289. *Properties of Conjugated Compounds. Part XVIII. Addition of Hypochlorous Acid to Sorbic Acid.*

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IF hypochlorous acid enters into reaction in a *molecular* condition, polarised exclusively in the manner $\overset{\delta+}{\mathrm{Cl}}\overset{\delta-}{\mathrm{OH}}$ (see preceding paper), it should be possible on the basis of Lapworth's classification of reagents (*Nature*, 1925, **115**, 625) to determine the point of additive attack in conjugated carbon chains.

The addition products of the butadiene-α-carboxylic acids with hypochlorous acid can be separated almost quantitatively, and therefore it is possible to determine the relative importance of opposing additive tendencies in this series with fair accuracy. Sorbic acid reacts fairly rapidly with cold aqueous hypochlorous acid, at a rate depending apparently to some extent on the purity of the unsaturated acid. The product is always a mixture of several substances, formed by reactions involving almost exclusively the γδ-double bond of the unsaturated acid. The chief solid product is a mixture of the acid $\mathrm{CHMeCl{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CO_2H}$ and its γ-lactone, representing 50—60% of the sorbic acid consumed : the two components (acid 80%, lactone 20%) undergo interconversion so readily that neither can be separated in pure form; their constitutions, however, have been fully established by reduction and degradative processes (p. 2074). The remainder of the addition product consists almost entirely of two substances, (*a*) a liquid lactone, stereoisomeric with the solid form, and (*b*) a dichlorohydrin —the two representing respectively 20—25% and 15—30% of the sorbic acid consumed. Still another addition product (apparently less than 1% of the total) is not isolable in its original form, but is converted into a crystalline saturated chloro-hydroxy-acid when the crude solid addition product is fully hydrogenated : it is almost certainly not an αβ-addition product, since the only solid chlorohydrin obtainable by the interaction of Δ^{α}-hexenoic acid with hypochlorous acid (preceding paper) differs from the reduced acid here obtained.

The total yield of simple addition product in which the components of the addendum are *unmistakably* oriented at the γδ-carbon atoms in the manner $>\mathrm{C_\delta Cl{\cdot}C_\gamma(OH)}<$ amounts to 70—85% of the sorbic acid consumed. But the dichlorohydrin mentioned above (*b*) is found on oxidation to contain a chlorine atom attached to $\mathrm{C_\delta}$ and may possibly be derived by the addition of a second molecule of the reagent to a primarily formed γδ-addition product; on the other hand, it may arise from a primarily formed αδ-chlorohydrin, thus having the formula  $CHMeCl\cdot\underbrace{CH\cdot CHCl\cdot CH(OH)\cdot CO}_{O}$, and this view receives a measure of support from the fact that the solid γδ-chlorohydrin shows no tendency, when isolated, to react with hypochlorous acid. There is, however, a further important possibility, *viz.*, that both double bonds of the conjugated acid have suffered attack simultaneously, each being separately polarised before addition commenced * : in this case the orientation of the addition might well be different from that arising by addition of the reagent first to a conjugated system and then to the resulting ethylenic system.

On the basis of the original assumption it is clear, therefore, that practically the whole of the conjugated material suffers attack (uniquely except in so far as simultaneous attack at the two ethylenic centres occurs) at the δ-carbon atom of the chain; the reservation with regard to the *complete* uniformity of additive attack at this point refers to the fact that a little of the sorbic acid (less than 1%) yielded, as stated, a solid addition product of undetermined orientation and also that the liquid addition products could have been contaminated with traces of isomeric compounds without detection.

The indications here provided with respect to the initiation of attack uniquely at a terminal carbon atom of the chain are in agreement with all the indications afforded by the work (mainly unpublished) of one of the authors on hydrogen bromide addition.† While the present investigation was in progress, however, there appeared a description of the manner of hypochlorous acid addition to the lower homologue of sorbic acid which seems to afford strong indication in the contrary sense. Muskat and Hudson (*J. Amer. Chem. Soc.*, 1931, **53**, 3178) have formulated the addition product of β-vinylacrylic acid with hypochlorous acid as γ-chloro-δ-hydroxy-Δ^{α}-pentenoic acid, $CH_2(OH)\cdot CHCl\cdot CH{:}CH\cdot CO_2H$. If this representation were correct, it would follow on the basic assumptions noted above that the butadiene chain is susceptible of attack at the γ-carbon atom. The present authors, however, early observed that

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* Results recently obtained in the catalytic hydrogenation of various butadiene-α-carboxylic acids leave little doubt that such simultaneous attack is quite distinct from rapidly occurring consecutive attacks; in the case of hydrogenation, however, only one double-addition product is of course obtainable.

† With respect to addenda of the Michael type—the most investigated of all the unsymmetrical addenda which have been employed with conjugated compounds—it is probable that attack can occur at a non-terminal carbon atom, but in this case the activation of the conjugated chain would be kationoid in character (compare Farmer and Mehta, J., 1930, 1610; 1931, 1904; Bloom and Ingold, J., 1931, 2765).

β-vinylacrylic acid, like sorbic acid, yielded a mixture of solid and liquid products with hypochlorous acid, the liquid product being mainly lactonic. Although no detailed investigation of this example has been carried out, the authors have now found that both the solid and the liquid product give much chloroacetic acid on oxidation : clearly, therefore, the additive mode recorded by Muskat and Hudson does not apply to the solid product or to (at least) a large proportion of the liquid product. Consequently the evidence in favour of attack at a non-terminal atom disappears and, in addition, the additive hypothesis of Muskat and Northrup (*J. Amer. Chem. Soc.*, 1930, **52**, 4043)—compounded of the well-known anionotropic principle and alternate polarity—falls completely to the ground.

EXPERIMENTAL.

Addition to Sorbic Acid.—HOClaq. (420 c.c. of 1·31%; 1·17 mols.) was added in small portions with shaking to a solution of sorbic acid (10 g.; 1 mol.) in Et_2O (1 l.) maintained at −5° to −6°, each portion being allowed to react completely before the succeeding portion was added. When only a trace of the reagent remained, the aq. layer was separated, saturated with NaCl, and extracted with Et_2O. The combined ethereal liquors were dried and evaporated: the oily residue deposited crystals of sorbic acid (1·5 g.) when strongly cooled, and after filtration set to an oily paste in a vacuum desiccator. This crude product was shaken with cold H_2O (20 c.c.) : the insol. portion was a viscous brown oil (2 g.), and the sol. portion, after re-extraction and drying, was a colourless oil which solidified almost completely. The latter product, drained on porous tile and crystallised from C_6H_6, formed hard nodules (4 g.), m. p. 75—81°, sol. in many of the usual org. solvents (not in petroleum); it was acidic and contained chlorine.

A similar addition of the reagent (exactly 1 mol.) to sorbic acid (10 g.) gave unchanged acid (2·5 g.), brown oil (3 g.), and solid addition product (6·5 g.).

(A) *The solid addition product.* This varied continuously in m. p. throughout a series of five crystns. from $CHCl_3$ (from 75—83° to 92·5—93°) and had a Cl content (Found, 23·1%) too high for the simple mono-addition product (Cl, 21·55%), much too low for a di-addition product or a chlorine addition product, and somewhat too low for a dehydrated mono-addition product. The basicity of the many times recryst. specimen (*M*, 196) corresponded to the presence of 83·6% of the simple (acidic) chlorohydrin $C_6H_9O_3Cl$, and 16·4% of the corresponding lactone, $C_6H_7O_2Cl$; the basicity of a once recryst. specimen corresponded to a lactone content of 20·5%. On account of their mutual relationship and for reasons which appear below, the two substances are regarded as δ-chloro-γ-hydroxy-Δ^{α}-hexenoic acid and the γ-lactone thereof. The *silver* salt of the mixture was obtainable free from AgCl in the usual way (Found : Cl, 13·2 ; Ag, 39·9. $C_6H_8O_3ClAg$ requires Cl, 13·1; Ag, 39·8%).

Hydrogenation of the solid lactone–acid mixture. The recryst. chlorohydrin (34 g.) was catalytically reduced in aq. solution in presence of colloidal Pd at atm. press. The product was a pale yellow, mobile oil containing a trace of cryst. matter; the latter was strongly acidic and could be extracted with $NaHCO_3$aq., but the oil (a solid below −10°) dissolved extremely slowly in $NaHCO_3$aq., producing no efferv., and only gradually in NaOHaq. The oil was stable towards $KMnO_4$, and distilled as a colourless mobile fragrant liquid, b. p. 120°/9 mm. (115°/5 mm.), m. p. 11·5° (approx.): from the evidence adduced hereafter, it is shown to be δ-chlorohexolactone (Found: Cl, 23·9. Calc. for $C_6H_9O_2Cl$: Cl, 23·9%). It has also been obtained by a method which leaves no doubt as to the γδ-position taken up by the components of the addendum (see preceding paper).

The residue (2·8 g.) remaining after the distillation was washed with $NaHCO_3$aq. and then yielded 1·2 g. of the same chloro-lactone (Found: Cl, 23·85%). From the washings an oil was regenerated which, after solidifying with difficulty, was triturated with hot C_6H_6; the solid obtained (0·15 g.), m. p. 141—142°, was readily sol. in H_2O, Et_2O, and Me_2CO, insol. in petroleum, C_6H_6, and $CHCl_3$, could not be crystallised, and appeared to be a chloro-hydroxy-acid (Found: Cl, 22·2. Calc. for $C_6H_{11}O_3Cl$: Cl, 21·3%).

Reduction and oxidation of the hydrogenation product. A solution of the sat. chloro-lactone (7 g.) in aq. EtOH was treated with 4% Na–Hg (150 g.) in a stream of CO_2. The Hg was washed, Na salts removed, and EtOH partly distilled at reduced press. The united Na salts and solution were acidified, and the reduced product extracted with Et_2O. The extract yielded (i) a trace of flocculent halogen-free acid, m. p. 55° (crude), and (ii) an oil, which distilled below 130°/20 mm., leaving a little viscous acid. The volatile product, washed ($NaHCO_3$aq.) and dried in Et_2O, gave 0·2 g. of a neutral halogen-free mobile oil with the odour of hexolactone.

The sat. chloro-lactone was oxidised by warm $K_2Cr_2O_7$–H_2SO_4, CO_2 being evolved. By extraction with Et_2O small quantities of succinic acid (confirmed by comparison with an authentic specimen), AcOH, and oily material were obtained.

Oxidation of the chloro-lactone with hot conc. (*d* 1·42) and fuming HNO_3 (1 : 1) produced a little succinic acid and a neutral oil.

Oxidation of the solid lactone–acid mixture. (a) *With ozone.* 5 G., m. p. 93—94°, were ozonised in purified AcOEt for 50 hrs. The product was freed from solvent, heated with H_2O, and extracted with Et_2O; from the mother-liquor, oxalic acid was pptd. as Ca salt. The ethereal extract yielded a little oxalic acid and 3·2 g. of unchanged chlorohydrin to $NaHCO_3$aq. and then contained a colourless oil, which gave a colour with Schiff's reagent and after standing for a few days with H_2O_2aq. yielded colourless prismatic crystals of a halogen-free substance, m. p. 87—94° after recrystn. from aq. EtOH, the constitution of which was not discovered.

(b) *With neutral permanganate.* The mixture (neutralised in H_2O with $NaHCO_3$) was treated with $KMnO_4$–$MgSO_4$aq. at 0°. Where 4O were supplied, the product consisted of oxalic acid and a very little oily chloro-acid but contained no AcOH. When 5O were supplied (the last O at room temp.), the same two products were obtained in rather larger yield. The oily acid distilled at 76—80°/9 mm. (approx.) as a colourless sharp-smelling oil, which appeared to be identical with the liquid chloro-acid described in (c).

(c) *With aqueous potassium dichromate–sulphuric acid.* The lactone–acid mixture (1·5 g.) was dissolved in a quantity of reagent sufficient to supply 6O per mol. of lactone. Reaction set in on warming and much CO_2 was evolved, but a considerable amount of $K_2Cr_2O_7$ remained even after boiling for a short time. The products, which were extracted in much Et_2O, consisted of an oily chloro-acid, a trace of AcOH, and fumaric acid (methyl ester, plates, m. p. 101°; mixed m. p. 100—101°). The oily acid, b. p. 74—

78°/9 mm. (approx.), was added to that obtained in (b) and redistilled. There was insufficient material to permit of adequate rectification, but the unsolidifiable distillate (b. p. 78—90°/9 mm.; 186—187°/776 mm.) appeared to be slightly impure α-chloropropionic acid (Found: Cl, 30·6; *M*, monobasic, 115. Calc.: Cl, 32·7%; *M*, 108·5). The oily acid was converted into methylmalonic acid by the aid of KCN: the dark sticky solid, m. p. 110—120°, first obtained was decolorised in H_2O with charcoal, and the solution concentrated over H_2SO_4; the white crystals obtained, m. p. 132°, depressed the m. p. of malonic acid but not that of methylmalonic acid.

The nature of the oxidation products obtained in this section furnishes abundant confirmation that the original lactone–acid mixture consisted of δ-chloro-γ-hydroxy-Δ^{α}-hexenoic acid and the corresponding γ-lactone.

(B) *The liquid addition products.* The brown oil which accompanied the solid addition product was a mixture of several substances. In order to facilitate the economical isolation of the latter in sufficiently large quantities and also to afford a means of determining the composition of the original crude addition product from experiment to experiment, the following separative procedure was adopted.

The ethereal solution of the crude addition product was concentrated to smaller bulk and extracted with $NaHCO_3$aq. The alkaline solution was extracted with fresh Et_2O, and the extract combined with the main ethereal solution. The ethereal liquor then contained an oily material (substance A). The alkaline liquor contained sorbic acid, the above-described solid lactone–acid mixture, and an oily addition product (substance B). On acidification the sorbic acid was pptd. together with substance B; the crystals of the former were filtered off and washed with H_2O, and substance B was obtained together with the solid lactone–acid mixture by repeated extraction of the oily filtrate with Et_2O and evaporation of the extract. The residue so obtained was *very thoroughly* agitated with a little H_2O: the solid lactone–acid mixture dissolved, and was recovered by extraction with Et_2O, whereas substance B remained undissolved.

Examination of substance B. This was a viscous oil which decomposed above 140°/5 mm., yielding a sublimate of sorbic acid. It reduced $KMnO_4$ rapidly and effervesced vigorously on treatment with $NaHCO_3$aq., but gave an indefinite end-point on titration with baryta. There is every indication that it is to be formulated as an unstable form (readily suffering ring-opening) of the *γ-lactone* of *δ-chloro-γ-hydroxy-Δ^{α}-hexenoic acid*, isomeric with the solid form already described (Found: Cl, 24·05. $C_6H_7O_2Cl$ requires Cl, 24·2%). Confirmation of this constitution was furnished by the nature of the products obtained (a) on hydrogenation and (b) on oxidation.

Hydrogenation. The chloro-lactone (20 g., dissolved in H_2O, 200 c.c., and Me_2CO, 300 c.c.) was catalytically reduced in presence of colloidal Pd, about 33% in excess of 1 mol. of H_2 being absorbed. A lactone–acid mixture (16 g.) was obtained, from an ethereal solution of which $NaHCO_3$aq. extracted the acidic portion (8 g.); this was regenerated and distilled, yielding some lactone (1·8 g.), which was combined with the lactonic material obtained from the ethereal liquor. From the acidic residue (5·1 g.), by re-treatment with $NaHCO_3$aq., a further small quantity of lactone was removed: the acid (4 g., obviously not homogeneous) (Found: Cl, 20·3%) could not be identified. The combined lactonic portions (7·5 g.) distilled at 80—100°/5 mm., but consisted almost entirely of two substances which were not completely separable by fractional distillation. The more volatile, b. p. 80—82°/5 mm., was nearly free from Cl and had the characteristics of hexolactone; the remainder, b. p. 82—106°/5 mm., was a mixture of this substance with a chloro-lactone, doubtless δ-chlorohexolactone.

Oxidation. The chloro-lactone (5·5 g.) was oxidised in the same way (b) as the solid lactone–acid mixture, the fifth O being supplied at room temp.: the rate of oxidation was slower than with the latter mixture. The reaction mixture was decolorised with SO_2, acidified with dil. H_2SO_4, and extracted with Et_2O. The extract yielded an oil (2·25 g.) which contained some oxalic acid but only a trace of AcOH (less than 0·05 g.). The main constituent of the oil was α-chloropropionic acid, which distilled as a colourless oil (0·7 g.), b. p. 60—80°/9 mm., leaving a dark undistillable residue (1·5 g.). The chloro-acid was readily convertible with the aid of KCN into methylmalonic acid.

Examination of substance A. This non-acidic mobile oil was stable in ethereal solution, but darkened rapidly after several days when freed from solvent. It contained Cl, reduced $KMnO_4$, and decomposed above 110°/5 mm. to give sorbic acid. Although it gave a pink colour with Schiff's reagent, it was not an aldehydic degradation product of a monochlorohydrin: rather it appeared to be the somewhat impure γ-lactone of a dichlorohydrin—either of αδ-dichloro-βγ-dihydroxyhexoic acid or of βδ-dichloro-αγ-dihydroxyhexoic acid. Attempts to obtain a Cl-free derivative by treatment with Na–Hg failed: the product was a mixture of a saturated lactonic oil and an unsaturated acidic oil, both of which contained Cl. Dehalogenation by means of Zn and EtOH was also unsuccessful. Proof, however, that in the formation of substance A 1 mol. of HOCl had become attached at the γδ-double bond of sorbic acid was obtained by oxidation. The oil (5·2 g.) was treated at 0° with 3% $KMnO_4$aq. (700 c.c.) which contained sufficient AcOH to neutralise the alkali liberated during oxidation, the temp. being finally allowed to rise to 20—25°. The product was α-chloropropionic acid, admixed of course with AcOH. The former was isolated by fractional distillation and converted into methylmalonic acid.

Attempted Formation of Dichlorohydrins.—To an ethereal solution of sorbic acid (5 g.), 1 mol. of HOCl was added, and then, when that had completely reacted (1½ hrs.), a second mol., which disappeared only after 60 hrs. No addition products other than those described above were found; some of the sorbic acid had, however, undergone oxidation to AcOH.

Addition product.	1 Mol. HOCl.	2 Mols. HOCl.
Solid *	3·5 g.	4·1 g.
Acidic oil	1·5	1·5
Non-acidic oil	0·75	2·4
Unchanged sorbic acid	1·0	0·0
	6·75	8·0

* Cl, 21·25%; lactone content, 23·6%.

The proportion of the non-acidic oil which contains the di-addition product (see above) increases somewhat with the increased proportion of the reagent.

Attempted addition of a second molecule of the reagent to the solid (γδ-) mono-addition product failed entirely: slight oxidation occurred but there was no addition.

Rate of Addition.—This was far from constant with different preps. of sorbic acid but was approximately the same for any one prep. The records of 9 experiments showed that the time of addition for very carefully purified specimens was only from $\frac{1}{2}$ to $\frac{1}{8}$ that required for less pure specimens.

Yield of Addition Products.—The percentages of the products isolated in the different experiments varied almost solely in accordance with the proportion of the sorbic acid which had entered into reaction. Special experiments in which considerable quantities of material were employed showed that the solid lactone–acid mixture is formed from about 50—60%, the acidic liquid isomeride of the lactonic component of this mixture (γ-lactone of δ-chloro-γ-hydroxy-Δ^{α}-hexenoic acid) from about 20—25%, and other products, including the di-addition product, from 15—30% of the sorbic acid consumed. $\gamma\delta$-Addition products (of the two varieties) thus appear to be formed from 70—85%, and possibly more, of the sorbic acid consumed.

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