CCCX.—*The Chemistry of the Three-carbon System. Part XVIII. Quantitative Investigations on the Influence of Alkyl Substituents on the $\alpha\beta$–$\beta\gamma$ Change in Unsaturated Acids: Observations on the Reduction of Sorbic Acid, and a New Synthesis of Pyroterebic Acid.*

By Alan August Goldberg and Reginald Patrick Linstead.

The position of equilibrium in the reversible change between αβ- and βγ-olefinic acids in the presence of alkali appears to be independent of the physical conditions under which the interconversion proceeds (Linstead, J., 1927, 362, 2579). It has, therefore, become possible to ascertain the effect of internal conditions, *i.e.*, molecular substitution, upon the position of equilibrium and upon the ease with which it is attained. The present communication describes an examination of the simplest mono-olefinic acids from this point of view.

In the two butenoic acids, *viz.*, vinylacetic (βγ-) and crotonic (αβ-), the change appears to be irreversible in the direction βγ ⟶ αβ, and the same preponderance of the αβ-form is met with in α- and β-alkylcrotonic acids, although, since in many instances only the αβ-forms have as yet been isolated, the evidence is not final. With

$$\text{(I.)}\quad CH_3\cdot CR_\gamma{:}CR_\beta\cdot CHR_\alpha\cdot CO_2H \overset{\text{KOH}}{\rightleftharpoons} CH_3\cdot CHR_\gamma\cdot CR_\beta{:}CR_\alpha\cdot CO_2H\quad \text{(II.)}$$

the pentenoic acids, a balanced reaction is possible, and we have therefore examined the unsubstituted pentenoic acids themselves

($R_{\alpha,\beta,\gamma} = H$), and two of the three monomethyl derivatives (R_α or $R_\gamma = Me$), the third possible series ($R_\beta = Me$) having already been studied (Kon and Linstead, J., 1925, **127**, 618; Linstead, J., 1927, 355). In addition, the effect of lengthening the chain ("δ-substitution," resulting in the *n*-hexenoic acids) was investigated, and the *cyclo*pentenylacetic acids (III and IV) were studied for comparison with the *cyclo*hexenyl analogues. The unsubstituted

(III.)  (IV.)

$$(\text{III.})\quad \begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\!>C\cdot CH_2\cdot CO_2H \overset{KOH}{\rightleftharpoons} \begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\!>C{:}CH\cdot CO_2H\quad (\text{IV.})$$

pentenoic and hexenoic acids were of especial interest as they were among the original substances studied by Fittig (*Annalen*, 1894, **283**, 47).

The preparation of the ten unsaturated acids used in this work is described in the experimental portion. The methods available for the preparation of α-methyl-Δ^α-pentenoic acid (II; $R_\alpha = Me$, $R_{\beta,\gamma} = H$) did not appear to be very satisfactory, but we find that it can readily be prepared in a state of purity from propaldehyde through the aldol $CH_3\cdot CH_2\cdot CH(OH)\cdot CHMe\cdot CHO$, by dehydration and oxidation by the method of Delépine and Bonnet (*Compt. rend.*, 1909, **149**, 39). A detailed investigation was made into the preparation of terebic acid which was required in the synthesis of pyroterebic acid (I; $R_\gamma = Me$, $R_{\alpha,\beta} = H$): the methods involving the oxidation of pinene and camphor appeared to afford uncertain yields and were not examined, but the remaining methods were investigated and much the best was found to be that due to Stobbe, in which teraconic acid is prepared from acetone and succinic ester and subsequently isomerised to terebic acid. We were able to improve upon Fittig's final method for the preparation of pyroterebic acid, but subsequently developed a new method (see pp. 2349, 2354).

Equilibration of the Acids.—In examining the interconversion between the pairs of acids, both the temperature and the concentration and excess of catalyst were maintained at the standard figures used in previous work, and analyses of the mixed acids were again carried out by iodometric methods. In all cases, when the pure isomeric acids were treated with 25% potassium hydroxide at 100°, the same equilibrium was reached in a few hours from either side. In the two pairs of acids already examined by Fittig we were able to confirm and amplify his statement that the equilibrium is on the αβ side, but our results differ in that, using 25% alkali (Fittig used 10 or 20%), we could detect only very slight formation of β-hydroxy-acid—generally about 2%. This absence of pronounced side reaction serves to support the evidence already obtained (J., 1927, 362) as to the tautomeric nature of the change.

The movement towards equilibrium is shown for three of the aliphatic series in Fig. 1 and for the alicyclic acids in Fig. 2, where the results previously obtained for the *cyclo*hexenylacetic acids are added for comparison. The more important data are summarised in Table I, the approximate time (in hours) required for equilibration being given in the last column.

FIG. 1.

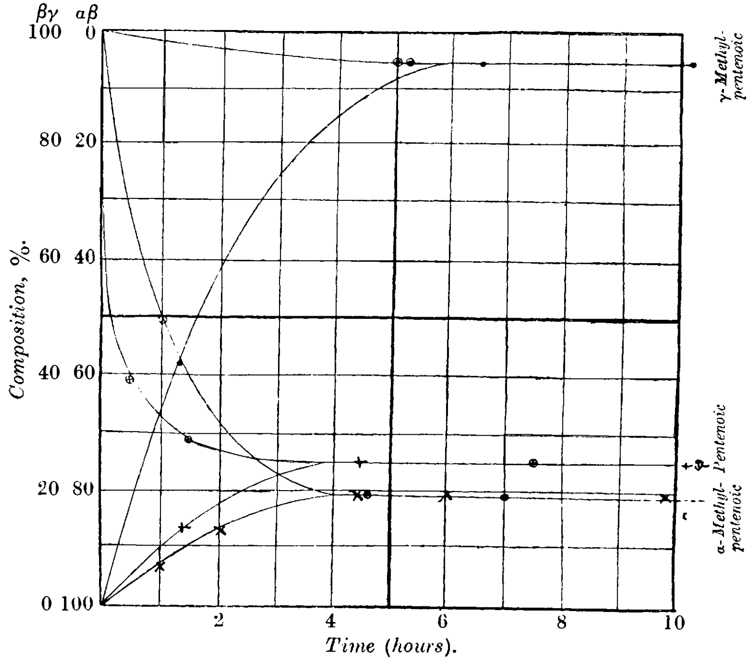


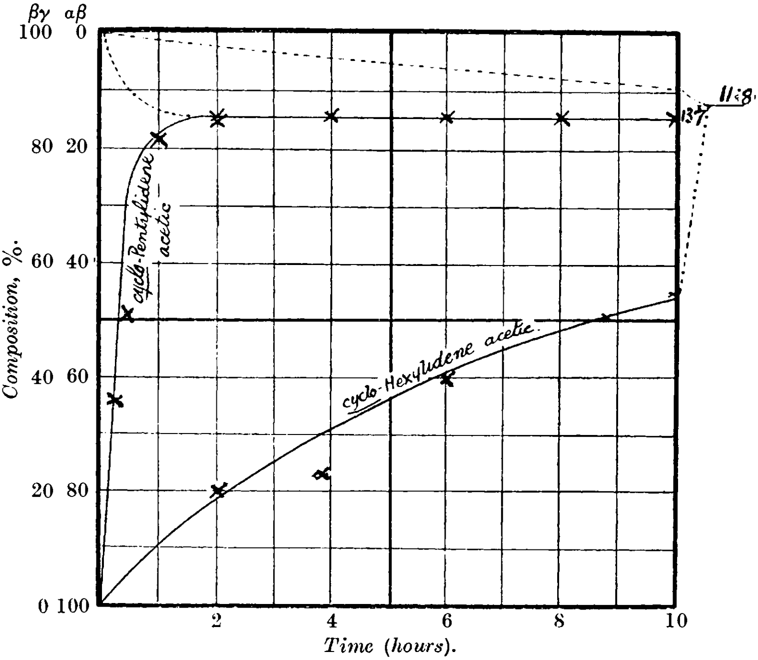
TABLE I.

Interconversion under Standard Conditions.

Acid (as αβ form).	From αβ-acid.	From βγ-acid.	Mean.	Time.
	% of αβ-acid at equilibrium.			
Δ^{α}-Pentenoic	75·6, 75·4, 75·2	75·6, 75·4	75·4	3
α-Methyl-Δ^{α}-pentenoic ...	80·9, 80·2, 80·5	81·2, 80·7	80·7	4½
γ-Methyl-Δ^{α}-pentenoic ...	6·0, 5·1, 5·4	5·4, 6·3	5·6	6
*cyclo*Pentylideneacetic ...	13·7 13·7 13·7 13·5	13·7	13·7	2

The Hexenoic Acids.—The results obtained from the hexenoic acids were abnormal and presented several features of interest. The αβ-acid behaved normally: treatment with alkali resulted in a fall in boiling point and an increase in affinity for iodine, indicating the production of the βγ-isomeride. After some 4 hours the iodine value of the product became constant (% addition of iodine, 19·9), and was unchanged by further treatment; when, however, the βγ-acid (hydrosorbic acid) was treated similarly, a very slow fall in the iodine value of the product was observed, becoming constant after about 20 hours' treatment at an addition value of 47·4%. Even on prolonged treatment with stronger alkali at the boiling point no further change could be effected. Hence, equilibrium was not attained, as shown in Fig. 3, where the time of reaction is plotted against the iodine addition of the product.

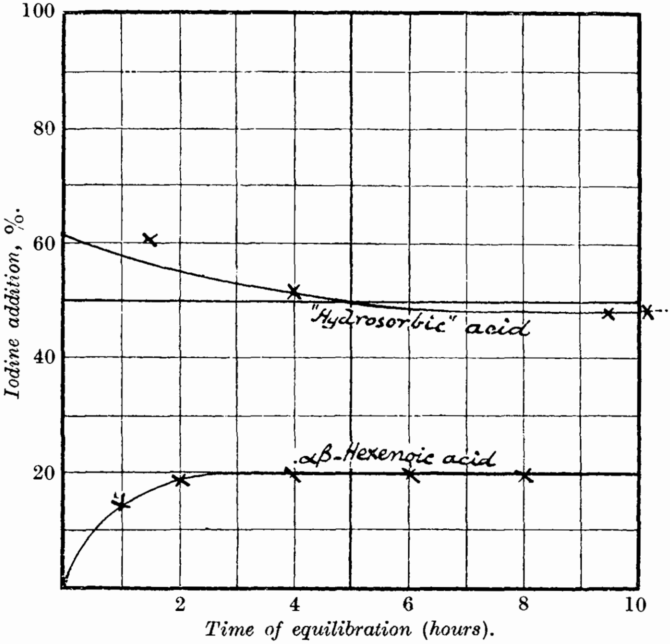
Fig. 2.



The three possible explanations of these anomalous results were: (1) the use of unsuitable experimental methods, (2) the presence of impurity in the acid used, or (3) definite abnormality of the βγ-acid in its behaviour with caustic alkali. The first explanation was not considered probable on account of the excellent results already obtained with other acids, whilst the third seemed unlikely, since the βγ-acid formed from the αβ-isomeride in equilibration behaved normally. On the other hand, the βγ-acid had been prepared from sorbic acid by the method due to Fittig and Baker (*Annalen*, 1894, **283**, 117) and subsequently used by a number of investigators.

The authenticity of our acid was carefully checked. It had a sharp boiling point, the correct physical properties, and gave the anilide, m. p. 55°, described by von Auwers and Henya (*Annalen*, 1923, **434**, 140). It was noticed, however, that the anilide had an indefinite m. p. even after repeated crystallisation, and that the difference between this and the m. p. of the anilide of the αβ-acid was unusually large, thus :

FIG. 3.



Series.	Pentenoic.	Hexenoic.	α-Methyl-pentenoic.	γ-Methyl-pentenoic.
M. p. of αβ-anilide......	100°	109—110°	84°	119°
M. p. of βγ-anilide......	75	54—56	75	106
Difference	25	55	9	13

This abnormality suggested the presence of impurity in the βγ-acid, which might be either the αβ- or the γδ-isomeride, formed by 3 : 4- and 1 : 2-addition of hydrogen to sorbic acid, respectively. The iodine addition was high, and therefore the presence of αβ-acid (or of fully reduced acid) was unlikely, and, moreover, acid containing αβ-acid as impurity would give normal results on equilibration. The γδ-acid, on the other hand, appeared to be a probable impurity : its physical properties closely resemble those of the βγ-isomeride (Fichter, *Ber.*, 1896, **29**, 2367), and its presence would account for the observed abnormalities, for it would be expected to resemble allylacetic acid in its inertness towards alkali. A study of the literature showed that Fittig's work, which established the presence of the βγ-isomeride in his hydrosorbic acid without, we think, proving its homogeneity, had always been accepted without verification. Indeed, in the course of one oxidation (*Annalen*, 1892, **268**, 38) he obtained a small quantity of succinic acid which could only have been derived from the γδ-acid. The bulk of the chemical evidence is ambiguous. We have oxidised samples of hydrosorbic acid prepared from sorbic acid by Fittig's method : with ozone, succinic acid and a mixture of acetaldehyde and propaldehyde were obtained, whilst with alkaline permanganate, succinic, propionic, and acetic acids were all identified. From the proportions of these oxidation products and from the equilibration experiments on the original acid, it is estimated that the " hydrosorbic acid " prepared in this way contained rather more than 50% of the γδ-isomeride. The reduction of sorbic acid was then repeated both with aluminium amalgam (which had little action) and with sodium amalgam under a variety of conditions ; we were unable to isolate the pure βγ-acid from any of the products, and indeed in one experiment a mixture containing about 90% of the γδ-acid was obtained, which was hardly affected by prolonged treatment with alkali. No separation of the acids could be effected by fractional crystallisation of the cadmium salts, as suggested by Fichter's work. The *p*-toluidide of our acid formed mixed crystals (well-defined needles, m. p. 74—77°), whereas the m. p. of the pure γδ-derivative is 103° and that of pure hydrosorbic acid (prepared from the corresponding paraconic acid) is 95·5° (Fichter and Pfister, *Ber.*, 1904, **37**, 1997). The preparation and equilibration of hydrosorbic acid will shortly be described, but it may be said that equilibrium is attained in about 4 hours at about 77% of αβ-acid.

Two points of interest arise. (1) It is believed that this represents the first proof of 1 : 2 addition to a conjugated system of this type, although it was predicted by Burton and Ingold (this vol., p. 913) ; more recently, in the course of their study of the hydrogenation of conjugated systems, Farmer and his collaborators have obtained other examples of the same kind of addition. (2) The results show that the production of a definite equilibrium furnishes an admirable test of the purity of an αβ- or βγ-unsaturated acid : the presence of any impurity (other than the isomeride) in such an acid will be shown by the inability of the sample to yield the correct equilibrium, which can be determined if only one of the two isomerides is available in a state of purity. An application is furnished by the pentenoic acids, for the βγ-acid yields the correct equilibrium value and therefore contains no $\gamma\delta$-acid ; hence 1 : 2-addition of hydrogen to vinylacrylic acid does not occur.

Synthesis of Pyroterebic Acid.—As shown in Table I, the equilibrium between the γ-methylpentenoic acids is 94·4% $\beta\gamma$- $\rightleftharpoons$ 5·6% $\alpha\beta$- ; this is so one-sided that the pure $\beta\gamma$-acid can readily be prepared from the equilibrium mixture by fractionation under reduced pressure, and pyroterebic acid can thus be obtained from its $\alpha\beta$-isomeride in 75% yield. As the latter acid can very easily be prepared from *iso*butaldehyde, the advantages of this method over those previously reported are obvious. The authenticity of the pyroterebic acid was checked by the preparation of derivatives, by oxidation, and by the determination of its iodine addition value, which agrees with the figure obtained for the acid prepared from terebic acid.

The Mobility of the Acids.—The mobility of the acids studied in this work was in every case greater than that of the *cyclo*hexenylacetic acids, in which series equilibrium was only reached after 21 hours' treatment under the standard conditions. As calculated from the equation previously used (J., 1927, 2579), but multiplying the results by 10 for convenience (instead of by 100, as formerly), the values for $10(k_1 + k_2)$ are : *cyclo*pentenylacetic acids 22, α-methylpentenoic acids 7, γ-methylpentenoic acids 4·5. The mobilities of the hexenoic and of the pentenoic acids (Figs. 1 and 2) are of the same order, about 7. These figures, calculated from the results given on p. 2358, serve to illustrate the important point, also made clear in the graphs, that alkyl substituents have little effect on the mobility of the change, if reversible, although a gradual decrease in mobility is to be expected with increase in molecular weight. The only exception lies in the large difference between the *cyclo*pentenylacetic acids (mobility = 22) and the *cyclo*hexenyl homologues (mobility = 1); this had been foreshadowed by earlier results, for it had been shown (Kon and Linstead, *loc. cit.*) that *cyclo*pentylideneacetic acid was completely equilibrated in less than 10 minutes with boiling 60% caustic potash, whereas the corresponding *cyclo*hexane acid required an hour's treatment under these conditions.

The Effect of Alkyl Substituents on Equilibrium.

The results so far obtained from the study of simple mono-olefinic acids containing no second unsaturated group * are summarised in Table II. (All values are reduced to whole numbers.)

From the figures in Table II, the following generalisations may be drawn regarding the comparative stability of the isomeric acids

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* The presence of such groups (*e.g.*, CO_2H,Ph) introduces complicating factors still under study.

TABLE II.

Series of acids.	Equilibrium, % αβ-acid.	Series of acids.	Equilibrium, % αβ-acid.
β-Methylbutenoic	100 [1]	Hexenoic	*ca.* 77
Pentenoic	75	β-Propylhexenoic	34 [3,4]
α-Methylpentenoic	81	δ-Methylhexenoic	*ca.* 82 [5]
β- ,,	26 [2]	β-*iso*Butyl-δ-methylhexenoic	49 [3,4]
γ- ,,	6	Δ^1-*cyclo*Pentenylacetic	14
β-Ethylpentenoic	5 [2]	Δ^1-*cyclo*Hexenylacetic	12 [2]
		Δ^1-*cyclo*Heptenylacetic	26 [3]

[1] Kon and Linstead, *loc. cit.* [2] Linstead, J., 1927, 361. [3] Kon and May, J., 1927, 1549. [4] Linstead and May, J., 1927, 2565.

[5] Fittig (*loc. cit.*) obtained a mixture of unsaturated acids of this composition by the action of alkali on Δ^{α}-*iso*heptenoic acid, and this probably represents an equilibrium value.

towards equilibrating agents (alkyl substituents only are referred to throughout): (1) Butenoic acids without γ-substituents show no stability of the βγ-form even when substituted on the β-carbon atom. (2) Butenoic acids with one γ-substituent show a small but definite stability of the βγ-form, which is not appreciably affected by the nature of the substituent or by the presence of α-substituents. (3) γ-Substituted butenoic acids having a second alkyl group on the γ-carbon show great stability of the βγ-form, and a similar but weaker effect is produced if the second substituent is on the β-carbon atom. The maximum effect in the β-position is given by an ethyl group. (4) These principles are still valid if the substituting groups form part of a polymethylene ring.

No exceptions to these rules are known at present, and it may therefore be predicted that the equilibrium in the methyl*cyclo*hexenylacetic acids derived from *o*-methyl*cyclo*hexanone will be more on the βγ-side than that in the *m*- and *p*-homologues; that di*iso*propylacrylic acid will give a much higher proportion of the βγ-isomeride on equilibration than di-*n*-propylacrylic acid; and that the acrylic acid derived from methyl *iso*propyl ketone will be converted almost completely into its βγ-isomeride on suitable treatment with alkali. It is hoped to test these predictions in the near future.

The theoretical significance of these results is obvious, particularly in the light of the electronic hypothesis of three-carbon tautomerism (Ingold, Shoppee, and Thorpe, J., 1926, 1477; Ingold, *Ann. Reports*, 1927, **24**, 109), but consideration of this point is reserved for a future communication.

EXPERIMENTAL.

A. *Preparation, Purification, and Characterisation of the Acids.*

Δ^{α}-*Pentenoic Acid* (II; $R_{\alpha,\beta,\gamma} = H$).—This was prepared from propaldehyde by the Döbner reaction, pyridine containing $\frac{1}{2}$% of piperidine being used as condensing agent; it had b. p. 105°/19 mm., m. p. 8° (compare von Auwers, *Annalen*, 1923, **432**, 46). Its identity was confirmed by the preparation of the acid chloride, b. p. 51°/24 mm., dibromide, m. p. 56°, and anilide, m. p. 100° (Wohlgemuth, *Ann. Chim.*, 1914, **2**, 332, gives 99°).

Δ^{β}-*Pentenoic acid* (I; $R_{\alpha,\beta,\gamma} = H$).—Vinylacrylic acid, prepared by the method of Kohler and Butler (*J. Amer. Chem. Soc.*, 1926, **48**, 1036), was purified by washing with light petroleum until it melted at 80° and was then immediately reduced with sodium amalgam by the method of Thiele and Jehn (*Ber.*, 1902, **35**, 2320), a 60% yield being obtained of the pure acid, b. p. 98°/19 mm. The acid chloride, b. p. 46°/23 mm., dibromide, m. p. 64° (Thiele gives 65°), and anilide, m. p. 75° (Wohlgemuth gives 73°) were prepared.

Δ^{α}-*Hexenoic Acid.*—This was prepared from *n*-butaldehyde by the method used for the lower homologue. The pure acid, flattened needles from alcohol, m. p. 32°, was obtained in 60% yield. The dibromide, m. p. 70°, and acid chloride, b. p. 70°/23 mm., were prepared. The latter was converted into the *anilide*, needles, m. p. 109—110° (Found: N, 7·5. $C_{12}H_{15}ON$ requires N, 7·4%).

Δ^{β}-*Hexenoic Acid* (Hydrosorbic Acid).—Sorbic acid was prepared from crotonaldehyde by the method of Döbner (*Ber.*, 1900, **33**, 2140), and the product (yield 35%) had m. p. above 132°. The reduction was carried out in the first place under the conditions used for vinylacrylic acid: Sorbic acid (25 g.), suspended in cold water (2 l.), was treated with 1300 g. of 3% sodium amalgam, the solution being kept neutral by passage of carbon dioxide. At the end of the reaction, the solution was decanted from the mercury, acidified with dilute sulphuric acid and extracted with ether. The product, after drying and removal of the solvent, gave a colourless, rancid-smelling oil, b. p. 98°/9 mm.; $n_{\mathrm{D}}^{19^\circ}$ 1·4398, $d_{4^\circ}^{19^\circ}$ 0·9632, $[R_L]_{\mathrm{D}} = 31{\cdot}21$; yield, 18 g., 72%. This substance gave an acid chloride, b. p. 52°/18 mm., and an anilide, needles, which in spite of recrystallisation from a variety of solvents melted at about 55° (Auwers and Henya, *loc. cit.*, give 54—56°) (Found: N, 7·3. Calc.: N, 7·4%). A solid dibromide could not be obtained. The acid added on 61·6% of iodine under the standard conditions, and, after equilibration, 47·6% (see p. 2358).

5 G. of the acid were dissolved in chloroform (30 c.c.) and treated with ozonised oxygen for 12 hours; the ozonide was freed from solvent and decomposed by water. The evolved gases were led through a solution of *p*-nitrophenylhydrazine in excess of dilute hydrochloric acid, and the thick, orange precipitate, after recrystallisation, melted at 117°: mixed with an authentic sample of acetaldehyde-*p*-nitrophenylhydrazone (m. p. 126°) it melted at 120°,

whereas the mixed m. p. with propionaldehyde-*p*-nitrophenylhydrazone (m. p. 118°) was 114°. When all the aldehyde had been evolved the residue was treated with perhydrol (20 c.c.) and allowed to stand over-night. On evaporation the solution gave succinic acid, m. p. 183° (Found : *M*, by titration, 119. Calc. : *M*, 118), which was further identified by a mixed m. p. determination.

Another sample (5 g.), prepared by the same method, was dissolved in 500 c.c. of water, excess of sodium bicarbonate was added, and the solution was treated slowly with 22 g. of potassium permanganate and 12 g. of magnesium sulphate in 750 c.c. of water. A further quantity of 7·1 g. of permanganate and 15 g. of magnesium sulphate was subsequently added (6 g.-atoms + 5%, in all). The product was worked up in the usual way, and the acid fraction yielded 2·55 g. of a semi-solid residue. The liquid portion of this (0·68 g.) was separated by filtration and converted into the acid chloride with phosphorus trichloride. Some two-thirds of this boiled between 50° and 60° and yielded aceto-*p*-toluidide on reaction with *p*-toluidine. The last few drops of the remaining liquid (b. p. about 75°) were also converted into a *p*-toluidide and gave bold needles of propion-*p*-toluidide, m. p. 123°, from light petroleum. The residual solid acid was succinic acid, m. p. 182°. The identities of these products were confirmed by mixed m. p. determinations.

Modified Reductions of Sorbic Acid.—(1) The reaction was carried out as before, except that dilute sulphuric acid was added at half-hour intervals until the solution was slightly acid (compare Fittig and Baker, *loc. cit.*). The product obtained as before boiled at 98—99°/9 mm., and had an " iodine value " of 57·3%, which after equilibration for 48 hours fell to 49·0%. Another sample had b. p. 204—206°/760 mm. and gave a *p*-toluidide forming well-defined tufts of needles, m. p. 74° (indefinite). The cadmium salt (compare Fichter, *Ber.*, 1896, **29**, 2367) was extracted with cold water until one-third remained as residue, and the solution, which should have contained the more soluble salt of the βγ-acid, was evaporated to dryness. The acid was extracted from the residue by treatment with dilute sulphuric acid and ether ; it boiled constantly at 101·5°/12 mm. and had $n_D^{18°}$ 1·4405, $d_{4°}^{18°}$ 0·9640, whence $[R_L]_D$ 31·23 (v. Auwers, *loc. cit.*, finds b. p. 112°/10 mm., $n_D^{20°}$ 1·4394, $d_{4°}^{20°}$ 0·9655, $[R_L]_D = 31·11$) ; it did not solidify in a freezing mixture, and gave an acid chloride, b. p. 50—51°/14 mm., and an anilide, m. p. 52—56°.

(2) Acetic acid was added during the reduction at such a rate as to keep the solution slightly *acid* throughout. In this way it was hoped to obtain addition of hydrogen to the molecule of sorbic acid as distinct from the ion. The product boiled at 101°/11 mm. and

had an "iodine value" of 52·6%, which fell to 48·9% after equilibration for 48 hours.

(3) Sorbic acid (10 g.), dissolved in moist ether (2000 c.c.), was reduced with aluminium amalgam (20 g.) in the usual way. The product yielded 2 g. of the pure reduced acid, b. p. 102°/12 mm., iodine value 59·8%, falling on equilibration for 48 hours to 50·6%. A considerable quantity of unchanged sorbic acid was recovered from the higher-boiling fractions.

γ-Methyl-Δ^{α}-pentenoic Acid (Δ^{α}-*iso*Hexenoic acid) (II; $R_{\alpha,\beta} = H$, $R_{\gamma} = Me$).—This was prepared from *iso*butaldehyde by the method used for Δ^{α}-pentenoic acid. After refractionation of the product, the pure acid was obtained in 66% yield; b. p. 113°/20 mm., 104°/10 mm. The *acid chloride* boiled at 67°/20 mm.; the *anilide* crystallised in fine needles from aqueous alcohol, m. p. 119° (Found : N, 7·4. $C_{12}H_{15}ON$ requires N, 7·4%); the dibromide crystallised in heavy white cubes, m. p. 124°.

Terebic Acid.—(1) Ethyl diaterebate was hydrolysed with concentrated hydrochloric acid (Simonsen, J., 1907, **91**, 184) but gave a poor yield, never exceeding 20% of terebic acid. Hydrolysis with 50% sodium hydroxide was very violent, but the use of potassium hydroxide gave better results : Ethyl diaterebate (30 g.) was poured into 50% aqueous potassium hydroxide solution (100 c.c.); hydrolysis, which was accompanied by the evolution of much heat, was completed by an hour's heating on the steam-bath, the solution was cooled, the unchanged ester extracted with ether, and the alkaline liquid acidified with concentrated hydrochloric acid and evaporated to dryness. The solid residue was exhaustively extracted with ether in a Soxhlet apparatus, and the solid obtained was repeatedly recrystallised from water. It melted between 162° and 166° and probably contained much teraconic acid. After being heated with concentrated hydrochloric acid and recrystallised, pure terebic acid was obtained, m. p. 175°; yield, nearly 50%.

(2) Ethyl carbethoxysuccinate was prepared in 60% yield by the action of ethyl chloroacetate on ethyl sodiomalonate; its sodio-compound readily reacted with *iso*propyl iodide and gave a 65% yield of ethyl α-carbethoxy-α-*iso*propylsuccinate, b. p. 153—155°/10 mm. This was boiled over-night under reflux with seven times its volume of concentrated hydrochloric acid, and the resulting solution gave *iso*propylsuccinic acid on evaporation to small volume, m. p. 110°; yield, 86%. This acid, when oxidised by the method of Lawrence (J., 1899, **75**, 527), yielded 51% of terebic acid, which melted sharply at 175° after one crystallisation from hot water, together with 20% of the unchanged starting material.

(3) Teraconic acid (Stobbe, *Ber.*, 1893, **26**, 2314) was converted

into terebic acid by boiling over-night with concentrated hydrochloric acid under reflux (compare Fittig and Frost, *Annalen*, 1884, **226**, 365), a 90% yield being obtained.

γ-Methyl-Δ^{β}-pentenoic Acid (Pyroterebic Acid) (I; $R_{\alpha,\beta} = H$, $R_{\gamma} = Me$).—(1) *By dry distillation of terebic acid.* The method of Fittig and Geisler (*Annalen*, 1881, **208**, 37) was improved as follows: Terebic acid, in 20 g. portions, was placed in a 100 c.c. distilling flask fitted with a thermometer, the bulb of which almost touched the bottom of the flask. To the side arm was attached a 50 c.c. distilling flask and to the side arm of this a small water condenser in a vertical position. The acid was heated *as quickly as possible* to 240°. At 175—180° it melted to a clear golden oil, and at about 240° water began to separate. The oil then distilled without charring. The distillate partly solidified on cooling, owing to the presence of unchanged terebic acid. It was distilled in steam, terebic acid and teraconic acid (2·8 g.) being left in the residue. The aqueous distillate was saturated with sodium bicarbonate and extracted with ether to remove *iso*caprolactone (0·5 g.). The alkaline solution was then acidified and extracted thoroughly with ether. The product, isolated after removal of the solvent and refractionation, distilled at 99°/10 mm.; yield, 6·5 g. (33%). The *acid chloride* boiled at 60°/15 mm. The *anilide* crystallised from alcohol and water in needles, m. p. 106° (Found: N, 7·5. $C_{12}H_{15}ON$ requires N, 7·4%). The dibromide was obtained as hard white crystals, m. p. 99°.

(2) *From Δ^{α}-*iso*hexenoic acid.* The αβ-acid (20 g.) was heated for 15 hours with a solution of potassium hydroxide (120 g.) in 250 c.c. of water. The solution was cooled, acidified, and extracted thoroughly with ether. After removal of the ether, the residual oil was distilled in steam and extracted as in the previous method. Almost the whole product distilled at 99—100°/10 mm., the last fractions, about 2 c.c., being rejected. On refractionation, 15 g. of a clear colourless oil were obtained, b. p. 99°/10 mm. (75% yield). This preparation gave the following derivatives: acid chloride, b. p. 62°/16 mm.; anilide, in needles from benzene–light petroleum, m. p. 104° [mixed m. p. with the αβ-anilide (of m. p. 119°) 85—87°; mixed m. p. with anilide prepared by method (1) 106°]; dibromide, m. p. 99°, not depressed in admixture with dibromide from preparation (1).

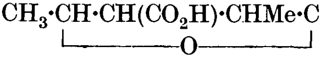
The new acid (5 g.), dissolved in dry chloroform (30 c.c.), was treated with dry ozonised oxygen for 20 hours; the precipitated white, solid *ozonide*, sparingly soluble in chloroform, had m. p. 110° (decomp.) after drying in a vacuum. A portion of the ozonide was treated with an excess of water, and the aldehyde evolved was converted into the *p*-nitrophenylhydrazone; this formed yellow needles from alcohol, m. p. 126°, and was identified as the acetaldehyde derivative by comparison with an authentic sample: a mixture with a specimen of the *p*-nitrophenylhydrazone of *iso*butaldehyde (m. p. 128°) melted at 103°. When all the acetaldehyde had been removed, the residual solution was heated under reflux for an hour, and a white,'crystalline deposit was formed in the condenser. An excess of sodium bicarbonate was added and the liquor slowly distilled under a column, the first 10 c.c. being collected. The presence of acetone in this was shown by the immediate formation of iodoform and by the preparation from it of dibenzylidene-acetone (m. p. 111°, identified by mixed m. p.). The white solid, volatile in steam, was undoubtedly acetone superoxide.

The remainder of the ozonide was left over-night with an excess of perhydrol, and the solution subsequently evaporated to small bulk; malonic acid crystallised on cooling, and was identified by its m. p. (129°), by its decomposition to acetic acid, and by a mixed m. p. determination.

α-Methyl-Δ^{α}-pentenoic Acid (II; $R_{\alpha} = Me$, $R_{\beta,\gamma} = H$).—α-Methyl-β-ethylacrolein (Döbner and Weissenborn, *Ber.*, 1902, **35**, 1144) was distilled, and the fraction of b. p. 55—60°/18 mm. was immediately oxidised. The aldehyde (40 g.), mixed with silver nitrate (230 g.), water (500 g.), and rectified spirit (200 c.c.), was stirred vigorously, and to it were added during 3 hours 75 g. of sodium hydroxide in 1 litre of water (compare Delépine and Bonnet, *loc. cit.*); reaction was completed by standing over-night. The filtered solution was acidified and thoroughly extracted with ether. The product, after drying and removal of the solvent, was fractionated, α-methyl-Δ^{α}-pentenoic acid being obtained as a colourless oil, b. p. 112°/12 mm. (yield, 25 g., 60%). On cooling in ice, the product solidified completely and melted at 22—23° (Lieben and Zeisel, *Monatsh.*, 1883, **4**, 46, give 24·4°).

The *acid chloride* boiled at 63°/16 mm. The *amide*, prepared from this by the action of dry ammonia in benzene solution, crystallised from benzene or carbon disulphide in plates, m. p. 80° (Found: N, 12·3. $C_6H_{11}ON$ requires N, 12·4%). All the crops obtained by fractional crystallisation of this substance melted sharply at 80°, and the m. p. could not be raised by further purification; we were unable therefore to obtain either of the amides, m. p. 65·5° and 96°, described by Macq (*Bull. Acad. roy. Belg.*, 1926, **12**, 753) as those of the *cis*- and *trans*-forms of this acid. The preparative method used by Macq (hydrolysis of the corresponding unsaturated nitrile) would, however, certainly lead to the production of a mixture, and it is probable that this was insufficiently separated (compare Newbery, J., 1925, **127**, 295; von Auwers, *Annalen*, 1923, **432**, 46).

The *anilide* of α-methyl-Δ^{α}-pentenoic acid, prepared from the acid chloride, crystallised from benzene–light petroleum in needles, m. p. 84° (Found: N, 7·2. $C_{12}H_{15}ON$ requires N, 7·4%). The dibromide crystallised from carbon disulphide in hard, white prisms, m. p. 96—97° (Lieben and Zeisel, *loc. cit.*, p. 77, give 97·6°).

α-Methyl-Δ^{β}-pentenoic Acid (I; $R_{\alpha} = Me, R_{\beta,\gamma} = H$).—This was prepared by the method of Fichter and Rudin (*Ber.*, 1904, **37**, 1615), who, however, gave scanty details. Ethyl α-methyl-β-acetosuccinate (100 g.), obtained in 62% yield from ethyl sodioacetoacetate and ethyl α-bromopropionate, was dissolved in 200 c.c. of rectified spirit and 150 c.c. of water, and cooled to 0°. To the mechanically stirred solution were added 1400 g. of 3% sodium amalgam in seven equal lots at one-hour intervals, 100 c.c. of water being added with each addition. The solution was kept over-night and the supernatant liquor separated from the mercury, carefully acidified with dilute sulphuric acid (evolution of carbon dioxide) and extracted with ether. The extract was dried and the residue after removal of the solvent was fractionated in a vacuum. The low-boiling fraction, 140—160°/12 mm. (15 g.), was presumably α-methyllævulic acid. At 195°/12 mm., αγ-dimethylparaconic acid,  $CH_3{\cdot}CH{\cdot}CH(CO_2H){\cdot}CHMe{\cdot}CO$, came over and solidified to a mass of long, white crystals (30 g., 40%), m. p. 130° after crystallisation (Fichter and Rudin report a 70% yield, but we were unable to obtain this in spite of many variations of conditions).

The paraconic acid (20 g.) was distilled from the same apparatus as that used for terebic acid, the temperature being raised *very gradually* to 240°; distillation commenced at 280° and continued up to 285°, there being no charring of the paraconic acid. The product was worked up as described for pyroterebic acid, and on fractionation gave 7·5 g. of a liquid, b. p. 101—103°/16 mm., and 102°/16 mm. after refractionation; yield, 33%. From the residue of the steam-distillation, 3 g. of the paraconic acid were recovered. Fichter and Rudin (*loc. cit.*), using a different method of separation, obtained only 16% of the unsaturated acid.

The *acid chloride* boiled at 47°/17 mm. The *amide*, prepared in the same way as the αβ-isomeride, crystallised from carbon disulphide or benzene in glistening plates, m. p. 74° (Found: N, 12·2. $C_6H_{11}ON$ requires N, 12·4%). The *anilide* crystallised from aqueous alcohol or benzene–light petroleum in needles, m. p. 76° (Found: N, 7·4. $C_{12}H_{15}ON$ requires N, 7·4%).

cyclo*Pentylideneacetic acid* (IV) (Kon and Linstead, *loc. cit.*)

boiled at 133°/15 mm. and solidified to a white mass which on crystallisation from alcohol melted sharply at 64°.

Δ^1-cyclo*Pentenylacetic acid* (III) was prepared by the action of a large excess of 40% potassium hydroxide on the αβ-isomeride for 1 hour. The acid, isolated in the usual way, was freed from adhering oil by washing with light petroleum, and recrystallised from aqueous alcohol, m. p. 52°; yield, 50%.

B. *Equilibration of the Acids.*

The same potassium hydroxide solution was used throughout: it contained 300 g. KOH per litre of solution, and was standardised from time to time against *N*-acid. Equilibrations were carried out by the standard procedure (J., 1927, 2579), 2 g. of the acid being sealed up with exactly ten times the theoretical amount of the alkali. The reaction mixture was then heated in a bath of boiling water. Owing to the formation of hydroxy-acids, the method of working up the product differed from that used previously. At the end of the required time the tube was opened and the contents were acidified and extracted with ether. The undried extract was freed from solvent under a good column and slowly distilled in steam for 1 hour. The mixed unsaturated acids in the distillate (about 1 litre) were isolated in the usual way after removal of lactone. The residual oil was washed into a tared beaker with pure ether and weighed after removal of the ether in a vacuum over paraffin wax. In every case about 1·7 g. of mixed acids (*ca.* 85%) were recovered in this way.

The residue from the distillation in steam was extracted with ether and the hydroxy-acids were isolated, after drying and removal of the solvent, as sweet-smelling viscous oils. The following amounts were obtained during the equilibrations: Pentenoic acids, traces; hexenoic acid, 22%; *iso*hexenoic acid, 5%; α-methylpentenoic acids, traces; *cyclo*pentenyl acids, nil.

The molecular weight of the β-hydroxy-*n*-caproic acid derived from Δ^α-hexenoic acid was found by titration with standard baryta to be 131 ($C_6H_{12}O_3$ requires 132). The other hydroxy-acids were not obtained in quantities sufficient for examination. In this respect the results are contrasted with those of Fittig, who obtained quantities of β-hydroxy-acids varying from 15 to 35%.

C. *Analysis of the Equilibrated Acids.*

The method of Linstead and May (*loc. cit.*) was used throughout. Data for reference were first obtained by determining the % addition of iodine under the standard conditions to mixtures of the isomerides of known composition, at least three determinations being made on every mixture. These data were then incorporated into reference curves, this "iodine value" being plotted against the % composition of the mixed acids. Quantities of the equilibrated acids equivalent to $M/300$ were then examined in the same way, three determinations of the iodine value being made in each case. The composition of the acid mixture was then found from the reference curve. The time of equilibration was increased until there was no further change in the iodine value of the product. The curves obtained from each pair of isomerides by plotting time of equilibration against composition of the product were of the exponential type, becoming asymptotic to each other at the equilibrium point (Figs. 1 and 2).

The following tables summarise this section of the experimental work.

Pentenoic acids : Reference data.

% αβ-Acid	100	80	66·6	50	33·3	20	0
Iodine value (10 mins.)	4·4	13·7	19·8	26·6	34·8	41·4	46·8

Equilibration data.

Starting acid :	αβ.	αβ.	αβ.	αβ.	βγ.	βγ.	βγ.	βγ.
Time of reaction (hrs.)	1½	4½	12	16½	½	1½	7½	17
Iodine value	9·8	15·7	15·8	15·9	22·5	17·4	15·7	15·8
% αβ-Acid	88·8	75·6	75·4	75·2	61·6	72·3	75·6	75·4

Mean iodine value at equilibrium : 15·8. αβ-Acid = 75·4%.

n-*Hexenoic acids.*

Iodine value for αβ-acid 1·4%, for βγ-acid (estimated) 70%.

Equilibration data.

Starting acid :	αβ.	αβ.	αβ.	αβ.	αβ.	βγ.*	βγ.	βγ.	βγ.	βγ.
Time of reaction (hrs.)	1	2	4	6	8	1½	2	4	21	24
Iodine value	14·3	18·4	19·9	20·0	19·9	61·6	61·6	52·6	47·4	47·8

* Hydrosorbic acid prepared by first method : iodine value 61·6%. The variation in the iodine values of other samples of hydrosorbic acid on equilibration has already been given (p. 2352).

Since the pure hydrosorbic (βγ-)acid was not obtained in the course of this work the position of equilibrium could only be determined approximately. It will be noticed from the figures given on p. 2352 that the samples of mixed βγ- and γδ-hexenoic acids which gave the lowest iodine values were also those whose iodine values *changed least on equilibration*, *i.e.*, were those containing the most γδ-acid. From a study of these results, we deduce that the iodine values of the βγ- and γδ-acids are approximately 70 and 50%, respectively, and assuming this figure for the pure βγ-acid, the equilibrium is of the order 22% βγ : 78% αβ. This equilibrium was also determined by Bougault's method (*Ann. Chim. Phys.*, 1908, **14**, 145), the unchanged αβ-acid being actually isolated (Linstead and May, *loc. cit.*). In three experiments, from 2 g. of the equilibrium mixture there were isolated 1·44 g., 1·60 g., and 1·57 g. of the solid αβ-acid, which give a mean value for the equilibrium of 77% αβ : 23% βγ. The variation in the above figures shows, however, that the method is by no means accurate.

γ-Methylpentenoic acids : Reference data.

% αβ-Acid	100	80	60	40	20	0*	0†
Iodine value (5 mins.)	1·8	17·8	34·2	49·0	63·1	73·4	73·1

Equilibration data.

Starting acid :	αβ.	αβ.	αβ.	αβ.	αβ.	βγ.*	βγ.†
Time of reaction (hrs.)	1¼	3¼	6½	15	26	5	5
Iodine value (5 mins.)	33·0	60·2	71·1	71·6	71·4	71·4	70·9
% αβ-Acid	61·8	24·5	6·0	5·1	5·4	5·4	6·3

Mean iodine value at equilibrium : 71·3. αβ-Acid = 5·6%.

* Pyroterebic acid from terebic acid. † Pyroterebic acid from αβ-acid.

The reaction of γ-methyl-Δ^{β}-pentenoic acid with iodine under the conditions was very rapid at first but appeared to stop after 5 minutes.

α-Methylpentenoic acids : Reference data.

% αβ-Acid	100	80	60	40	20	0
Iodine value (10 mins.)	0	11·1	21·0	30·5	39·9	44·1

Equilibration data.

Starting acid :	αβ.	αβ.	αβ.	αβ.	αβ.	βγ.	βγ.	βγ.
Time of reaction (hrs.)	1	2	4½	6	10	1	4½	7
Iodine value (10 mins.)	3·7	7·75	10·6	11·0	10·8	25·8	10·4	10·7
% αβ-Acid	93·9	87·0	80·9	80·2	80·5	50·5	81·2	80·7

Mean iodine value at equilibrium : 10·7. αβ-Acid = 80·7%.

cyclo*Pentenylacetic acids : Reference data.*

% αβ-Acid	100	80	66·6	50	33·3	20	0
Iodine value (10 mins.)	12·8	34·0	45·2	58·3	72·5	80·3	87·7

Equilibration data.

Starting acid :	αβ.	αβ.	αβ.	αβ.	αβ.	αβ.	αβ.	αβ.	βγ.
Time of reaction (hrs.)	¼	½	1	2	4	6	8	10	2
Iodine value (10 mins.)	47·8	61·0	81·4	82·6	83·4	83·5	83·4	83·4	83·4
% αβ-Acid	64·3	49·0	18·7	15·6	13·7	13·5	13·7	13·7	13·7

Mean iodine value at equilibrium : 83·4. αβ-Acid = 13·7%.

In this series, the residual iodine was titrated with thiosulphate without previous acidification, and there is a slight absolute error which does not extend to the interconversion curves and the position of equilibrium.

Much of the heavy cost of this investigation has been defrayed by grants from the Government Grant Committee of the Royal Society and from the Chemical Society, to whom we wish to acknowledge our indebtedness. Our thanks are also due to Professor J. F. Thorpe, F.R.S., and Dr. G. A. R. Kon for their interest in the progress of the work.

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[*Received, June* 21*st*, 1928.]