288. *Reactions of Olefinic Compounds. Part I. Additivity of Olefinic Acids towards Hypochlorous Acid and Ethyl Hypochlorite: Orientation in Relation to Additive Mechanism.*

By G. F. Bloomfield and E. H. Farmer.

The addition of hypochlorous acid to an olefin $C_1 : C_2$, being a reactivity characteristic of the ethylenic linkage *per se*, will yield in the general case the two position isomerides $C_1Cl{\cdot}C_2(OH)$ and $C_1(OH){\cdot}C_2Cl$, except in so far as the polarisability of the olefinic linking in the contrary senses expressed by $\overset{\delta\pm}{C_1} : \overset{\delta\mp}{C_2}$ is restrictively influenced by the groups attached to C_1 and C_2. Where the two components of an unsymmetrical addendum are *electrically* very dissimilar and readily ionise, *e.g.*, hydrogen bromide, it is doubtless legitimate to assume that the relative extent of formation of positionally isomeric addition products in a given example is directly related to (probably constitutes a measure of) the inverse polarising tendencies of the olefin under the conditions of experiment. Where, however, the addendum is such that either component can normally function as a stable anion (*e.g.*, ICl, HOCl, ROCl), there is less certainty that a similar assumption may generally be made; for although the olefinic compound would be expected to exhibit anionoid reactivity exclusively (compare Lapworth, *Nature*, 1926, **115**, 625), there is no more than a strong presumption that the addendum will be limited to uniform polarisation in only one of the two possible ways (*e.g.*, $\overset{+\,-}{\mathrm{ICl}}$, $\overset{+\,-}{\mathrm{ClOH}}$, $\overset{+\,-}{\mathrm{ClOEt}}$, etc.) when entering reaction in *molecular* condition.

The manner of hypochlorous acid addition has been the subject of prolonged controversy, and much of the confusion has arisen from misconception of the electrical condition of the addendum.

In 1906 Michael sought to replace the view then current, that the hypochlorous acid molecule divides into chlorine and hydroxyl components when entering into reaction, by one involving the attachment of the ions of hypochlorous acid ($H^{\cdot}$ and OCl') to the ethylenic carbon atoms : this view necessitated the assumption that isomerisation of the first-formed product immediately occurred,

$$>C(OCl){\cdot}CH< \longrightarrow >C(OH){\cdot}CCl<.$$

Noyes and Wilson (*J. Amer. Chem. Soc.*, 1922, **44**, 1630; see also Noyes, *Rec. trav. chim.*, 1922, **41**, 557) have shown that the degree of ionisation of hypochlorous acid in aqueous solution is low, the ions being almost entirely $H^{\oplus}$ and $OCl^{\ominus}$; nevertheless these authors are of opinion that ionisation is amphoteric, since a current of air removes from the solution not hypochlorous acid but chlorine monoxide, $\overset{+}{H}\overset{-}{O}Cl + \overset{+}{Cl}\overset{-}{O}H \longrightarrow Cl_2O + H_2O$. Chlorohydrins, however, may be additively formed either by means of aqueous hypochlorous acid or by chlorination of an aqueous solution of the olefinic compound; and, analogously, chloro-alkoxy-addition products of olefinic compounds appear to be obtainable either by employment of the preformed alkyl hypochlorites (Goldschmidt, *Ber.*, 1925, **58**, 572) or by chlorination of the olefinic compound in alcoholic solution (Conant and Jackson, *J. Amer. Chem. Soc.*, 1924, **46**, 1727; Jackson, *ibid.*, 1926, **48**, 2166; Jackson and Pasuit, *ibid.*, 1927, **49**, 2071). The condition or nature of the addendum is therefore not necessarily always the same, and in studying the relationship between olefinic constitution and the orientation of hypochlorous acid addition products cognisance must be taken of the method of addition employed.

The experiments herein described were initiated to show conclusively the potential ability of an olefinic linking to yield structurally isomeric chlorohydrins and also for the purpose of observing the restrictive influence exerted by a carboxyl group situated near to the unsaturated centre. Δ^{α}-, Δ^{β}-, and Δ^{γ}-Hexenoic acids (probably all *trans*) seemed well suited to the purpose. Aqueous solutions of hypochlorous acid—chlorine-free but containing dissolved calcium chloride *—only were employed, in which, owing to the low degree of ionisation, the addendum would be presented under conditions favourable to attachment in *molecular* condition. A parallel, though less extensive, series of experiments with ethyl hypochlorite was carried out in which the reagent necessarily came into reaction in molecular condition.

Δ^{γ}-Hexenoic acid, $CHMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, in which the

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* Such solutions were used in preference to pure aqueous solutions of hypochlorous acid on account of the great saving in time which their use permitted during a long series of operations.

double bond is sufficiently remote from the carboxyl group to escape participation in the αβ,βγ-changes which characterise its Δ^{α}- and Δ^{β}-isomerides, might be expected to behave essentially as an unsymmetrically substituted ethylene. In practice it yields about 95% of a volatile δ-*chlorohexolactone* (I), the remainder of the product consisting of a gummy non-lactonising chloro-acid, doubtless the γ-chloro-δ-hydroxy-acid (II).

(I.) 

$\mathrm{CHMeCl{\cdot}\underset{\llcorner O}{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{\lrcorner}{C}O}$

$\mathrm{CHMe(OH){\cdot}CHCl{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$ (II.)

$\mathrm{CH_2Me{\cdot}CHCl{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H}$ (III.)

 (IV.)

$\mathrm{CH_2Me{\cdot}\underset{\llcorner O}{C}H{\cdot}CHCl{\cdot}CH_2{\cdot}\underset{\lrcorner}{C}O}$

(V.) $\mathrm{CH_2Me{\cdot}CH_2{\cdot}CH(OH){\cdot}CHCl{\cdot}CO_2H}$

(VI.) $\mathrm{CH_2Me{\cdot}CH_2{\cdot}CHCl{\cdot}CH(OH){\cdot}CO_2H}$

Δ^{β}-Hexenoic acid, which combines more rapidly than the Δ^{γ}-acid and much more rapidly than the Δ^{α}-acid with the addendum, yields about 20% of a crystalline non-lactonising chloro-hydroxy-acid (probably III). The major product (nearly 80% yield), however, is a liquid mixture of a volatile chloro-lactone and an undistillable chloro-lactone representing stereoisomeric forms of β-chloro-γ-hexolactone (IV).

Δ^{α}-Hexenoic acid combines with hypochlorous acid so slowly that much of the latter is lost by decomposition. The product contained, in addition to much unchanged hexenoic acid, two substances the constitutions of which were extremely difficult to demonstrate convincingly.* One of these is α-chloro-β-hydroxy-hexoic acid (V) and the other is a rather impure, stereoisomeric form of the same compound free from any material quantity of the structural isomeride (VI).

The following scheme symbolises the results :

C_{δ}═══C_{γ}	C_{γ}═══C_{β}	C_{β}═══C_{α}
Cl · · · · · OH (95%)	Cl · · · · · OH (20%)	Cl · · · · · OH (0%)
OH · · · · Cl (<5%)	OH · · · · Cl (80%)	OH · · · · Cl (100%)

It is seen that addition of hypochlorous acid to the αβ-double bond follows the same course as in hydrogen halide addition : all tendency

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* This applies to the chlorohydrins of most Δ^{α}-acids. Even in the case of cinnamic acid, the interaction of which with aqueous hypochlorous acid and with chlorine water has frequently been studied, no rigid demonstration of the constitution of the solid chlorohydrin as $\mathrm{CHPh(OH){\cdot}CHCl{\cdot}CO_2H}$ appears to have been furnished; moreover, so far as the authors are aware, the complete non-formation of a structural isomeride of the main product has only recently been shown (by Mr. C. Hose).

to addition in the reverse way is suppressed. The low degree of reactivity of the Δ^{α} in comparison with the Δ^{β}- and Δ^{γ}- acids indicates that the carboxyl group has a powerful deactivating influence while at the same time co-operating with the propyl group attached to C_{β} in negatively polarising C_{α}.* The effect of CO_2H, however, is apparently not transmitted to any significant extent through one or more methylene groups, since the results obtained for the Δ^{β}- and the Δ^{γ}-acid are precisely of the kind to be anticipated from well-known considerations affecting the comparative activating (electron-repelling) properties of alkyl groups (Allan, Oxford, Robinson, and Smith, J., 1926, 405). The influence of the ethyl group attached to C_{γ} of the Δ^{β}-acid in activating (negatively polarising) C_{β} outweighs, but does not suppress, that of the group $\cdot CH_2\cdot CO_2H$ attached to C_{β} in activating C_{γ}. Similarly, the action of the group $\cdot CH_2\cdot CH_2\cdot CO_2H$ attached to C_{β} of the Δ^{γ}-acid in activating C_{δ} outweighs, and nearly suppresses, the opposing influence of the methyl group attached to C_{δ} (compare Ingold and Ingold, J., 1931, 2354). The dominant polarisations may therefore be represented thus :

$$\overset{\delta-}{C_{\delta}}=\!=\overset{\delta+}{C_{\gamma}} \qquad \overset{\delta+}{C_{\gamma}}=\!=\overset{\delta-}{C_{\beta}} \qquad \overset{\delta+}{C_{\beta}}=\!=\overset{\delta-}{C_{\alpha}}$$

Crotonic acid yielded with ethyl hypochlorite a mere trace of addition product, and sorbic acid a small yield of material which was at least partly ethoxylated. Even with the hexenoic acids the slow rate of reaction and the spontaneous decomposition of the reagent rendered the study of the Δ^{α}- and the Δ^{γ}-isomeride unprofitable (in the latter case the cost of material was too great to allow working on a large scale). With the Δ^{β}-acid, however, addition occurred to the extent of 92% when a carbon tetrachloride solution of ethyl hypochlorite (Taylor, MacMullan, and Gammal's reagent; *J. Amer. Chem. Soc.*, 1925, **47**, 395) was employed : the product was not a chloro-ethoxy-hexoic acid but consisted entirely of the two stereoisomeric forms of β-chlorohexolactone previously mentioned; moreover, when an ethereal solution of nearly pure ethyl hypochlorite was used in place of Taylor, MacMullan, and Gammal's

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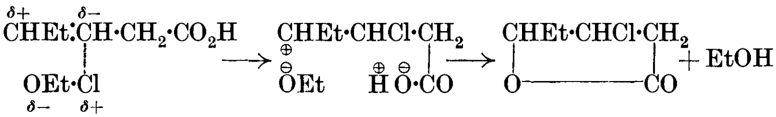
* The influence of the carboxyl group in securing the addition of hydrogen halides to $\alpha\beta$-unsaturated acids so diverse as acrylic, α-methylacrylic, and crotonic, in the general manner $>CHal\cdot\dot{C}H\cdot CO_2H$, appears to be the dominant one. Hypochlorous acid addition, however, does not necessarily follow a parallel course and the interesting case afforded by α-methylacrylic acid requires investigation (Melikoff's statement, *Annalen*, 1886, **234**, 197, that this acid reacts with hypochlorous acid to give a β-chloro-α-hydroxy-derivative is not proved). In the conjugated series the course of hypochlorous acid addition definitely differs from that of hydrogen bromide addition in the first example examined by the authors.

reagent, addition was almost quantitative, at least 93% of the acid being converted into the mixture of isomeric β-chlorohexolactones, and less than 1% yielding a chloro-ethoxy compound—presumably the γ-chloro-β-ethoxy-acid.

Since there can be little doubt as to the *molecular*, though polarised, condition of ethyl hypochlorite in entering reaction, the simplest assumption as to the course of reaction is that an ethoxyl ion is lost after the inception of addition, thus :



$$\begin{array}{c}\overset{\delta+}{\text{CHEt}}\colon\overset{\delta-}{\text{CH}}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}\\ |\\ \underset{\delta-}{\text{OEt}}\cdot\underset{\delta+}{\text{Cl}}\end{array}\longrightarrow\begin{array}{l}\overset{\oplus}{\text{CHEt}}\cdot\text{CHCl}\cdot\text{CH}_2\\ \overset{\ominus}{\text{OEt}}\qquad\overset{\oplus}{\text{H}}\,\overset{\ominus}{\text{O}}\cdot\text{CO}\end{array}\longrightarrow\begin{array}{l}\text{CHEt}\cdot\text{CHCl}\cdot\text{CH}_2\\ \text{O}\text{————}\text{CO}\end{array}+\text{EtOH}$$

Although ethyl hypochlorite and hypochlorous acid differ slightly in their tendency to yield positionally isomeric addition products, the results obtained with the two reagents are so similar that there is no adequate reason for supposing that the addendum furnished by the aqueous hypochlorous acid is other than *molecular* hypochlorous acid, or that reaction in the two cases follows a different course. The authors have found, moreover, that chlorination of Δ^{β}-hexenoic acid at −8° in ether or *n*-hexane results solely in the formation of β-chlorohexolactone and hydrogen chloride, the latter being liberated from the *outset* of reaction (change of solvent affects the speed of reaction and the relative proportion of the stereoisomeric lactonic forms). Therefore it would appear that the addition of chlorine may be represented analogously to that of ethyl hypochlorite and of hypochlorous acid, the addition in all three cases being initiated mainly or wholly at the C_{β}-atom of Δ^{β}-hexenoic acid.

It has been shown by Conant, Jackson and their collaborators (*loc. cit.*) that chlorinated alcohols yield chloro-alkoxy-addition products comparatively readily with cinnamic acid, whereas a solution of ethyl hypochlorite in carbon tetrachloride does not. It appears certain, therefore, that the addendum in the former case is not an alkyl hypochlorite existing in molecular condition, although it may well be molecular chlorine acting in conjunction with ethoxyl ions as has been suggested by Ingold (*Ann. Reports*, 1928, 132). Probably the difference in condition of the addendum in the two cases affects additive reactivity and not the orientation of the addition products; at any rate it appears quite unlikely from the observations here described that molecular ethyl hypochlorite would differ from chlorinated alcohol in giving an α-ethoxy-β-chloro-derivative with cinnamic acid (presumably corresponding to polarisation in the manner $\overset{\delta+}{\text{OEt}}\overset{\delta-}{\text{Cl}}$) as Ingold (*loc. cit.*) has suggested.

EXPERIMENTAL.

(A) *Products Derived by Use of Hypochlorous Acid.*

Preparation of Hypochlorous Acid.—A slow stream of Cl was passed into a well-stirred suspension of pptd. $CaCO_3$ (50 g.) in water (1 l.) until the concn. of HOCl (estimated iodometrically in a 2 c.c. sample) reached about 2%. Stirring was continued for a while to ensure removal of free Cl, and the HOCl–$CaCl_2$ solution, now colourless or only very faintly yellow, was filtered into an ice-cold flask. The final strength was rapidly estimated, and the desired quantity calculated and put into use as soon as possible.

Addition to Δ^{β}-Hexenoic Acid.—To a solution of the acid (Boxer and Linstead, J., 1931, 748) (30 g.) in Et_2O (1200 c.c.) cooled in a freezing mixture, 2·26% HOCl aq. (620 c.c.) was added gradually. After 12 hrs., the aq. layer was run off, saturated with NaCl, and extracted with Et_2O. The united ethereal solutions, dried over Na_2SO_4, left on removal of the solvent under a column a residue in nearly quantitative yield.* This was separated by $NaHCO_3$ aq. into non-acidic lactone (A) (54%) and an acidic substance (B) (46%) still containing some lactone.

On distillation (B) yielded (i) a non-acidic lactone (9·1 g.), b. p. 90—100°/3 mm., which was added to (A); (ii) an oily acid (8·9 g.), b. p. 127°/3 mm.; (iii) a non-acidic residue (0·7 g.). Fraction (ii) solidified almost completely and gave, as a white crystalline powder, m. p. 83—84° after two crystns. from C_6H_6, a saturated acid which was a simple hypochlorous acid addition product and showed no tendency to lactonise; it is represented as *β-hydroxy-γ-chloro-*n*-hexoic acid* (III) (Found: C, 43·45; H, 6·7; Cl, 21·35; *M*, monobasic, 167·7. $C_6H_{11}O_3Cl$ requires C, 43·35; H, 6·65; Cl, 21·3%; *M*, 166·5).

The total crude lactonic material from (A) and (B) was distilled and yielded (i) a colourless pleasant-smelling oil, b. p. 80°/5 mm., which was saturated, homogeneous, and without immediate action on $NaHCO_3$ aq., and (ii) a residue which began to lose HCl. The oil (redistillable without residue) is regarded, owing to its spontaneous formation during the addition reaction, as *β-chlorohexolactone* (Found: Cl, 23·9. $C_6H_9O_2Cl$ requires Cl, 23·9%). The decomposable residue appeared to be a stereoisomeride of β-chlorohexolactone † (which itself rapidly darkened after 2 months); after a year, it began to crystallise, contemporaneously with the (more rapid) crystn. of a similar residue derived by interaction of Δ^{β}-hexenoic acid with ethyl hypochlorite (see p. 2071) and then formed colourless prisms, m. p. 175°, from C_6H_6 (Found: C, 48·7; H, 6·1; Cl, 23·95%. $C_6H_9O_2Cl$ requires C, 48·5; H, 6·1; Cl, 23·9%). Rather less than 80% of the hexenoic acid had suffered conversion into chlorolactones, and of this proportion about 5/7 yielded the more stable (volatile) form. Owing to the ready loss of halogen with alkali neither form of the lactone could be converted into the corresponding β-chloro-γ-hydroxyhexoic acid.

Addition to Δ^{γ}-Hexenoic Acid.—To a solution of the acid (Eccott and Linstead, J., 1929, 2163) (20 g.) in Et_2O (700 c.c.), the requisite quantity of HOCl was added (9·2 g. in about 3% solution), none of which remained after

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* The loss of material was negligible, but owing to the considerable difference in the molecular weight of the products an exact figure cannot be given. A similar difficulty applies in other instances which occur below.

† The analogous δ-chlorohexolactone (see below) could be kept indefinitely without undergoing decomp.

55—60 hrs. at 0°. The addition product, obtained in quant. yield (taking into consideration its composition), was separated by $NaHCO_3$ treatment into a crude lactonic portion (13 g.) and an " acidic " portion (13·5 g.). The latter, which contained a little AcOH, was, however, chiefly lactonic : it yielded (i) a small liquid fraction, b. p. 90—105°/6 mm., consisting of a lactone admixed with some volatile acid—probably wholly AcOH, (ii) a neutral lactonic liquid, b. p. 105—115° (chiefly 108—115°)/5 mm., which together with (i) weighed 9·3 g., and (iii) a saturated, feebly acidic residue (3·3 g.). The main lactonic portion gave on distillation the same neutral lactonic liquid, b. p. 90—116°/6 mm. (10·9 g.), as constituted fraction (ii), but left a small non-acidic residue (1·8 g.) which appeared to be slightly impure lactone (Found : Cl, 25·0. Calc. for $C_6H_9O_2Cl$: Cl, 23·9%). Fraction (iii), again treated with $NaHCO_3$ aq., yielded a further quantity of lactonic material, and a saturated gummy acid (1·3 g., still not entirely free from lactonic matter) which formed the sole acidic addition product and represented not more than 4·5% of the hexenoic acid employed.

The main lactonic portion was combined with the lactonic material from fractions (i) and (ii) and (iii), and the whole distilled. Two fractions were collected : (*a*) b. p. 90—105°/5 mm., small in amount, and (*b*) b. p. 105—116°/5 mm.; there was no residue. Redistillation of fraction (*b*) gave pure δ-*chlorohexolactone*, a colourless oil, b. p. 115—116°/5 mm. (Found : Cl, 23·8%). This lactone, characterised by a high degree of stability towards nitric and chromic acids, with both of which it gave small yields of succinic acid on heating, was examined side by side with the reduction product (catalytic) of the αβ-unsaturated chloro-lactone derived from sorbic acid and HOCl. The two saturated chloro-lactones were indistinguishable in ordinary properties, but identity of constitution was not directly demonstrated by degradation : the unsaturated chloro-lactone from sorbic acid, however, was definitely shown to have the constitution $CHMeCl\cdot CH\cdot CH{:}CH\cdot CO\cdot O$.

Addition to Δ^{α}-*Hexenoic Acid.*—To the pure Δ^{α}-acid (Goldberg and Linstead, J., 1928, 2351) in cold Et_2O, the requisite quantity of 2% HOCl aq. was gradually added. Absorption required 80 hrs. at 0° for completion, but the bulk of the reagent disappeared in a much shorter time. The product was a colourless, rather viscous acidic oil, the Cl content (18·45%) and basicity (M, 172) of which were too low to correspond to those of the expected chlorohydrin ($C_6H_{11}O_3Cl$ requires Cl, 21·3%; M, monobasic, 166·5). On distillation the product separated into two almost equal fractions : (i) of b. p. 95—118°/5 mm., solidifiable in a freezing mixture, and (ii) of b. p. 134—136°/5 mm., which solidified on cooling. The second was a chloro-hydroxy-acid (colourless prisms, m. p. 82°, from C_6H_6) (Found : Cl, 21·3%; M, 168·5) which was definitely different from the acid of m. p. 83—84° obtained (see above) from Δ^{β}-hexenoic acid. The first fraction remained only partly solid at room temp., and from it could be separated by further fractional distillation and crystn., unchanged Δ^{α}-hexenoic acid,* a further quantity of the chloro-hydroxy-acid, and a liquid product. Complete separation of the reaction products was effected by repeatedly extracting the crude liquid product with H_2O until no further contraction in vol. occurred and submitting the sol. and the insol. portion to rigorous fractional distillation and crystallisation. The proportion of

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* The hexenoic acid thus isolated was shown to be largely, if not entirely, present *as such* in the crude addition product.

unchanged acid in any sample could be determined with fair accuracy by titration with $KMnO_4$, since the chloro-addition products were stable to this reagent at room temp. In the table is shown the composition of the crude addition product in a typical experiment in which 25 g. of Δ^{α}-hexenoic acid were employed; of the latter, about 70% suffered conversion into chlorohydrins or their derivatives. In the last col., *R* is the wt. (g.) of Δ^{α}-hexenoic acid corresponding to the wt. of product in the preceding col.

			(g.).	*R*.
Sol. in H_2O	(*a*)	Solid chlorohydrin, m. p. 82°	8·73	5·98
	(*b*) Oil	Δ^{α}-hexenoic acid	1·68	1·68
		oily addition products (mixed)	9·5	6·5
Insol. in H_2O	(*c*) Oil	(i) b. p. 98°/3 mm. (Δ^{α}-hexenoic acid)	3·3	3·3
		(ii) b. p. 100—110°/3 mm. 85% Δ^{α}-hexenoic acid	2·55	2·55
		15% oily addition products	0·45	0·31
		(iii) b. p. 110—128°/3 mm., oily addition products (mixed)	4·4	3·02
		(iv) residue	2·0	1·25
			32·6	24·6

Constitution of the solid addition product. The solid chloro-hydroxy addition product (m. p. 82°) yielded a similar chlorine-free oil, probably consisting of β-hydroxyhexoic acid (α-hydroxyhexoic acid is cryst. at room temp.) or $\alpha\beta$-oxidohexoic acid, when reduced with Na–Hg and H_2O and with Zn dust and AcOH. Direct oxidation of these substances having provided no satisfactory evidence of constitution, attempts were made to achieve regulated degradation of the original chloro-hydroxy-acid. This acid was stable to 80% H_2SO_4, to P_2O_5, and to oxidising agents. Dehydrochlorination with 2 mols. of alc. NaOH produced instantaneously and quantitatively an acid which gave no colour with $FeCl_3$, was stable to $KMnO_4$, and was doubtless $\alpha\beta$-oxidohexoic acid, from the further investigation of which no useful evidence could be derived.

The chloro-hydroxy-acid was acetylated by excess of hot Ac_2O–AcOH containing a trace of H_2SO_4. The oily product was a slightly impure *chloroacetoxyhexoic acid* (Found: Cl, 15·45. $C_8H_{13}O_4Cl$ requires Cl, 17·0%) which did not lose HCl when titrated with alc. NaOH. On treatment with Na–Hg in presence of CO_2 reduction took place unaccompanied by serious hydrolysis. The derived oily acetoxyhexoic acid was kept over KOH in an evacuated desiccator for several days and then hydrolysed with alc. KOH. The product was an oil which, oxidised with alkaline $KMnO_4$, yielded first butaldehyde * and later small quantities of butyric and oxalic acids: a much larger yield of butyric acid (b. p. 70—80°/10 mm.) was obtained by oxidation on a steam-bath with $K_2Cr_2O_7$ and H_2SO_4 (4 O supplied).

There was little doubt from the foregoing that the solid chloro-hydroxy-acid contained a β-hydroxyl group. Additional proof that it was, indeed, *α-chloro-β-hydroxyhexoic acid* was afforded by its behaviour with $K_2Cr_2O_7$–H_2SO_4: oxidation was slow in the cold, but the odour of butyric acid (not butaldehyde) soon became apparent; on warming, the production of butyric acid

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* Since this aldehyde was not isolable either as such or as its *p*-nitrophenylhydrazone, it was probably derived from a trace of $\alpha\beta$-unsaturated acid present as impurity. No butyrylacetic acid was isolated at this stage, but a small yield of a *p*-nitrophenylhydrazone, m. p. 197°, was obtained.

was accelerated, and 90% of the chlorohydrin was thus converted into this acid, the remainder being recovered unchanged.

Constitution of the liquid addition products. After separation of the bulk of the two main constituents of the water-soluble portion of the addition product in solid condition (see table, p. 2069) there remained an oil which still contained about 15% of hexenoic acid as estimated by $KMnO_4$ titration. This deposited on long standing about ⅓ of its wt. of the same (very sticky) chlorohydroxy-acid and there remained after filtration an oily acid, which could not be freed from residual hexenoic acid and consisted mainly of a liquid addition product (chlorohydrin), the proportion of which in the original mixture of addition products amounted at most to 16%. It was more resistant to $K_2Cr_2O_7$–H_2SO_4 than the solid chloro-hydroxy-acid, but on gentle warming (the equivalent of 4 O per mol. of chloro-hydroxy-acid was taken) a mixture of fumaric acid and various fatty acids was obtained. The fatty acid mixture on distillation yielded much butyric acid, but no α-chlorovaleric acid. It was probable, therefore, that the chlorine atom was attached exclusively to the α-carbon atom.

As in the case of the solid chloro-hydroxy-acid the liquid addition product was converted *via* its acetyl derivative and the chlorine-free acetoxy-compound into a colourless, H_2O-sol., oily acid. The amount of this was very small, but on oxidation with slightly warm alkaline $KMnO_4$ it gave the products butyric and oxalic acids to be expected from β-hydroxyhexoic acid. It was therefore concluded that the liquid addition product consisted essentially of α-chloro-β-hydroxyhexoic acid.

The oily material composing fraction (*c*) (iii) of the crude addition product (see p. 2069) yielded on long standing a little more of the chlorohydrin, m. p. 82°. Although the residual oil was still adulterated with a little Δ^{α}-hexenoic acid, its halogen content was greater than that required for a simple chlorohydrin (Found : Cl, 28·9%) and it doubtless contained chloro-hydroxy-acids admixed with dichlorinated material.

The viscous residue composing fraction (*c*) (iv) of the crude addition product (see p. 2069) was insol. in H_2O and therefore probably consisted of intermolecular condensation products of the simple chlorohydrins together with a little polymerised hexenoic acid (Found : Cl, 20·2%).

(B) *Products derived by Use of Ethyl Hypochlorite.*

Solutions of Ethyl Hypochlorite.—Solution (1), in CCl_4, was prepared by Taylor, MacMullan, and Gammal's method (*loc. cit.*). Solution (2) was obtained by preparing EtOCl in nearly pure condition in a dark room, drying it over $CaCl_2$, and dissolving it in dry Et_2O in a blackened glass-stoppered vessel (about 10% solution).

Addition to Sorbic and Crotonic Acids.—Samples of each acid (5 g.) in solutions (1) and (2) were kept in the cold until no EtOCl remained (about 20 hrs.). Most of the acid was recovered unchanged, the reagent having decomposed into $CH_3{\cdot}CHO$ and HCl, but from sorbic acid, in either solution, 0·6—0·7 g. of crude addition product was obtained which was shown by interaction with HI aq. to contain some ethoxylated material.

Addition to Δ^{β}-Hexenoic Acid.—This acid, unlike sorbic and crotonic acids, did not promote the decomposition of EtOCl. On the contrary the two substances reacted at a fairly constant rate below 0°, addition becoming complete in about 3 days.

(1) The product obtained from 10 g. of Δ^{β}-hexenoic acid by treatment with the calc. quantity of solution (1) was washed with $NaHCO_3$ aq. and freed from CCl_4 without the application of heat. The oily residue, which deposited a few crystals, m. p. 169—170°, was filtered and distilled. It yielded (i) a colourless lactonic oil (2·7 g.) b. p. 80°/5 mm. (Found : Cl, 22·2%), resembling the volatile form of β-chlorohexolactone (p. 2067), and (ii) a decomposable lactonic residue (5 g.), which slowly yielded more of the cryst. solid, m. p. 169—170° : this solid, m. p. 175° after recrystn. from C_6H_6, was identical with the solid β-chlorohexolactone (p. 2067). The total yield of lactone was 92% of the theoretical.

(2) The product obtained by treating Δ^{β}-hexenoic acid (24 g.) with the calc. quantity of solution (2) was similarly washed with $NaHCO_3$ aq. and freed from solvent. The oily residue yielded the volatile form (b. p. 80°/5 mm.) of β-chlorohexolactone (15·6 g.) (Found : Cl, 23·7%) and a rather smaller quantity of decomposable lactone (12·9 g.) which appeared to be identical with the crude stereoisomeric form of β-chlorohexolactone. The $NaHCO_3$ washings yielded an oil (1·42 g.) which contained both lactonic and acidic material. The acidic material appeared to be unchanged hexenoic acid, and the lactonic material contained some ethoxylated material. The former of these was estimated by $KMnO_4$ titration, and the latter by the Zeisel method : the figures obtained indicate that the portion of the addition product sol. in $NaHCO_3$ aq. consisted of chloroethoxyhexenoic acid, 19·4%, Δ^{β}-hexenoic acid, 37·4%, and chlorohexolactone, 43·2%, which corresponded closely to the determined halogen content of the mixture (Found : Cl, 13·7. Calc., 13·8%) and reasonably well to the observed basicity. The quantity of the chloro-ethoxy-compound thus estimated represents less than 1% of the Δ^{β}-hexenoic acid originally taken.

(C) *Lactone Formation by Halogen Addition.*

Chlorination of Δ^{β}-Hexenoic Acid in Hexane and in Ether.—An ice-cold solution of Cl in *n*-hexane (37 c.c. of 6·7% solution) was gradually added to a cold solution of the acid in the same solvent (4 g. in 60 c.c. at −8°). HCl was at once evolved, and β-chlorohexolactone separated. The product consisted of a mixture of distillable β-chlorohexolactone (2·3 g.) (b. p. 80°/4 mm.) (Found : Cl, 23·85%) and a decomposable lactonic residue (2·7 g.) similar to those previously obtained (total yield of lactone, 96%).

When chlorination was conducted in an ethereal medium under conditions similar to those used in carrying out the above-described additions of HOCl and EtOCl, HCl was again liberated continuously through the reaction and the products were identical in nature, and nearly so in proportion, with those obtained in hexane solution. Total yield of lactone, 97%.

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