CCLXIV.—*The Modes of Addition to Conjugated Unsaturated Systems. Part II. The Reduction of Conjugated Unsaturated Acids by Metals dissolving in Aqueous Media.*

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IN Part I of this series (J., 1928, 904) dealing with conjugative additions, we classified addenda into three categories according to whether (*Case* 1) both parts are stable as anions (*e.g.*, Br_2), (*Case* 2) one part is stable as an anion and the other as a kation (*e.g.*, HBr, HCN), or (*Case* 3) both parts are stable as kations (*e.g.*, H_2); and we included in the paper a detailed discussion of part of the field relating to Cases (1) and (2). The present paper contains a partial survey of the portion of the subject represented by Case (3).

Our immediate object is to consider the reduction of conjugated unsaturated compounds by metals dissolving in aqueous (or alcoholic) media, but it is necessary first briefly to refer to reduction by such agents in a more general way.

The view that hydrogen generated at the surface of a metal is in a chemically distinct (" nascent ") form is widely held, and the established fact that changes in chemical and physical conditions alter the manifestation of reducing power does not, of course, dispose of this chemical theory, since the activity of a reactive entity formed at a surface will naturally depend on its immediate environment. The theory has, however, for a long time been closely linked with the idea that the active form consists of uncombined hydrogen atoms,* and this, we presume, would imply that the simplest reductions at olefinic or other double linkings involve the successive addition of two hydrogen atoms. This view will not be pursued here, for we do not find that it leads to a satisfactory theory of the reduction of organic compounds generally. We shall assume a three-stage process which may be described for the olefinic linking as follows:

(i) The unsaturated molecule, polarised in the electric field at the surface of the metal, extracts a proton from the aqueous or alcoholic solution; this proton becomes attached to that atom (C_α) which most readily tolerates the negative polarisation charge developed prior to co-ordination :

$$\overset{\curvearrowright}{C_\beta{=}C_\alpha}\longrightarrow X+\overset{\oplus}{H}\rightleftharpoons\overset{\oplus}{C_\beta}-CH-X.$$

It seems best to regard this process as reversible, and as almost

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* The same view is reflected in its application to electrolytic reduction (compare, for instance, Allmand and Ellingham, " Applied Electro-chemistry," 1924, pp. 96, 99).

entirely dependent for its left-to-right progress on a speedy metamorphosis of the unstable complex kation.

(ii) The kation possesses an electron-sextet at C_β and its electron-affinity exerted in the region of the metallic surface locally breaks down—temporarily punctures, as it were—the electrostatic potential barrier inhibiting the escape of metallic electrons. The successive absorption of the two electrons necessary to complete the octet converts * the kation into an anion $\overset{\ominus}{C_\beta}—C_\alpha H—X$.

(iii) The anion extracts a second proton from the solution, giving $C_\beta H{\cdot}C_\alpha H{\cdot}X$.

Consideration of stage (i) shows that this picture of the process offers an immediate explanation of the well-known fact that the only aliphatic olefinic acids which are reducible by metals in aqueous media are the αβ-unsaturated acids. We see, further, that the possession of this structure is but one of the ways in which an olefinic substance can satisfy the more general theoretical requirement that for facile reduction at least one ethenoid carbon atom must be attached to an electron-sink.† By an electron-sink we mean either an electron-attractor, the permanent state of polarisation of which confers on the adjoining carbon atom an affinity for a negative charge, or a charge-distributing mechanism, the polarisability of which endows the carbon atom with a toleration for such a charge, or a group which acts in both ways. It is necessary, in short, to envisage the operation of both the inductive and tautomeric effects, and the category of facilitating groups is thus the same as that which confers prototropic mobility on the $CH{\cdot}C{:}C$ system (Ingold, *Ann. Reports*, 1927, **24**, 106; 1928, **25**, 118). A noteworthy point is that the aryl group must be added to the usual series of electron-absorbing radicals of the type of carboxyl and carbonyl (compare Ingold and Shoppee, this vol., pp. 447, 1199), and this agrees with the facile reduction, not only of αβ-unsaturated acids, ketones, etc., but also of αβ-unsaturated aromatic compounds such as styrene, stilbene, indene, benzylidenefluorene, and numerous substances of similar type. The above considerations leave untouched the question whether those groups, which can in themselves provide a seat for the negative charge, act in this way, as an indirect route for the entrance of the first hydrogen : it can at least be said

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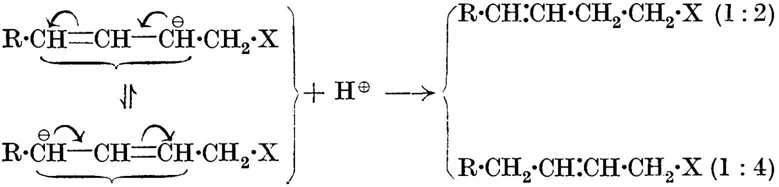
* Sometimes the " puncture " may " heal " after the escape of one electron; the product will then be a radical from which a pinacol-like polymeride would normally be formed.

† This definition may be too narrow : possibly it should be widened by the inclusion of the condition that one ethenoid carbon atom should bear a *strongly* electron-releasing or -repelling group (electron-source), in which case reaction would commence at the other ethenoid carbon, or at a distant point in the case of conjugated systems (compare p. 2025, footnote).

that, in the analogous problem which arises in connexion with the internal facilitation of prototropy, the answer appears to be an affirmative (Part I, *loc. cit.*).

At the conclusion of stage (ii), which is regarded as an almost immediate sequel to the first stage, *negative* hydrogen ($\mathrm{H}^{\cdot}$,2e) has been added to the double linking. We now perceive a close analogy with the halogen additions discussed in Part I; for just as in these additions unstable positive halogen first unites, leaving the ordinary halide ion to combine later, so, according to this hypothesis of reduction, unstable negative hydrogen is first added on, leaving the ordinary positive hydrogen ion to unite later. The advantage of this analogy is that it persists in the subsequent pursuit of the theory in relation to stage (iii), and especially to the complications which affect this stage in the reduction of conjugated unsaturated compounds. We find, indeed, that, just as the course followed by the addition of halogens to conjugated olefinic systems bearing electron-releasing groups can be correlated with the principles of anionotropy (see Part I, *loc. cit.*), so also the course of addition of hydrogen to conjugated unsaturated systems bearing electron-absorbing groups can be correlated with the principles of prototropy; for in conjugated compounds stage (iii) represents the final union of the ions of a prototropic system (three-carbon in the case of butadiene derivatives), and the proportion in which the products will appear should therefore depend on the distribution of the charge in the electromeric anion, as determined by the relative degrees of electron-absorption of the groups (R, CH_2X) terminating the system (Ingold, *loc. cit.*; Ingold and Shoppee, *loc. cit.*). As in the case discussed in Part I, the correlation leads to a simple and definite theory of the course of addition. It remains now to be seen to what extent its consequences accord with established fact.



$$\left.\begin{array}{c} R\cdot CH{=}CH{-}\overset{\ominus}{C}H\cdot CH_2\cdot X \\ \updownarrow \\ R\cdot\overset{\ominus}{C}H{-}CH{=}CH\cdot CH_2\cdot X \end{array}\right) + H^{\oplus} \longrightarrow \left\{\begin{array}{l} R\cdot CH{:}CH\cdot CH_2\cdot CH_2\cdot X\ (1:2) \\ \\ R\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot X\ (1:4) \end{array}\right.$$

Two extreme cases may first be considered on account of their simplicity. In the first place any butadiene, hexatriene, or octatetraene, etc., which is terminated at both ends by electron-absorbing groups (*e.g.*, CO_2H, Ph) and is otherwise free from such groups, will add hydrogen terminally, because the anionic charge, the location of which controls stage (iii), will be stabilised terminally. Well-established illustrations are available on the exclusive 1 : 4-reduction of muconic acid, $\Delta^{1:3}$-dihydroterephthalic acid, cinnamylideneacetic acid, cinnamylidenemalonic acid, αδ-diphenylbutadiene, and naphthalene; examples of the terminal reduction of longer unsaturated chains are available in the 1 : 6-reduction of αζ-diphenylhexatriene, the 1 : 8-reduction of αθ-diphenyloctatetraene, and the 1 : 10-reduction of ακ-diphenyldecapentaene (Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 123). We know of no exception to this general rule. It is interesting to observe, by comparison with Part I, the difference between the theoretical requirements regarding the addition of bromine and hydrogen to αδ-diphenylbutadiene, and the agreement, in each case, of observation with these requirements.

It is an equally definite consequence of the theory that any butadiene which bears two groups of the type considered in the 1 : 2-positions and is otherwise free from such groups will add hydrogen in the 1 : 2-positions. A similar rule can be formulated for variously substituted hexatrienes and octatetraenes, but we know of no investigation bearing on the point, which thus awaits future experimental test.*

Our own investigation has been concerned with cases, lying between these two extremes, for which the theory predicts a mixture of dihydro-isomerides and gives some indication of the proportions to be expected. This group of conjugated unsaturated compounds includes most of the simpler alkyl derivatives of vinylacrylic acid. Prior to the commencement of the work the reduction of several of these acids had been investigated, but the general conclusion reached, *viz.*, that the products were in all cases those of 1 : 4-addition, was strongly at variance with expectation based on theory. The following is a tabular summary of the work referred to, the reducing agent in every case being sodium amalgam.

Acid reduced.	Medium.	Addition.	Authors.
Vinylacrylic	Acid; alkaline	1 : 4	T.
Sorbic	,, ,,	1 : 4	F., R.
α-Methylsorbic	Acid	1 : 4	A.
α-Ethylsorbic	,,	1 : 4	A.
γ-Methylsorbic	,,	1 : 4	A.
βδ-Dimethylsorbic	Acid; alkaline	1 : 4	L., A.

T = Thiele and Jehl, *Ber.*, 1902, **35**, 2320.
F = Fittig and others, *Annalen*, 1872, **161**, 309; 1880, **200**, 42; 1894, **283**, 117.
R = Rupe, *ibid.*, 1902, **327**, 115.
L = Rupe and Lotz, *ibid.*, 1909, **369**, 348.
A = Auwers and Heyna, *ibid.*, 1923, **434**, 140.

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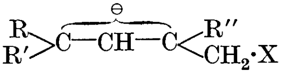
* Pending an investigation indicated below, we are prepared, for reasons already given (Part I; Ingold, *Ann. Reports*, 1928, 152; Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1929, **1**, ix, 421), also to entertain the view that phenyl may act in the manner indicated in the footnote on p. 2023. The alternative has no practical consequences regarding any of the examples of orientation quoted in the text; but it has for certain alphyl derivatives of α-phenylbutadiene, the reduction of which it is proposed to re-examine.

The acids which we have examined include three from the above list. Whilst this work, which aimed at quantitative estimation of the dihydro-isomerides, was still in progress,* Evans and Farmer (J., 1928, 1644) and Goldberg and Linstead (*ibid.*, p. 2343) independently established the presence of a large proportion of the 1 : 2-dihydro-compound in the reduction product of sorbic acid, thus providing the first experimental indication that the conclusions summarised above require revision. Similarly we find that (with a qualification to be mentioned later) vinylacrylic, sorbic, and β-methyl- and βδ-dimethyl-sorbic acids all give substantial quantities of 1 : 2-reduction product.

We have employed three methods of estimation (measurement of refractive index, permanganate oxidation, and ozonolysis, standardised in each case against synthesised dihydro-compounds), which, where they have been applied to the same reduction product, have given results in close agreement. The following table records our estimates of the proportion of 1 : 2-dihydro-isomerides formed from the above four acids by sodium amalgam in both acid and alkaline media. The reduction of sorbic acid by metals other than sodium will be referred to later.

	1 : 2-Dihydro-isomeride formed from			
Medium (aqueous).	Vinylacrylic acid.	Sorbic acid.	β-Methyl-sorbic acid.	βδ-Dimethyl-sorbic acid.
$NaHCO_3$	0%	40%	28%	38%
$CH_3{\cdot}CO_2H$	18	55	—	—

It is not difficult to see that these results are in excellent general agreement with the theory given, according to which the proportions are determined by the relative toleration of C_β and C_δ for the negative charge in an electromeric anion of the type



$$\begin{matrix}R\\R'\end{matrix}\!>C-\overset{\ominus}{CH}-C<\!\begin{matrix}R''\\CH_2{\cdot}X\end{matrix}$$

The repulsion of electrons by the groups attached at each end of the three-carbon system will decrease, and the absorption of electrons by these groups will increase, the toleration of the corresponding carbon atom for the anionic charge. In the examples mentioned, R,R′, and R″ are either H or CH_3, and X is CO_2H or $CO_2^{\ominus}$ according as the medium is acid or alkaline. Since all the groups are saturated at the point of union with the three-carbon system, their inductive effects constitute the primary polar influence; the series has, in fact, been chosen so that the tautomeric effect, which in general it

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* A brief outline of the theory here described, and of its application to the reduction of sorbic acid, was published at the time (Ingold, *Chem. and Ind.*, 1928, **47**, 269).

would be necessary to take into account, does not complicate the problem in this preliminary study. In theory, the direct effect should also be envisaged; but since the study of aromatic substitution has shown that this is a feeble polar influence, and that, in any event, it follows the inductive in sign and magnitude as regards its origination, it is legitimate as an approximation to regard its specific influence as absorbed in that attributable to the inductive effect. A completely general treatment would take count of spatial influences in addition, but again the examples under discussion are such that these are expected to be negligible.

The order of inductive electron-repulsion, $CH_3 > H$, is well known, and the order $CH_2{\cdot}CO_2^{\ominus} > CH_3 > CH_2{\cdot}CO_2H$ follows from the known electron-attraction of the carboxyl group and electron-repulsion of the carboxylate ion. The order $CH_2{\cdot}CO_2H > H$ may be inferred from the order $CH_2{\cdot}CO_2Et > H$ established by the unpublished experiments by Dr. F. R. Shaw on the nitration of ethyl phenylacetate. The complete sequence is therefore

$$CH_2{\cdot}\overset{\ominus}{C}O_2 > CH_3 > CH_2{\cdot}CO_2H > H.$$

It follows immediately that the reduction of vinylacrylic acid in acid solution should lead to an excess ($CH_2{\cdot}CO_2H > H$) of the 1 : 4-dihydro-derivative (Found : 82%), and that its reduction in alkaline solution ($CH_2{\cdot}\overset{\ominus}{C}O_2 >>> H$) should produce a much larger excess (Found : 100%). In the reduction product of sorbic acid in acid solution ($CH_3 > CH_2{\cdot}CO_2H$), however, the 1 : 2-compound should be the major constituent (Found : 55%); but in alkaline solution ($CH_2{\cdot}\overset{\ominus}{C}O_2 > CH_3$) the 1 : 4-isomeride should again predominate (Found : 60%). Under the same conditions, the 1 : 4-compound should predominate more strongly in the reduction product of β-methylsorbic acid than in that of sorbic acid (Found : 72%), owing to the electron-repulsion of the additional β-methyl group; but the introduction of a δ-methyl group should produce an effect in the opposite sense, and in the reduction product of βδ-dimethylsorbic acid the 1 : 4-dihydro-compound should still predominate, but less strongly than for the β-methyl acid; in short, the proportion should lie between 50% and 72% (Found : 62%).

In the circumstances, we are not disposed to accept as final the conclusions of Auwers and Heyna regarding the nature of the reduction products of α-methyl-, α-ethyl-, and γ-methyl-sorbic acids by sodium amalgam in acid solution. We have not revised these experiments, but when they are repeated it should be found that the proportion of 1 : 2-addition product should not be very different from that given by sorbic acid under the same conditions.

We had intended to include in this communication a quantitative study of the reduction of sorbic acid by a variety of metals, ranging in the electrochemical series from sodium to tin, in media of increasing acidity, the object being to vary independently the ease of access of electrons and protons to the unsaturated system. Unfortunately, experimental difficulties have so far defeated detailed study of several of the most interesting cases, and our results are too fragmentary to merit theoretical discussion. The reduction of sodium sorbate in neutral and in alkaline aqueous solution with aluminium amalgam was successfully carried out, and gave 45% as the proportion of 1 : 2-addition product, that is, a few units % more than was found for reduction with sodium amalgam. Reduction of sorbic acid in mineral acid solutions with zinc, tin, and stannous ion led to the formation of the caprolactone of Fittig and Hjelt (*Annalen*, 1881, **208**, 67).

γ-Caprolactone is known (Fichter and Langguth, *ibid.*, 1900, **313**, 377) to be produced by hydration of the 1 : 2-dihydro-acid.

Some new synthetic work, relating to certain unsaturated acids required for this investigation, is described in the experimental section.

EXPERIMENTAL.

(1) *Preparation of Materials.*

Vinylacrylic Acid.—Malonic acid (300 g.) was dissolved in dry pyridine (500 g.), and acraldehyde (150 g.) gradually added to the cooled mixture. After standing at 0° for a few hours and at the room temperature over-night, the mixture was heated on the steam-bath under reflux for 4 hours, poured on crushed ice, acidified with hydrochloric acid (Congo-red), and thoroughly extracted with ether. The vinylacrylic acid which crystallised at the ordinary temperature from the concentrated ethereal solution was collected in fractions until the viscosity of the solution inhibited filtration. The liquid was then evaporated in a current of dry air, and the viscous residue rapidly distilled in four portions under 5 mm. pressure; the distillate then crystallised and was drained. The crude acid (90 g.) was crystallised from ether–ligroin (1 : 3) between the b. p. and 0°. Other preparations were crystallised from water between 55° and 15°, a small amount of a white rubber-like polymeride (increasing if the preparation suffers undue delay) being filtered from the warm solution. The m. p. (74—76°) was not changed by further crystallisation (compare Kohler and Butler, *J. Amer. Chem. Soc.*, 1926, **48**, 1036) (Found: C, 61·2; H, 6·3. Calc.: C, 61·2; H, 6·2%).

β-*Methylsorbic Acid.*—Auwers and Heyna state that they were unable to obtain this substance by a method identical in principle with that described below.

A mixture of zinc turnings (66 g.), ethyl bromoacetate (167 g.), ethylideneacetone (93 g.), and dry benzene (300 c.c.) was warmed on the steam-bath under reflux until a vigorous reaction had been initiated. When the initial reaction had subsided, the mixture was boiled for 20 minutes and decomposed with ice and dilute sulphuric acid. Separation of the benzene layer, followed by extraction of the aqueous layer with benzene, evaporation of the combined benzene solutions, and distillation gave *ethyl* β-*hydroxy*-β-*methyl*-Δ^{γ}-*hexenoate*, $CHMe{:}CH{\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2Et$, b. p. 89—93°/12 mm. (Found : C, 62·75; H, 9·3. $C_9H_{16}O_3$ requires C, 62·8; H, 9·4%), in 50% yield.

When the hydroxy-ester was heated with half its weight of finely powdered, anhydrous potassium hydrogen sulphate, water was eliminated, but the formation of a high-boiling product impaired the yield of ethyl β-methylsorbate. It was found better to distil the hydroxy-ester (110 g.) directly under ordinary pressure. Ethyl β-methylsorbate (75 g.) and water passed over below 205°, and a less volatile residue remained. Hydrolysis of the ester with an excess of 15% alcoholic potassium hydroxide yielded an acid product which on analysis gave the correct figures for β-methylsorbic acid, but was obviously a mixture. Crystallisation from the minimum quantity of hot alcohol yielded a pure β-*methylsorbic acid*,

$$CHMe{:}CH{\cdot}CMe{:}CH{\cdot}CO_2H$$

(28 g.), which separated in either colourless needles or glistening plates, m. p. 120° (Found : C, 66·5, 66·55; H, 7·9, 7·9. $C_9H_{10}O_2$ requires C, 66·65; H, 8·0%). Dilution of the mother-liquor with ice-water gave a crystalline product, m. p. 60—74°, which was extremely soluble in the usual solvents (except water), and tended to separate from dilute alcohol as an oil. After many crystallisations from this solvent, it had m. p. 74—76°, and analysis indicated it to be an *isomeride* of the β-methylsorbic acid described above (Found : C, 66·25; H, 7·9%). We are not certain that our specimen was perfectly free from the higher-melting form, as there was insufficient for purification by regeneration from a derivative. The less fusible acid was converted by treatment with thionyl chloride into its chloride, b. p. 94—95°/15 mm., and thence into its *amide* and *anilide*; the former crystallised from benzene in prismatic needles, m. p. 147—148° (Found: C, 67·2; H, 8·8. $C_7H_{11}ON$ requires C, 67·2; H, 8·8%), and the latter from alcohol in needles, m. p. 134—135° (Found: C, 77·3; H, 7·4. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%).

Δ^{β}-*Pentenoic Acid.*—This was prepared in the usual way by reduction of vinylacrylic acid with sodium amalgam in alkaline solution, and freed from any trace of an isomeric acid by conversion into its crystalline dibromide, m. p. 64°, and regeneration from the fully purified substance by treatment with excess of zinc dust and alcohol.

β-Methyl-Δ^{γ}-hexenoic Acid.—A mixture of ethyl α-bromobutyrate (200 g.) and diethylaniline (300 g.) was vigorously boiled under reflux for 6 hours, and then crystallised on cooling; it was thereupon treated with rather more than the calculated amount of 15% hydrochloric acid, and thoroughly extracted with ether. The ethyl crotonate obtained by distillation of the residue from the extract was collected at 130—145° (47 g.) and the greater portion had b. p. 135—137°.

Ethyl crotonate (160 g.) was treated below 10° with a solution (600 g./l.) of hydrogen bromide in glacial acetic acid. After 18 hours the mixture was poured into water, and the heavy oil separated, washed with aqueous sodium carbonate, dried, and distilled. A volatile fraction (30 g.) was collected, together with ethyl β-bromobutyrate, b. p. 74—76°/13 mm. (175 g.).

A solution of ethyl β-bromobutyrate (142 g.) in alcohol (150 c.c.) was gradually added to a well-cooled solution of ethyl sodioacetoacetate prepared from sodium (16·75 g.), absolute alcohol (350 c.c.) and ethyl acetoacetate (95 g.). The mixture, after being kept for some time at the ordinary temperature, was heated on the steam-bath for 4 hours, distilled to remove the bulk of the alcohol, and mixed with water. The oil, which was extracted with ether and fractionated, yielded a considerable amount of a mixture of ethyl crotonate and ethyl acetoacetate, together with 35 g. of *ethyl α-acetyl-β-methylglutarate*, b. p. 148—150°/10 mm. (Found: C, 59·0; H, 8·5. $C_{12}H_{20}O_5$ requires C, 59·0; H, 8·2%). The ester gave a violet colour with ferric chloride, and is presumably a mixture of the tautomerides $CO_2Et{\cdot}CH_2{\cdot}CHMe{\cdot}CH(CO_2Et){\cdot}COMe$ and $CO_2Et{\cdot}CH_2{\cdot}CHMe{\cdot}C(CO_2Et){:}CMe{\cdot}OH$.

A solution of the ester (60 g.) in alcohol (140 c.c.) and water (100 c.c.) was treated at 0° with 1000 g. of 3% sodium amalgam and 500 c.c. of water, each added in ten equal portions at intervals of 1 hour. Reduction and hydrolysis occurred together, and after being kept over-night at the ordinary temperature, the solution was separated from the mercury, acidified with dilute sulphuric acid, and extracted with ether. Some decomposition with loss of carbon dioxide occurred during distillation of the product and was completed by heating the distillate, b. p. 160—240°/10—20 mm., rapidly to 240° (thermometer in liquid) at the ordinary pressure. Distillation then commenced, and the product, which passed over below 320°, was distilled in steam, and the distillate made alkaline with sodium hydrogen carbonate, and extracted with ether to remove any lactone. *β-Methyl-Δγ-hexenoic acid*, $CHMe{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$, was obtained from the acidified solution by extraction with ether as an oil, b. p. 103—105°/9 mm. (Found : C, 65·3; H, 8·8. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%). On ozonolysis it gave methylsuccinic acid in excellent yield, but since the unsaturated acid, unlike its analogues, became slightly coloured on keeping, the specimen must have contained some small amount of impurity which distillation did not remove.

Other Materials.—The other acids utilised in the work were all prepared by recorded methods, excepting sorbic acid, a pure specimen of which, purchased from T. Schuchardt, G.m.b.H., was used throughout. An attempt to exploit the synthesis described in the preceding section for the preparation of βδ-dimethyl-Δγ-hexenoic acid by replacing the reduction stage by a Grignard reaction between the ketonic ester and magnesium methyl iodide failed—we believe because the enolic form of the ester decomposed the Grignard reagent.

(2) *Preparation and Analysis of the Reduction Products.*

Preparation.—In order to obtain trustworthy analytical results it was necessary to ensure that the mixtures of 1 : 2- and 1 : 4-dihydro-compounds resulting from reduction should be free from other substances. The separation by distillation of small amounts of pinacol-like reduction products, or polymerides of high molecular weight, when these were present, gave no difficulty. Partial reduction to saturated acids was not contemplated as a serious possibility, since βγ- and γδ-unsaturated acids are known to resist the action of the reducing agents we employed; furthermore, βγ-unsaturated acids are not isomerised to their readily reducible αβ-unsaturated isomerides in sodium hydrogen carbonate, the most alkaline solutions used in our reductions. Undetected contamination by small amounts of unconverted diolefinic acid was, however, a danger which required special attention. Although the dihydro-compounds boil only about 10° lower than the diolefinic acids from which they are derived, it was found possible to effect quantitative removal of the latter substances by distillation under reduced pressure provided that certain conditions were satisfied, *viz.*, (1) that the heating be conducted with a liquid bath kept at approximately the b. p. of the diolefinic acid under the pressure used, (2) that the distillation proceed slowly (about 2 drops per minute), (3) that an adequate column (sealed to the flask) be employed, and (4) that the pressure be steady. The following are some illustrative tests.

Δγ-Hexenoic acid (10·0 g.) and sorbic acid (0·2 g.) were distilled together at 16 mm. under the conditions stated; the distillate weighed 9·85 g. and the sorbic acid, which crystallised on the sides of the flask but not in the column, was almost completely recovered. Δ^{γ}-Hexenoic acid (10·0 g.), sorbic acid (0·2 g.), and 2·5 g. of a "bimolecular product" (Section 3), obtained as a residue in a large-scale reduction of sorbic acid, were similarly distilled; the result was as before except that only part of the sorbic acid crystallised on the sides of the flask, part presumably remaining dissolved in the non-volatile bimolecular product at the bottom. Contamination by 2% of unreduced material could in general be detected with certainty, excepting that, in the case of the reduction product of vinylacrylic acid, the slow distillation was found to polymerise this acid to a non-volatile rubber which was thus automatically removed. A second distillation was usually carried out as an additional precaution. Reduction products in which any unaltered material was detected were either set aside or subjected to further action by the reducing agent. Too prolonged treatment, or treatment with an excessive quantity of reducing agent was, however, detrimental, and some of the products had to be discarded from this cause also. Apparently some form of polymerisation was induced: the prepared reduction products developed a haze on keeping, and in extreme cases of over-reduction the yield was impaired by the formation of high-boiling material.

Analysis.—(a) *Refractive indices.* The measurements were made with a Pulfrich instrument, using the green line of the mercury arc and an auxiliary slit to increase the accuracy of setting. The drum of the instrument was used as is customary in measurements of dispersion, so that the differences between the observed indices are more accurate than their absolute values. The reduction products and corresponding synthetic isomerides were measured rapidly one after another at the same temperature.

(b) *Oxidation with permanganate.* Estimation of the succinic acid formed by oxidation with permanganate was employed only for the reduction products of sorbic acid, since the correction for incomplete formation of succinic acid from the Δ^{γ}-isomeride was too great in the other cases. Even for Δ^{γ}-hexenoic acid the percentage conversion was not high, but it was constant (68%) and, under the standard conditions used throughout, could at any time be reproduced to within 2%. Extraction of the succinic acid with organic solvents was quantitatively unsatisfactory, since the material thus obtained, after drying to constant weight, was contaminated with oxalic acid and small amounts of a coloured oil, and therefore could not be weighed as *pure* succinic acid without further treatment involving losses. A separation of the acid products through their barium salts was finally resorted to.

The acid, or mixture of acids, to be examined (2—3 g.) was dissolved in the calculated amount of standard potassium hydroxide and the solution diluted to 1 l., and mechanically stirred at the ordinary temperature whilst a 3% solution of potassium permanganate, equivalent to 7 atoms of available oxygen, was delivered from a dropping funnel at an approximately constant rate during 7 hours. The mixture was stirred for a further 16 hours, and the excess of permanganate destroyed by the addition of aqueous formaldehyde. The oxides of manganese were filtered off and repeatedly extracted with boiling water, and the combined filtrates were evaporated to a small bulk, filtered from a small further precipitate of manganese oxides, acidified (Congo-red) with hydrochloric acid whilst still hot, and boiled to expel carbon dioxide. The solution was then neutralised (phenolphthalein) with carbonate-free, pure sodium hydroxide, and treated with a solution of barium chloride (15—20 g.) in the minimum quantity of boiling water. The mixture was boiled for 30 minutes, and the crystalline precipitate collected (Gooch), washed with sufficient boiling water to make the total volume of the filtrate 100 c.c., and dried to constant weight at 120°. The mixture of barium succinate and oxalate was washed with 50% acetic acid (50—60 c.c.), then with water, and again dried to constant weight. The difference of the weights, plus 0·165 g. (the correction, previously determined under the same conditions, for the solubility of barium succinate in the 100 c.c. of neutral filtrate), gave the weight of barium succinate. Succinic acid, subsequently isolated, was quite pure and colourless.

(c) *Oxidation with ozone and hydrogen peroxide.* Fission with ozone followed by oxidation of the products with hydrogen peroxide under the conditions described below led in all four cases to the formation of pure succinic or methylsuccinic acid in high yield. With the synthetic Δ^{γ}-isomerides the conversions were so close to 90% that this figure has been employed uniformly in correcting the results obtained from products of reduction. The procedure differed slightly according as succinic or methylsuccinic acid was the product to be estimated.

(i) In the former case, the acid to be examined (5—7 g.) was treated in chloroform solution at 0° with ozonised oxygen during 36 hours. The chloroform was then removed in a vacuum at the ordinary temperature, and the residue, which was largely solid, was boiled with water under reflux for 2 hours, cooled, mixed with 40—50 c.c. of 20-vol. hydrogen peroxide, and kept over-night. The solution was then evaporated on the steam-bath, and the residue dissolved in water. The solution was distilled to dryness at about 60° under reduced pressure, and the residue heated under a short reflux condenser at 150° (bath temperature) for 1 hour. The cooled product was extracted with water, and the solution filtered from a trace of flocculent material, and evaporated. The residual succinic acid (m. p. 184°) was dried to constant weight.

(ii) In those cases in which methylsuccinic acid was the final product, the heating at 150° and the third evaporation were omitted; the scarcely ponderable trace of flocculent substance, which appeared in these experiments also, was removed by filtration before the second evaporation. The resulting methylsuccinic acid had m. p. 111°.

(3) *Details of the Reductions and Analyses.*

Vinylacrylic Acid.—Expt. 2. The acid (19·6 g.) was dissolved in saturated sodium hydrogen carbonate (300 c.c.), and the solution, diluted to 1200 c.c., was treated at 40—45° with continuous stirring and passage of carbon dioxide with 3% sodium amalgam (3 kg.), gradually added during 96 hours. During this period further small amounts of water were added, and the stirring was continued for 48 hours after the whole of the amalgam had been introduced. After separation of the mercury, the solution was acidified (Congo-red), and the reduction product extracted with ether, dried with sodium sulphate, and prepared for analysis as described in Section 2. The final specimen (16·0 g.) had b. p. 94—96°/17 mm. (Found : C, 59·9; H, 8·0. Calc. : C, 60·0; H, 8·0%). (Method *a*.) Δ^{β}-Pentenoic acid had $n_{5461}^{10^\circ}$ 1·44090, the reduction product $n_{5461}^{10^\circ}$ 1·44100, and Δ^{γ}-pentenoic acid $n_{5461}^{10^\circ}$ 1·43528; hence, Δ^{γ}-pentenoic acid = 0%.

Expt. 3. The previous experiment was duplicated. The product (16·0 g.) had b. p. 95—97°/18 mm. (Found : C, 59·7; H, 7·9%). (Method *c*.) Succinic acid, nil. Found : Δ^{γ}-Pentenoic acid, 0%.

Expt. 5. A solution of vinylacrylic acid (19·6 g.) in acetic acid (300 c.c.) and water (600 c.c.) was treated at 15—25° with 3% sodium amalgam (6 kg.) added gradually during 48 hours. During this period acetic acid (total 300 c.c.) and water (total 400 c.c.) were added in portions at intervals, and when the introduction of the amalgam had been completed the solution was diluted with a further quantity of water, kept for 24 hours, acidified with concentrated hydrochloric acid (1 l.), and extracted repeatedly with ether (total, 4 l.). The product, b. p. 95—97°/18 mm., was isolated as before, excepting that the use of a moderately long column was necessary for the removal of the acetic acid (Found : C, 59·8; H, 8·0%). (Method *a*.) Δ^{β}-Pentenoic acid had $n_{5461}^{10^\circ}$ 1·44100, the reduction product $n_{5461}^{10^\circ}$ 1·44000, and Δ^{γ}-pentenoic acid $n_{5461}^{10^\circ}$ 1·43528; hence, Δ^{γ}-pentenoic acid = 17·5%.

Expt. 6. The preceding experiment was duplicated. The product (12·0 g.) had b. p. 95—97°/18 mm. (Found : C, 59·8; H, 7·9%).

(Method *c.*) 5·40 G. gave 1·07 g. of succinic acid, *i.e.*, 17%. Found : Δ^{γ}-Pentenoic acid, 19%.

Sorbic Acid.—Expt. 7. A solution of sorbic acid (11·2 g.) in the calculated quantity of dilute sodium hydroxide solution was treated at about 40° with 3% sodium amalgam (1·5 kg.) during 72 hours, throughout which mechanical stirring and a stream of carbon dioxide were maintained. After a further 24 hours, the product was worked up as described for Expt. 2. The analytical specimen of dihydro-acids (7·2 g.) had b. p. 109—110°/18 mm. (Found : C, 63·2; H, 8·5. Calc. : C, 63·2; H, 8·8%); a viscous residue (2 g.), b. p. about 247°/18 mm., was also obtained (see Expt. 10). (Method *b.*) 1·605 G. gave 1·9150 g. of barium succinate. Found : Δ^{γ}-Hexenoic acid, 38·5%.

Expt. 8. The preceding experiment was duplicated; the yield and b. p. were the same (Found : C, 62·8; H, 8·8%). (Method *c.*) 5·70 G. gave 2·16 g. of succinic acid, *i.e.*, 36·5%. Found : Δ^{γ}-Hexenoic acid, 40·5%.

Expt. 10. Sorbic acid (50 g.) was reduced in the same way. The dihydro-product was used in an unsuccessful attempt to separate the isomerides through their cadmium salts. The high-boiling residue (9·5 g.) had b. p. 245—247°/17 mm. We presume that this consists partly of one or more pinacol-like reduction products from 2 mols. of sorbic acid, but analysis indicated that impurities of another composition were also present; and this conclusion is confirmed by the fact that the analogous product from β-methylsorbic acid (see below) was only partly solid, and that only the solid portion gave correct analytical figures for a compound of an analogous constitution.

Expt. 11. A solution of sorbic acid (11·2 g.) in acetic acid (300 c.c.) and water (100 c.c.) was treated at 15—20° during 48 hours with 3% sodium amalgam. After the first 24 hours further quantities of acetic acid (250 c.c.) and water (200 c.c.) were added, and 24 hours after the introduction of the amalgam had been completed the product was worked up as described for Expt. 5. The dihydro-specimen (6·5 g.) had b. p. 108—109°/17 mm. (Found : C, 63·3; H, 8·7%). (Method *b.*) 1·669 G. gave 1·379 g. of barium succinate. Found : Δ^{γ}-Hexenoic acid, 55%.

These estimates of the proportions of Δ^{γ}-acid formed on reduction of sorbic acid by sodium amalgam in alkaline and acid solution, *viz.*, 40 and 55% respectively, may be compared with the " minimum proportions," 30 and 40% respectively, found by Evans and Farmer (*loc. cit.*), who, however, used extraction with organic solvents to estimate the succinic acid formed by oxidation (see Section 2, method *b*).

Expt. 14. A solution of sorbic acid (11·2 g.) in *N*-sodium hydrogen carbonate (500 c.c.) was treated at 16—27° each day for three successive days with thin amalgamated aluminium foil (30 g.) and *N*-sodium hydrogen carbonate solution (100 c.c.). After a further 24 hours the product was exactly neutralised and filtered, and the residue thoroughly extracted with water. The combined filtrates were acidified and worked up as in Expt. 7. The dihydro-preparation (7·5 g.) had b. p. 107—108°/16 mm. (Found : C, 63·3; H, 8·5%); a high-boiling residue was also obtained. (Method *b*.) 2·963 G. gave 2·006 g. of barium succinate. Found : Δ^{γ}-Hexenoic acid, 45%.

Expt. 16. The neutral solution from sorbic acid (11·2 g.), together with the calculated quantity of standard sodium hydroxide solution, was treated at the ordinary temperature with moderately stout amalgamated aluminium foil (36 g.). After four days the product was filtered and worked up as in the preceding experiment. The specimen of dihydro-acids (6·22 g.) had b. p. 118°/22 mm. (Found : C, 63·0; H, 8·8%); a high-boiling residue was also obtained. (Method *b*.) 2·600 G. gave 1·732 g. of barium succinate. Found : Δ^{γ}-Hexenoic acid, 44%.

Expt. 17. The preceding experiment was duplicated; the product had b. p. 108—109°/17 mm. (Method *b*.) 3·044 G. gave 2·099 g. of barium succinate. Found : Δ^{γ}-Hexenoic acid, 46%. The mean for the three reductions by aluminium amalgam is therefore 45%.

Expts. 19—25. The reductions of sorbic acid with sodium amalgam and hydrochloric acid and with zinc and acetic acid were incomplete. Reduction at 85° with zinc, tin, and stannous chloride, in a mixture of concentrated hydrochloric and acetic acids led to the formation of the caprolactone described by Fittig and Hjelt (*loc. cit.*), b. p. 107—109°/17 mm., 216—218°/760 mm., as the main product. The specimens gave no immediate evolution of carbon dioxide with saturated sodium hydrogen carbonate, and hence contained no substantial quantity of either of the dihydrosorbic acids. This lactone is characterised by its dissolving in 5—6 parts of water at 0° to a solution, which, on being warmed, becomes strongly turbid between 20° and 40° and clears again above 60°.

β-*Methylsorbic Acid.*—*Expt.* 27. A solution of the acid (10·0 g.) in a slight excess of sodium hydrogen carbonate solution was treated at 40—45° with 3% sodium amalgam (1·5 kg.) under the conditions of Expt. 7. The analytical sample of reduction product (7·7 g.) had b. p. 117—118°/16 mm. (Found : C, 65·5; H, 9·4. Calc. : C, 65·6; H, 9·4%). (Method *c*.) 5·90 G. gave 1·44 g. of methylsuccinic acid. Found : β-Methyl-Δ^{γ}-hexenoic acid, 27%.

Expt. 28. Duplication of the preceding experiment gave a product

(7·7 g.), b. p. 117—118°/16 mm. (Method *c.*) 7·00 G. gave 1·87 g. of methylsuccinic acid. Found : β-Methyl -Δγ-hexenoic acid, 29%.

The less volatile residues from Expts. 27 and 28 partly solidified. They were combined, drained, and crystallised from dilute alcohol, from which colourless needles, m. p. 198—199°, separated. Analysis (Found : C, 66·15, 66·1; H, 8·85, 8·8. $C_{14}H_{22}O_4$ requires C, 66·15; H, 8·7%) indicated one or other of the constitutions,

$$CHMe{:}CH{\cdot}CMe(CH_2{\cdot}CO_2H){\cdot}CMe(CH_2{\cdot}CO_2H){\cdot}CH{:}CHMe,$$
$$CO_2H{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CHMe{\cdot}CHMe{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CO_2H,$$
$$CHMe{:}CH{\cdot}CMe(CH_2{\cdot}CO_2H){\cdot}CHMe{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CO_2H.$$

βδ-*Dimethylsorbic Acid.*—*Expt.* 30. A solution of the acid (14·0 g.) in a slight excess of sodium hydrogen carbonate was treated with 3% sodium amalgam (1·55 kg.) under the conditions of Expt. 27. The sample of reduction product (11·0 g.) had b. p. 120—120·5°/14 mm. (Found : C, 67·5; H, 9·7. Calc. : C, 67·6; H, 9·9%). (Method *c.*) 4·00 G. gave 1·25 g. of methylsuccinic acid. Found : βδ-Dimethyl-Δγ-hexenoic acid, 38%.

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