily by-product was also obtained, which was esterified with methyl alcohol, and the esters were separated by distillation into two principal fractions. The less volatile of these had b. p. 118°/0·5 mm., and on analysis gave figures agreeing with those required for a methyl bromohydroxyhexenoate (Found : C, 37·3; H, 4·8. Calc. : C, 37·6; H, 4·9%). The more volatile fraction, b. p. 148—150°/0·5 mm., yielded a solid, which crystallised from chloroform in colourless needles, m. p. 154—155° [Found : C, 35·4; H, 4·7; Br, 33·0; M (Rast), 250. $C_7H_{11}O_4Br$ requires C, 35·1; H, 4·6; Br, 33·4%; M, 239]. When an ethereal solution of sorbic acid was treated with an aqueous solution of hypobromous acid, the product, isolated as in the corresponding experiment with hypochlorous acid, proved to be identical with the bromohydroxyhexenoic acid described above. This substance was ozonised precisely as described for the corresponding chloro-compound in the preceding section; the identified products were ethylglyoxal, which was isolated as its 2 : 4-dinitrophenylosazone, and oxalic acid. Brief reference may be made to two further experiments. Bromine was added to methyl sorbate in suspension in a large amount of water. The product, b. p. 107—111°/0·5 mm., consisted principally of methyl γδ-dibromo-Δ^α-hexenoate, since on ozonolysis it gave α-bromocrotonaldehyde, which was isolated as its 2 : 4-*dinitrophenylhydrazone*. This substance crystallised from ethyl acetate in deep red needles, m. p. 220° (decomp.) (Found : C, 36·8, 36·7; H, 2·9, 2·7; N, 15·9, 16·3; Br, 24·4. $C_{10}H_9O_4N_4Br$ requires C, 36·5; H, 2·7; N, 17·0; Br, 24·3%). Bromine was added to sorbic acid dissolved in absolute ethyl alcohol, the solution

was neutralised with dilute ethyl-alcoholic potassium hydroxide, and evaporated until a test portion gave a crystalline precipitate on acidification. The whole solution was then poured into dilute hydrochloric acid; the precipitate obtained crystallised from benzene in needles, m. p. 135°, and was shown to be γ-bromosorbic acid (Found : C, 38·2; H, 3·7; Br, 41·4. Calc. : C, 37·7; H, 3·7; Br, 41·9%), an acid for which Farmer and Healey (*loc. cit.*) record m. p. 140°. The same substance, m. p. 135°, was obtained by treating γδ-dibromo-Δ^α-hexenoic acid with dilute ethyl-alcoholic potassium hydroxide, and the constitution assigned to it was confirmed by ozonolysis, the products of which were acetaldehyde, isolated as its 2 : 4-dinitrophenyl-hydrazone, and oxalic acid.

In the course of these experiments acetaldehyde 2 : 4-dinitrophenylhydrazone was obtained in two modifications possibly identical with the two recently described by Bryant (*J. Amer. Chem. Soc.*, 1933, **55**, 3201), although this author does not record the m. p. of his less stable form. Our less stable modification was precipitated in alcoholic sulphuric acid, and could be purified by crystallisation from benzene without change. It formed orange-red needles, m. p. 146° (Found : C, 43·4; H, 3·6. $C_8H_8O_4N_4$ requires C, 42·9; H, 3·6%), and when crystallised from ethyl alcohol reverted to the more stable modification, which forms yellow plates, m. p. 162°.

(7) *Addition of Hydrogen Chloride to Sorbic Acid.*—Hydrogen chloride (26 g.), dried by passage over phosphoric oxide, was condensed in a thick-walled glass tube, cooled in liquid air. Sorbic acid (8 g.) was added, and the tube was closed, kept at the ordinary temperature for several days, and then opened in order to allow the excess of hydrogen chloride to escape. The product, an oil which decomposed on distillation, consisted largely at least of δ-chloro-Δ^β-hexenoic acid (Found : Cl, 21·7. $C_6H_9O_2Cl$ requires Cl, 23·9%), since its ozonide, produced in chloroform solution, gave, when decomposed with water, methylglyoxal, which was isolated in the form of its 2 : 4-dinitrophenylosazone, m. p. 293—294° (decomp.) (Found : C, 41·8; H, 2·8; N, 26·0%).

(8) *Addition of Bromine to Ethyl Muconate.*—The dibromide, m. p. 81° (Found : C, 33·9; H, 4·1; Br, 44·3. Calc. : C, 33·5; H, 3·9; Br, 44·7%), was treated with ozonised oxygen in chloroform solution, and the ozonide, after removal of the solvent, was decomposed with water. The neutral product contained ethyl β-bromo-β-aldehydoacrylate, the 2 : 4-*dinitrophenyl-hydrazone* of which separated from ethyl acetate in yellow plates, m. p. 193—194° (Found : C, 37·1; H, 3·0; Br, 20·4. $C_{12}H_{11}O_6N_4Br$ requires C, 37·2; H, 2·8; Br, 20·6%). The acid fraction contained oxalic acid, which was removed as its calcium salt, and also a soluble crystalline acid, which sublimed at 250—260°. On esterification with ethyl alcohol in the presence of sulphuric acid this yielded a crystalline ester, which was identified as ethyl *i*-dibromosuccinate, m. p. and mixed m. p. 58° (Found : C, 29·1; H, 3·7. Calc. : C, 28·9; H, 3·6%).

(9) *Addition of Iodine Monochloride to Ethyl Muconate* (with H. G. Smith).—A solution of ethyl muconate (6 g.) and freshly distilled iodine monochloride (6 g.) in glacial acetic acid (100 c.c.) was kept at room temperature over-night, and the solution was then poured into water and extracted with ether. The extract, washed with dilute sodium carbonate solution, sodium thiosulphate and water, yielded a solid product, which, after crystallisation from light petroleum, had m. p. 68°. This compound is believed to be *ethyl β-chloro-α-iodo-Δ^γ-dihydromuconate* (Found : C, 33·2; H, 3·7. $C_{10}H_{14}O_4ClI$ requires C, 33·3; H, 3·9%), because, on warming with very dilute sodium carbonate solution, it yielded ethyl muconate, and, on boiling with alcoholic potassium hydroxide, gave muconic acid. It is thought that an addition product containing chlorine in the α-position would yield a chloro-muconic ester or acid under these conditions. When a solution of the iodochloride in chloroform was treated with a stream of ozonised oxygen, a slow precipitation of muconic acid was observed. On boiling the ozonides with water, iodine was liberated, but the only other recognised product was oxalic acid.

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