

196. *Reactions of Olefinic Compounds. Part II. The Orienting Influence of the Carboxyl Group.*

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IN Part I (J., 1932, 2062) Bloomfield and Farmer showed that the orientation of the addition products obtained by the interaction of simple Δ^α -, Δ^β -, and Δ^γ -ethylenic acids with aqueous hypochlorous acid was essentially that which would be expected if the carboxyl groups exerted little or no directive influence. Thus in the system $R^1\dot{C}_1\dot{C}_2R^2$, the formation of the products $R^1\dot{C}_1Cl\dot{C}_2(OH)R^2$ and $R^1\dot{C}_1(OH)\dot{C}_2ClR^2$ was determined by the nature of the hydrocarbon systems present in the groups R^1 and R^2 , the result being apparently little affected by the carboxyl group in such groups as $\cdot CH_2\cdot CH_2\cdot CO_2H$ and $\cdot CH_2\cdot CO_2H$ or even when occurring alone in direct attachment to one of the ethylenic carbon atoms. This result, however, applies only to the particular addendum and to the conditions of reaction employed; with other addenda and under other conditions of reaction the orienting influence of the carboxyl group may be of considerable importance. Moreover, even in the cases cited, only specially devised comparisons could show whether the carboxyl group is *entirely* without orienting influence.

In all additions to ethylene and to other symmetrical olefins the tendencies for polarization to occur in the reverse senses $>\overset{\delta+}{C}_1\overset{\delta-}{C}_2<$ and $>\overset{\delta-}{C}_1\overset{\delta+}{C}_2<$ are presumably equal; in additions to unsymmetrical systems ($R^1\dot{C}_1\dot{C}_2R^2$), on the other hand, the tendencies are unequal and are governed by the nature of R^1 and R^2 .* How potent the orienting influence of alkyl or aryl groups attached to an ethylenic centre can be is shown by all observations which have so far been made, and this is in sharp contrast to the corresponding behaviour displayed in the addition of hydrogen bromide to conjugated diene-acids. In the latter type of additivity all the available evidence points to exclusive $\alpha\beta$ -addition, the inherent

* This takes no account of the part played by the solvent or medium in modifying or transmitting the influence of the groups, or of the direct or indirect influence of catalysts on the additive process.

ability of the addendum to add to an ethylenic centre *per se* being suppressed by the occurrence of a specialised additive mechanism, *viz.*, the overwhelming tendency for the hydrogen component of the addendum to become attached to the carboxylic oxygen atom, so enabling addition to occur at the terminals of the conjugated system $\cdot\text{CH}:\text{CH}:\text{C}:\text{O}\cdot$ * But even with addenda such as hypochlorous acid and iodine chloride, the fundamental ability of which to add at an ethylenic centre is quite unaffected by any attraction of the carbonyl oxygen atom for one of the addendal components, the orienting influence of the carboxyl group as exercised in determining the polarisations $>\overset{\delta+}{\text{C}}_1:\overset{\delta-}{\text{C}}_2<$ and $>\overset{\delta-}{\text{C}}_1:\overset{\delta+}{\text{C}}_2<$ is not necessarily negligible: on the contrary, our results for hypochlorous acid show that this influence may be quite definite and specific in the case of Δ^α -unsaturated acids, but it is markedly affected by the condition—free (that is to say, presumably, ionisable) or esterified (non-ionisable)—of the carboxyl group, and may apparently be completely outweighed by the influence due to a large alkyl group attached to the β -carbon atom, as is indicated by the orientation figures previously quoted (Part I) for Δ^α -hexenoic acid, $\text{Pr}^\alpha\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$.

If it be assumed that the relative degree of formation of positionally isomeric addition products furnishes a direct measure of ethylenic polarisability in opposite senses under the conditions of experiment, it is possible to gain some idea of the carboxylic influence. Thus if the introduction of a carboxyl group in *s*-dimethylethylene (I) destroys the tendency for the addendum to add to equal extents in opposite directions, then the departure from equality (*i.e.*, 50% orientation) in one direction or the other affords a measure of the carboxylic influence. In the case of tiglic acid (II) this departure amounts to somewhat

$\text{Me}\cdot\text{CH}=\text{CHMe}$ $\text{Cl}\text{---}\text{OH}$ 50% $\text{OH}\text{---}\text{Cl}$ 50% (I.)	$\text{Me}\cdot\text{CH}=\text{CMe}\cdot\text{CO}_2\text{H}$ $\text{Cl}\text{---}\text{OH}$ 62% $\text{OH}\text{---}\text{Cl}$ 38% (II.)	$\text{CH}_2=\text{CMe}\cdot\text{CO}_2\text{H}$ $\text{Cl}\text{---}\text{OH}$ 90% $\text{OH}\text{---}\text{Cl}$ 10% (III.)	$\text{Me}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$ $\text{Cl}\text{---}\text{OH}$ 26% $\text{OH}\text{---}\text{Cl}$ 74% (IV.)
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over 10%, the carboxylic influence being exercised in the direction of depressing the negative polarisation of the adjacent carbon atom and correspondingly enhancing that of the more remote.

It is not then surprising to find that in passing from α -methylacrylic acid (III) to crotonic acid (IV),† whereby only the position of the carboxyl group in the carbon chain is altered, the proportion of the major addition product falls by nearly 20%; for in the former acid the alkyl and the carboxyl group co-operate in bestowing a negative polarity on the β -carbon atom, whilst in the latter they work in opposition.

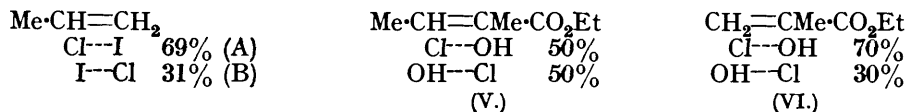
No exact figures can be quoted for hypochlorous acid addition to the propylene system itself,‡ but Ingold and Smith (J., 1931, 2742) have recorded the following figures for the analogous iodine chloride addition, effected in dilute hydrochloric acid. Accepting these values, it is then apparent that the introduction of a carboxyl group to form α -methylacrylic acid increases the orientation in the direction (A) (the direction to be expected) by about 20% (see above). Clearly then no constant figure representing the usual orienting

* The determination of the constitution of the hydrobromides of sorbic acid and its homologues is unusually difficult owing to the instability of these compounds and, although recent investigations by Mr. M. Brent have disclosed no example of $\gamma\delta$ -addition, the orientation data are too fragmentary in a quantitative sense, and the conditions of reaction so far employed in the formation of the hydrobromides (dry hydrogen bromide in a chloroform medium) too restricted, to permit of certainty as to the entire non-formation of $\gamma\delta$ -products.

† Melikoff (*Ber.*, 1882, **15**, 2586; 1883, **16**, 1268; *Annalen*, 1886, **234**, 197; 1890, **257**, 116; 1891, **266**, 358; *J. pr. Chem.*, 1900, **61**, 555) has stated that crotonic, *isocrotonic*, tiglic, and angelic acids all yield positionally isomeric addition products, but only the formation of α -chloro- β -hydroxy-forms has been definitely shown in these examples.

‡ Although the well-known controversy between Markownikoff and Henry left little doubt as to the fact of the formation of isomeric chlorohydrins from propylene, the proportions of the isomerides remained undetermined. The literature, however, gives reason to believe that the proportion of the chlorohydrin $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ greatly exceeds that of its isomeride, as would be expected.

influence of the carboxyl group under the conditions of experiment here employed can be assigned.



The result obtained, however, on esterifying tiglic acid is striking. Tiglic ester (V) shows the same orientation as was assumed above for *s*-dimethylethylene, indicating that the carbethoxyl group has no *orienting* influence; and this conclusion is supported by the orientation figures for α -methylacrylic ester (VI), which are practically identical with Ingold and Smith's figures for propylene (see above). Now, although the quantitative determination of orientation in the case of tiglic and α -methylacrylic esters is much more difficult and likely to be less accurate than in the case of the corresponding acids, there is nevertheless strong indication that the orienting influence of the carboxyl group is due entirely to the free charge on the organic anion $\text{R}^1\dot{\text{C}}:\text{CR}^2\cdot\text{CO}\cdot\text{O}^\ominus$ and is not directly connected with carbonyl unsaturation or the direction of the dipoles present in the carboxyl and the carbethoxyl group. This appears the more probable since the orientation figures for sodium tiglate (VII) (an addition which proceeds very rapidly) show a considerably enhanced proportion of the β -chloro- α -hydroxy-product. Probably the organic anion $\text{R}^1\dot{\text{C}}:\text{CR}^2\cdot\text{CO}_2^\ominus$



suffers addition preferentially to the undissociated acid, since it is always found that the esters yield chlorohydrins much more slowly than do the corresponding free acids. It is not possible to employ hypochlorous acid as an addendum in a non-aqueous medium (ethyl hypochlorite, which might serve as a substitute, is unreactive towards Δ^α -acids), so that any exact correlation between the ionising capacity of the acids and the orienting influence of the carboxyl group is out of the question for this reagent; interesting comparisons are, however, to be expected from experiments which have been initiated on the additivity of the nitriles and sodium salts of sundry ethylenic acids. With respect to the manner in which the orienting influence of the anionic charge is propagated—whether through the carbon chain or through the medium—there is nothing in the present experiments to indicate; but one notable characteristic of all the above-cited additions to Δ^α -acids which deserves attention is their great slowness compared with additions to Δ^β -acids and to Δ^γ -acids. A further interesting point encountered is that, although the orienting influence of the two alkyl groups present in $\beta\beta$ -dimethylacrylic acid (VIII) is precisely of the kind to be expected (enhancing the negative polarisation on the Δ^α -carbon atom), there appears in this example a well-marked tendency for the loss of the carboxyl group from the α -chloro- β -hydroxy-form of the chlorohydrin—a tendency which is an important feature of chlorohydrin formation from cinnamic acid and other phenylated acids, but which can be avoided to some extent by decreasing the concentration of the reactants.

EXPERIMENTAL.

Preparation of Hypochlorous Acid.—The reagent employed in all experiments was the aqueous solution of hypochlorous acid (containing calcium chloride) described by Bloomfield and Farmer (*loc. cit.*).

Addition to α -Methylacrylic Acid.—*iso*Butyric acid was brominated and esterified by the method of Auwers (*Ber.*, 1891, **24**, 2220), and the resulting ethyl α -bromoisobutyrate dehydrobrominated by heating with dimethylaniline (compare Sudborough and Davies, *J.*, 1909, **95**, 977). It was found advantageous to distil off the crude ethyl α -methylacrylate (b. p. below 125°) every 30 minutes, the distillate being collected in an ice-cold receiver and finally fractionated under reduced pressure (b. p. 63—65°/100 mm.). The reaction was complete after about 4 hours; two layers then appeared and frothing (red) commenced. Yield, 42%. The ester (15 g.) was

hydrolysed by adding it to an aqueous-alcoholic solution of caustic alkali (8 g. of sodium hydroxide or 11 g. of potassium hydroxide). After 20 hours the alcohol was removed, and the residual liquor made neutral to litmus, extracted with ether, and evaporated to dryness. The residue yielded, on extraction with hot alcohol, sodium (potassium) α -methylacrylate in pure condition.

The potassium salt (20 g.; 1 mol.) was dissolved in water, cooled to -5° , and cautiously acidified with dilute sulphuric acid (0.96 mol.). To the solution, aqueous hypochlorous acid (1 mol.) was slowly added with shaking. Addition was rapid and some heat was evolved. After standing over-night, the product was freed from calcium sulphate by filtration and then thoroughly extracted with ether. The dried ethereal liquor yielded, on evaporation, an oil which soon solidified. This crude solid, when crystallised from benzene, yielded (a) colourless prisms (8.75 g.), m. p. 109° , (b) crystals (0.95 g.), m. p. $75-90^\circ$, and (c) a syrupy liquid (0.9 g.). The crystalline acid, m. p. 109° (Melikoff, *loc. cit.*, gives 106°), was evidently a β -chloro- α -hydroxy-compound, since, like other β -chloro- α -hydroxy-derivatives of fatty acids encountered, and unlike the isomeric α -chloro- β -hydroxy-acids, it remained unreduced when, in the form of its sodium salt and in the presence of excess of carbon dioxide, it was submitted to the action of a large excess of 3% sodium amalgam. (This method of reduction, under standardised conditions of operation, afforded a convenient and reasonably accurate means of estimating the proportions of α - and β -chloro-compound in a mixture.) Its identity as β -chloro- α -hydroxyisobutyric acid (Found: Cl, 25.8. Calc. for $C_4H_7O_2Cl$: Cl, 25.6%) was fully confirmed by synthesis of the latter in the way described below. The lower-melting addition product (b) was a slightly impure form of the same acid, m. p. 109° , and from its crystallisation liquors was obtained a trace of syrupy liquid, which, together with the fraction (c), represented approximately 10% of the total addition product. This non-crystallisable acidic product, reducible with sodium amalgam under the standard conditions, must represent the chlorohydrin α -chloro- β -hydroxyisobutyric acid (Found: Cl, 26.1%), since the production of isolable stereoisomeric forms of either chlorohydrin is not theoretically to be expected.

Synthesis of β -Chloro- α -hydroxyisobutyric acid.—Fourneau and Tiffeneau (*Bull. Soc. chim.*, 1914, 15, 24) record the formation of a chlorohydroxybutyric acid from chloroacetone cyanohydrin which must necessarily be the β -chloro- α -hydroxy-compound. The m. p. of the acid is given as 110° , but no details of its synthesis are recorded. The following procedure was found to be successful. Chloroacetone (18.5 g.) (Kling, *Bull. Soc. chim.*, 1905, 33, 322) was gradually added to the greenish solution obtained by passing sulphur dioxide into a solution of sodium carbonate (29 g.). To the product, after 12 hours, was gradually added a concentrated solution of potassium cyanide (13 g.), and the whole after 1 hour was extracted with ether. The dried ethereal extract yielded the crude cyanohydrin, which, after the addition of 2 drops of concentrated sulphuric acid, distilled without decomposition (b. p. $107-108^\circ/20$ mm.). Yield, 15 g.

The cyanohydrin (5 g.) was hydrolysed by heating on a steam-bath for 10 hours with concentrated hydrochloric acid (10 c.c.). After cooling, sufficient water was added to dissolve the precipitated ammonium chloride, and the resulting solution in turn neutralised with sodium carbonate, extracted with ether, acidified, and re-extracted with ether. The second ethereal extract yielded an oily acid which soon solidified. This, on crystallisation from benzene, formed colourless prisms, m. p. 110° .

Addition to Ethyl α -Methylacrylate.—The carefully fractionated ester obtained above was sufficiently pure for use. The freshly distilled ester (16 g.), dissolved in 250 c.c. of ether, was treated at -5° with a solution containing 7.4 g. of hypochlorous acid. The mixture was vigorously shaken at intervals for about $1\frac{1}{2}$ hours; disappearance of the hypochlorous acid (much slower than in the case of the free acid) was then practically complete. After 24 hours, the ethereal layer was removed, and the aqueous layer re-extracted with ether. The combined ethereal extracts, dried with sodium sulphate, yielded on distillation much unchanged ester and a liquid chlorohydrin (8.5 g.), b. p. $77-90^\circ/17$ mm., which contained a more highly chlorinated product as impurity (Found: Cl, 26.3. $C_6H_{11}O_2Cl$ requires Cl, 21.3%). There is little doubt that the latter product was the corresponding dichloro-ester, thus present to the extent of 30%. The estimation of the components of the mixture could not be effected with any high degree of accuracy, since analysis showed that no really satisfactory separation of the more highly chlorinated material could be brought about by fractionation or by partial hydrolysis of the mixture. After, however, the mixture had been hydrolysed by long heating with dilute hydrochloric acid on a steam-bath (compare Fourneau and Tiffeneau, *Bull. Soc. chim.*, *loc. cit.*, p. 19), the amount of crystalline β -chloro- α -hydroxyisobutyric acid (see above) which separated when the hydrolysis product was taken up in hot benzene represented at least 70% of the total amount

of chlorohydrin produced during the addition, assuming for the purpose of calculation that the more highly chlorinated by-product of the addition consisted wholly of the dichloro-ester, $\text{CH}_2\text{Cl}\cdot\text{CMeCl}\cdot\text{CO}_2\text{Et}$. The non-crystallisable portion of the hydrolysis product, although consisting without doubt mainly of the isomeric chlorohydrin, α -chloro- β -hydroxyisobutyric acid, contained even after the above-mentioned treatment appreciable quantities of the more highly chlorinated compound (Found : Cl, 28.2%).

Addition to Tiglic Acid.—Tiglic acid (20 g.), m. p. 64°, was suspended in water and thoroughly agitated with the requisite quantity of hypochlorous acid solution, added in portions. When dissolution, which was rapid, was practically complete, the solution was filtered and extracted with ether. A convenient modification of this procedure consisted in gradually adding the requisite quantity of hypochlorous acid solution to tiglic acid (10 g.) dissolved in ether (250 c.c.) and allowing the mixture to stand over-night before extracting the addition product with ether. Some heat was evolved during the reaction, but by both methods a nearly quantitative yield of a pale yellow, and but slightly impure, addition product was obtained (Found : Cl, 22.0. $\text{C}_8\text{H}_9\text{O}_3\text{Cl}$ requires Cl, 23.3%).

Although about one-quarter of this liquid product solidified, after very long keeping, yielding a chlorohydrin which crystallised from benzene in colourless prisms, m. p. 113° (Found : Cl, 23.5%), no reasonably accurate estimate of the proportions of the isomeric addition products present could be made by separative means. The solid compound was clearly the α -chloro- β -hydroxy-form of the addition product (actually α -chloro- β -hydroxy- α -methylbutyric acid), since its sodium salt was readily and completely reducible by sodium amalgam in the presence of carbon dioxide to the sodium salt of the corresponding hydroxy-acid (colourless oil, b. p. 116—120°/1—2 mm.); the residual liquid consisted mainly, but not entirely, of a slightly impure chlorohydrin (Cl, 20.9%) which was not so reduced, *i.e.*, the β -chloro- α -hydroxy-isomeride (actually β -chloro- α -hydroxymethylbutyric acid). Careful estimates of the proportions of the components by reducing (*a*) the original unseparated oily addition product (chlorine content of the reduction product, 14.2%) and (*b*) the non-crystallisable portion of the addition product, b. p. 118—122°/3—4 mm. (chlorine content of the reduction product, 17.1%), gave the values 38% and 39% respectively for the proportion of α -chloro- β -hydroxy-addition product. On keeping the oily reduction product for several weeks a portion of the β -chloro- α -hydroxy-acid crystallised; this separated from benzene in colourless needles, m. p. 89°,* and was identical with the β -chloro- α -hydroxy- α -methylbutyric acid subsequently obtained from sodium tiglate (below).

Addition to Ethyl Tiglate.—The ester (16 g.), obtained by the action of ethyl iodide on silver tiglate, was dissolved in ether (250 c.c.) and treated at -5° with an aqueous solution containing 6.6 g. of hypochlorous acid. When addition was complete (after about 4 hours) the aqueous layer was separated and extracted with more ether, and the combined ethereal liquors dried over sodium sulphate and evaporated. The oily product, on distillation, gave (i) unchanged ester (2.35 g.), b. p. 61—65°/25 mm., (ii) an oil (2.4 g.), largely unsaturated, b. p. 65—80°/25 mm., and (iii) an oil (13 g.), b. p. 75—95°/18 mm., which contained the chlorohydrin mixed with unchanged ester and a lower-boiling chloro-ester (almost certainly tiglic ester dichloride). The last fraction was extracted 20 times with hot water to remove the chlorohydrin, and the extract re-extracted with ether. The soluble and the insoluble oil thus obtained were then separately distilled. There were thus obtained two fractions : (1) 2 g. of a sweet-smelling oil, b. p. 40—62°/3 mm. but mainly 50—56°/3 mm., which contained unchanged ester and the chlorinated by-product (Found : Cl, 16.3%), and (2) 8.5 g. of chlorohydrin of b. p. 69—72°/3 mm. (Found : Cl, 19.4. $\text{C}_7\text{H}_{13}\text{O}_3\text{Cl}$ requires Cl, 19.6%).

The chlorohydrin fraction was hydrolysed with 10% hydrochloric acid. The syrupy hydrolysis product, after separation from a trace of unhydrolysed ester, was neutralised with bicarbonate and reduced with sodium amalgam under the standard conditions (above). The product (Found : Cl, 12.7%) contained reduced and unreduced components in approximately equimolecular proportion (0.5 mol. $\text{C}_5\text{H}_9\text{O}_3\text{Cl}$ + 0.5 mol. $\text{C}_5\text{H}_{10}\text{O}_3$ requires Cl, 13.0%). An independent estimate of the approximate proportion of the components became possible after the chlorohydrin component of the reduction product had been allowed to crystallise; then, from 2.3 g. of the mixed acids, 1.2 g. of crude crystalline material separated; the latter material,

* Melikoff records the production, by the addition of hypochlorous acid to tiglic acid, of two chlorohydrins, m. p.'s 111° and 75°, the latter of which was considered to be the acid $\text{CHMeCl}\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}$, because it was identical with the product obtained by adding hydrogen chloride to the corresponding glycidic acid.

when crystallised from benzene, yielded 1.1 g. of a pure chlorohydrin forming characteristic plates, m. p. 114° (Found: Cl, 23.4. $C_5H_9O_2Cl$ requires Cl, 23.3%). This chlorohydrin, which is β -chloro- α -hydroxy- α -methylbutyric acid, is a stereoisomeric form of the chlorohydrin, m. p. 89°, formed by addition of hypochlorous acid to tiglic acid.

Addition to Sodium Tiglate.—Tiglic acid (10 g.) was neutralised with sodium hydrogen carbonate solution, diluted to 500 c.c., and treated at 0° with 460 c.c. of a solution containing 5.2 g. of hypochlorous acid. Addition proceeded rapidly and after standing over-night the solution was acidified and thoroughly extracted with ether. The dried ethereal extract yielded a crude liquid chlorohydrin, containing a little unchlorinated acid (Found: Cl, 20.9%). When a portion of this chlorohydrin was neutralised with sodium hydrogen carbonate and reduced with sodium amalgam under the standard conditions there was obtained an oily acid which contained 17.2% of chlorine. Taking into consideration the initial chlorine content of the crude addition product, this figure corresponds to the presence of 80% of the β -chloro- α -hydroxy-form of the chlorohydrin. On keeping the reduction product, partial crystallisation of the unreduced chlorohydrin occurred: from 1.9 g. of material, 0.7 g. of a solid chlorohydrin was isolated, which separated as needles, m. p. 89°, from benzene. This was β -chloro- α -hydroxy- α -methylbutyric acid (Found: Cl, 23.4%). The original crude addition product also yielded crystals of this substance when inoculated with a crystal from the reduction product.

Addition to Crotonic Acid.—A solution containing 4.9 g. of hypochlorous acid was gradually added to 8 g. of crotonic acid dissolved in 160 c.c. of water, at 0°. Reaction was practically instantaneous, and the product was extracted with ether (8 extractions), dried over sodium sulphate, and distilled. The oil obtained, although undoubtedly consisting mainly of the α -chloro- β -hydroxybutyric acid as shown by Melikoff (*loc. cit.*) (Found: Cl, 25.7. Calc. for $C_4H_7O_2Cl$: Cl, 25.6%), also contained some of the β -chloro- α -hydroxy-isomeride (β -chloro- α -hydroxybutyric acid) as shown below. Yield, 12.8 g. (99% of the theoretical).

A portion of the addition product (2.1 g.) was heated with 60 c.c. of 10% potassium dichromate solution on a steam-bath. The oxidation product consisted mainly of acetic acid, but on distillation a very small quantity of α -chloropropionic acid was isolated, the identity of which was confirmed by conversion with the aid of potassium cyanide into duly authenticated methylmalonic acid.

A larger quantity of the addition product was oxidised with 6 times its weight of concentrated nitric acid. Reaction was vigorous and was completed by heating the mixture for a short time on a steam-bath. After cooling, the product was first freed from residual nitric acid by saturation with sulphur dioxide, and was then extracted with ether. The oxidation products consisted mainly of acetic and oxalic acids, but from the former was isolated a quantity of α -chloropropionic acid (b. p. 80–85°/10 mm.) which corresponded in amount to the presence of 8% of β -chloro- α -hydroxybutyric acid in the α -chloro- β -hydroxybutyric acid constituting the main addition product. This procedure, however, was unsuitable for determining the proportion of the isomeric chlorohydrins and when the addition product was submitted to reduction under the standard conditions, the proportion of β -chloro- α -hydroxy-acid, as calculated from the final chlorine content (9.2%), was 26%.

Addition to $\beta\beta$ -Dimethylacrylic Acid.—To the acid (20 g.), suspended in water (400 c.c.), a 2.1% solution containing 10.5 g. of hypochlorous acid was added, and the mixture shaken until the reaction was about complete ($\frac{1}{2}$ hour). After standing over-night, the product was neutralised with sodium hydrogen carbonate, and the neutral material formed in the reaction extracted with ether (extract A). The mother-liquor was re-acidified and first extracted with light petroleum (extract B) and then with ether (extract C). Each extract was dried over sodium sulphate.

The extract A yielded (i) a liquid, b. p. 42–65°, which contained, in addition to a little ether, a neutral chloro-compound which corresponded in properties with α -chloroisobutylene, $CMe_2 \cdot CHCl$, and (ii) a non-homogeneous residue (2.2 g.), which was divided into two fractions of b. p. 50–60°/14 mm. (1.4 g.) and 65–85°/14 mm. respectively. The first of these two fractions was doubtless a further hypochlorination product of α -chloroisobutylene (Found: Cl, 48.2. $C_4H_8OCl_2$ requires Cl, 49.6%), and the second probably a dimeride of chloroisobutylene [Found: Cl, 38.2. $(C_4H_7Cl)_2$ requires Cl, 39.2%]. In view of the well-known strong tendency of acids of the types $R \cdot CH(OH) \cdot CHHal \cdot CO_2H$ and $R \cdot CHHal \cdot CHHal \cdot CO_2H$ to suffer decarboxylation during their conversion (by dehydration and hydrogen halide fission respectively) into the α -halogeno-acids of the type $R \cdot CH \cdot CHal \cdot CO_2H$, all the above neutral chloro-compounds are regarded as secondary derivatives of the chlorohydrins $CMe_2(OH) \cdot CHCl \cdot CO_2H$ and are accounted as such in arriving at a quantitative estimate of the opposite modes of hypochlorous acid addition which occur in the reaction.

The extract B yielded only $\beta\beta$ -dimethylacrylic acid (1.75 g.), and the extract C the same acid (1.5 g.) together with a liquid chlorohydrin (13.3 g.). The last two substances were separated by solution in water (150 c.c.) and extraction (3 times) with light petroleum. The chlorohydrin remained in the aqueous liquor and on re-extraction with ether was obtained as a yellow oil which largely solidified on keeping. The solid portion, which crystallised from benzene in large nodules, m. p. 69°, and formed 68% of the total chlorohydrin which escaped decarboxylation, represented α -chloro- β -hydroxy- β -methylbutyric acid* (Found: Cl, 23.5. $C_5H_9O_2Cl$ requires Cl, 23.3%). The residual liquid portion could not be further crystallised, and, since stereoisomeric forms of the chlorohydrins cannot arise in this case, it represented β -chloro- α -hydroxy- β -methylbutyric acid admixed with α -chloro- β -hydroxy- β -methylbutyric acid but otherwise nearly pure (Found: Cl, 23.4%). The percentage of the former of these chlorohydrins was estimated by reducing the original oily mixture with sodium amalgam under the standard conditions and analysing the product (Found: Cl, 4.3%). Taking into account the recovered dimethylacrylic acid and the secondary products of reaction, this amounted to about 7% of the total primarily-formed chlorohydrin.

The constitution of the solid chlorohydrin followed from its ready reducibility with sodium amalgam and the fact that it readily yielded α -chloro- $\beta\beta$ -dimethylacrylic acid, m. p. 84° (Found: Cl, 26.3. Calc. for $C_5H_7O_2Cl$: Cl, 26.4%), after it had been heated for 2—3 minutes with a little concentrated sulphuric acid and then poured into water (compare Prentice, *loc. cit.*).

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