CCLXXVII.—*Investigations of the Lower Olefinic Acids. Part I.* n-*Hexenoic Acids.*

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The primary object of the present series is a thorough investigation of the tautomeric changes of unsaturated acids, but as this will necessitate the preparation of a large number of these substances, it is intended not to restrict the study to this one aspect of their chemistry. The need for a wide approach to the subject has been emphasised by recent observations (Goldberg and Linstead, J., 1928, 2343) on the reduction of sorbic acid (I), which suggest that even so well known a reaction as this has been insufficiently studied. The present paper represents the second stage in the investigation of the reduction products.

It was found in the earlier work (*loc. cit.*) that " hydrosorbic acid " failed to pass into the equilibrium mixture of $\alpha\beta$(II)- and $\beta\gamma$(III)-*n*-hexenoic acids readily obtained by the action of caustic alkali on $\alpha\beta$-hexenoic acid. (The term " hydrosorbic acid " is used in this paper for the acid mixture obtained by reduction of sorbic acid and not as a pseudonym for $\beta\gamma$-hexenoic acid.) This provided the first indication that sorbic acid gave other than the generally accepted complete 1 : 4 addition (compare Evans and Farmer, J., 1928, 1644). Oxidation showed the presence in hydrosorbic acid of the βγ- and γδ-isomerides (III and IV),

(I.) $CHMe{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$ $CH_2Me{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H$ (II.)

(III.) $CH_2Me{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$ $CHMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ (IV.)

formed by 1 : 4- and 1 : 2-addition respectively, and the proportion of the isomerides did not appear to be affected to any great extent by the conditions of reduction.

The abnormal results of equilibration were attributed to the fact that of the two unsaturated acids only the βγ- was affected by treatment with alkali, the γδ-isomeride remaining unchanged and obscuring the results of iodometric analyses.

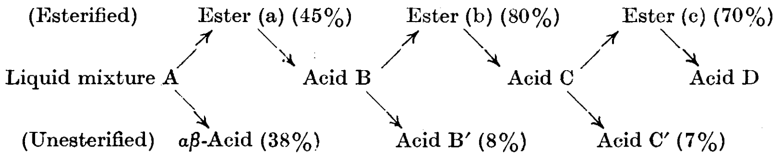
It was clearly desirable to obtain further evidence in support of this view, and following a suggestion by Dr. J. L. Simonsen, the synthesis and examination of the pure βγ- and γδ-isomerides has been undertaken.

It was known that the βγ-hexenoic acid formed from the αβ-acid during equilibration behaves normally to alkali (*loc. cit.*), the reaction being of the usual reversible type, and hence it was decided to attempt the separation of this acid from the equilibrated product. Experiment showed that a partial separation could readily be effected by distillation of the product, for on cooling the distillate in ice a large amount of unchanged αβ-acid separated out in the usual solid form, m. p. 32—33°. Iodometric titration showed that the residual liquid acid (A) was more reactive (30% addition) than either the equilibrium mixture (18%) or the pure αβ-acid (1%) and by analogy with other series might be supposed to contain 50% or more of the required βγ-acid. For further separation we endeavoured to make use of the well-known fact that βγ-acids are stronger than their αβ-isomerides by means both of partial neutralisation and of partial esterification. A small additional degree of separation was effected by partial neutralisation (compare Wechsler, *Monatsh.*, 1893, **14**, 462), but as anticipated, this was insufficient for the purpose in view, and the possibilities of methods based on fractional esterification were then examined.

Sudborough and his collaborators (J., 1907, **91**, 1033; 1909, **95**, 319; 1910, **97**, 2450), having found that βγ-acids are esterified with much greater facility than their αβ-isomerides, utilised this fact in the separation of two typical mixtures (Sudborough and Thomas, J., 1911, **99**, 2307). The same two authors (*loc. cit.*) attempted the separation of αβ- and βγ-hexenoic acids, using an equilibrated acid prepared from "hydrosorbic acid"; they were able to separate unesterified solid αβ-acid—formed from the βγ-isomeride in the hydrosorbic acid (compare Fittig and Baker, *Annalen*, 1894, **283**, 117; Goldberg and Linstead, *loc. cit.*, p. 2359)—but they apparently did not attempt to isolate βγ-acid from the esterified portion. That their material must have contained a large amount of γδ-acid is clearly shown by the small proportion of αβ-acid isolated in this work.

A method based on Sudborough's principle, but with certain experimental modifications, has now been developed and applied with success to the complete separation, not only of the acids now under discussion, but also to a considerable number of other isomeric pairs investigated in these laboratories. The great value of the method lies in the fact that liquid βγ-acids can now be isolated in a state of definite instead of assumed purity: several, indeed, have been obtained in a solid form for the first time.

The liquid mixture of αβ- and βγ-hexenoic acids (A) (see above) shows an exaltation in $[R_L]_D$ of 0·54 unit. On controlled esterification with cold alcoholic hydrogen chloride (p. 2160), it yields over half its weight of an ester and a smaller quantity of unchanged acid, which is the almost pure αβ-isomeride. On hydrolysis of the ester, an acid (B) is obtained, which boils 12° below the αβ-acid and has a low molecular refractivity (exaltation, 0·32 unit) and an iodine addition (43·6%) approaching that (46·8%) of the lower homologue, βγ-pentenoic acid (Goldberg and Linstead, *loc. cit.*). This acid solidifies readily in ice, melts at about 4°, and is nearly pure βγ-hexenoic acid (III). In order to obtain the acid perfectly pure, the partial esterification process was repeated twice, but only very small amounts of αβ-acid were separated and the improvement in properties was slight. The full process may be illustrated by the following scheme:



The high yield of ester from acids B and C confirmed the fact that they were essentially βγ-; moreover, in the final esterification the small *unesterified* portion (C′) had properties approaching those of the βγ-acid. The last sample (D) being regarded as pure βγ-acid, iodometric analysis gives the following proportions of this acid in the intermediate products:

Acid	A	B	C	D	A′	B′	C′
Composition, % βγ...	56	90	96	100	(0)	41	71

The pure βγ-acid gives distinct derivatives. It boils at 107°/15 mm. and melts at 4—5°, the m. p. being depressed to below −15° by admixture with the solid αβ-acid. On oxidation it yields propionic acid but no succinic acid (contrast hydrosorbic acid; Fittig, *Annalen*, 1892, **268**, 38; Goldberg and Linstead, *loc. cit.*; Evans and Farmer, *loc. cit.*). The general properties of the acid obtained by one partial esterification (*e.g.*, B) suggest that it contains more than the 90% of βγ-acid indicated by iodine titration, which may be taken to represent a minimum value; this specimen gives the derivatives yielded by the pure acid and would seem to be suitable for preparative work. Over 10% of it can be obtained from the readily available αβ-acid in one series of operations.

It was a matter of great interest to examine the action of alkali on the new acid. When it was equilibrated under the standard conditions (J., 1927, 2579), a product was obtained identical in every way with that formed from the αβ-acid. This completely confirms the original ideas on the abnormality of "hydrosorbic acid." The equilibrium mixture contains 30% of βγ-acid and this value has been confirmed from the αβ-side. The approximation previously given (25% βγ-) was based on mistaken ideas as to the reactivity to iodine of the βγ- and γδ-acids. The effect of the γ-ethyl group is thus slightly greater than that of the γ-methyl in stabilising the βγ-phase in the three-carbon system.

It remained to synthesise γδ-hexenoic acid and confirm Fichter's observation that it is unaffected by caustic alkalis (*Ber.*, 1896, **29**, 2370). As in our experience the pyrogenic decomposition of lactonic acids is the least satisfactory of all methods for the preparation of unsaturated acids, the original synthesis (*ibid.*) was not at first repeated, but the acid was prepared by a new method from crotonaldehyde through crotyl bromide (VI) and the corresponding Δ^{β}-*butenylmalonic acid* (VIII) :

$$\begin{tikzcd}
\mathrm{CHMe{:}CH{\cdot}CHO} \arrow[r] & \underset{\text{(V.)}}{\mathrm{CHMe{:}CH{\cdot}CH_2{\cdot}OH}} \arrow[r] & \underset{\text{(VI.)}}{\mathrm{CHMe{:}CH{\cdot}CH_2Br}} \arrow[d] \\
\text{(IV.)} & \underset{\text{(VIII.)}}{\mathrm{CHMe{:}CH{\cdot}CH_2{\cdot}CH(CO_2H)_2}} \arrow[l] & \underset{\text{(VII.)}}{\mathrm{CHMe{:}CH{\cdot}CH_2{\cdot}CH(CO_2Et)_2}} \arrow[l]
\end{tikzcd}$$

This synthesis leaves no doubt as to the position of the double bond, and gives a pure product. The acid obtained has the normal optical properties and yields acetic and succinic acids on oxidation with permanganate. It also gives the crystalline cadmium salt (compare Fichter, *loc. cit.*) and the *p*-toluidide, m. p. 103° (Fichter and Pfister, *Ber.*, 1904, **37**, 1997), and we have further characterised it by the preparation of the *anilide*, m. p. 87°. Here, however, the resemblance to the acid of Fichter ended, for we were unable to induce our acid to solidify even when kept for long periods in a freezing mixture, whereas Fichter's acid is described as readily yielding a solid melting at 0°. In order to determine whether this was due to some accidental impurity, a sample of Fichter's acid was prepared and characterised by the preparation of the cadmium salt, the *p*-toluidide, and the anilide, which were identical in every way with those given by the acid prepared by the new method. The Fichter acid, however, readily solidified in a freezing mixture and melted sharply at 0°. On seeding a sample of the new acid cooled below 0° with the solid Fichter acid, no solidification occurred. Further, the two acids showed marked differences in density and refractivity. The sharpness of the boiling point and of the melting points of the derivatives, and also the results of analysis show clearly that the new acid is a chemical individual and it is therefore necessary to assume that the two acids are *cis-trans*-isomerides about the double bond. These would be expected to give identical oxidation products and the same series of derivatives, as the acid chloride would be that of the stable form (compare Newbery, J., 1925, **127**, 295). The only unexplained feature is the formation from both acids of what is apparently the same cadmium salt.

Both forms of the acid have a considerable affinity for iodine, but the reaction of the Fichter acid, which it is proposed to call the " α "-form, is lower (80%) than that of the new " β "-acid (92%). Fichter (*loc. cit.*) states that his acid is unchanged by boiling alkali, but he gives no details of the properties of the recovered acid. We have been unable to repeat the experiment on the α-acid owing to lack of material. The β-acid is, however, completely unchanged by 25% caustic potash at 100° even after 24 hours' treatment. The recovered acid has the high iodine addition of the β-acid, yields the characteristic *p*-toluidide, and will not solidify in a freezing mixture. It is therefore clear that, whichever of these forms of the γδ-acid is present in " hydrosorbic " acid, the observed incomplete equilibration is fully accounted for. The fact that the two γδ-acids have dissimilar iodine additions makes it impossible to give more than an approximate estimate of the relative amounts of 1 : 2- and 1 : 4-reduction products in hydrosorbic acid. This is unfortunate in view of the theoretical importance of this reduction. The change in iodine addition on equilibration is shown below (round figures) for the pure acids and for several samples of " hydrosorbic " acid (Goldberg and Linstead, *loc. cit.*) :

Acid :	αβ-.	βγ-.	γδ- (α-Form).	γδ- (β-Form).	" Hydrosorbic." * (1).	(2).	(3).
Before equilibration	1	47	80	91	62	57	60
After equilibration	18	17	—	93	48	49	51

* Prepared by reduction with (1) sodium amalgam and carbon dioxide, (2) sodium amalgam and sulphuric acid, (3) aluminium amalgam.

If it is assumed that the γδ-acid is present in hydrosorbic acid as the α-form, then the iodine additions of the three samples of the acid agree with those of a roughly equal mixture of βγ- and γδ-acids, and this is in agreement with the iodine values obtained after equilibration. If the γδ-acid is present as the more reactive β-form the proportion of this must be lower.

The results from this point of view suggest that 1 : 2-addition of hydrogen to sorbic acid occurs to the extent of 40—50%, in agreement with the results of Evans and Farmer (*loc. cit.*), who give values of 35, 40, and 30% for the lower limit of 1 : 2-addition in reductions by three similar methods.

Both the beautifully crystalline *p*-toluidides (Fichter and Pfister, *loc. cit.*) and anilides serve to characterise the *n*-hexenoic acids, and the m. p.'s of the derivatives and of the acids are summarised below :

Acid :	αβ-.	βγ-.	γδ- (α-Form).	γδ- (β-Form).
M. p. of acid	32— 33°	4—5°	0°	Liquid
,, anilide	109—110*	76	87	
,, *p*-toluidide ...	125†	95	103†	

* Goldberg and Linstead, *loc. cit.* † Fichter and Pfister, *loc. cit.*

"Hydrosorbic acid" gives fairly well-defined crystalline derivatives which melt indefinitely and appear to be composed of mixed crystals. The melting points of hydrosorbic anilide (about 55°) and *p*-toluidide (about 74°) are raised by admixture with either the corresponding pure βγ- or the pure γδ-derivative.

The new data throw light on some other aspects of the chemistry of hexenoic acids. Fittig and Landsberg (*Annalen*, 1880, **200**, 43) noticed that addition of hydrobromic acid to hydrosorbic acid yielded a bromocaproic acid which on treatment with water regenerated an unsaturated acid apparently isomeric but not identical with hydrosorbic acid. Hjelt (*Ber.*, 1882, **15**, 617) found that the product of the same reaction contained, in addition to caprolactone (Fittig and Hjelt, *Annalen*, 1881, **208**, 67), an unsaturated acid resembling that of Fittig and Landsberg. This acid differed from hydrosorbic acid in that it solidified at −12° and melted at −10°. It now seems probable that this unsaturated acid was impure

$\beta\gamma$-hexenoic, the bulk of the $\gamma\delta$-acid having been removed as lactone. The only other reference to a " solid " hydrosorbic acid seems to be that of Wahlbaum (*J. pr. Chem.*, 1917, **96**, 245), who isolated the phenylacetate of a $\beta\gamma$-hexenol from Japanese oil of peppermint. The position of the double bond was fixed by oxidation, the alcohol yielding the β-hexenyl ester of $\beta\gamma$-hexenoic acid, which on hydrolysis (under unspecified conditions) yielded an acid, b. p. 215—218°, solidifying in a freezing mixture. Wahlbaum considered this to be impure $\alpha\beta$-acid, but, unless the hydrolysis was conducted under extremely vigorous conditions, it was most probably an impure sample of the solid $\beta\gamma$-acid.

Reference must finally be made to the $\beta\gamma$-hexenoic acid of Fittig and Delisle (*Annalen*, 1889, **255**, 61), prepared by pyrogenic decomposition of the corresponding paraconic acid. This resembled hydrosorbic acid superficially, but from its method of preparation it must have been the chemically pure $\beta\gamma$-acid, a view which is strengthened by the fact that Fichter and Pfister isolated a *p*-toluidide from this acid with a melting point (95·5°) identical with that of our derivative. Fittig and Delisle, however, definitely state that their acid remains liquid at $-18°$, and it would appear that this represents an example of *cis-trans*-isomerism analogous to that of the $\gamma\delta$-acids. At present we have been unable to confirm this owing to difficulties encountered in the preparation of the necessary intermediate paraconic acid.

EXPERIMENTAL.

Δ^{β}-*n-Hexenoic Acid.*—The best yields were obtained by the following process: Δ^{α}-Hexenoic acid, m. p. 32° (Goldberg and Linstead, *loc. cit.*) is equilibrated in 200—300 g. quantities by 8 hours' heating under reflux (brine bath at 105°) with 10 equivs. of 40% caustic potash, the temperature inside the 3-litre flask remaining at 100° ± 1°. The product is cooled in ice, acidified with 50% sulphuric acid, and extracted exhaustively with ether. The solvent is removed from the dried extract, and the residue distilled under reduced pressure. Some water first passes over from the decomposition of hydroxy-acid. Distillation of the unsaturated acids commences at about 112°/15 mm. and all the distillable product is collected, no attempt at fractionation being made. The distillate is cooled in ice (*not* in a freezing mixture), and the $\alpha\beta$-acid which separates is removed by filtration at the pump through a funnel cooled at 0°. The liquid filtrate yields no solid $\alpha\beta$-acid on cooling at 0° and seeding. 220 G. of the $\alpha\beta$-acid yield 77 g. of the liquid mixture (A).

If the unsaturated acids are separated from the hydroxy-acid by distillation in steam, the yield is lower. The αβ-acid removed by filtration and the hydroxy-acid remaining as residue after the vacuum distillation can be treated again with caustic potash and yield further quantities of βγ-acid. After a second treatment in this way, however, the accumulation of hydroxy-acid makes it advisable to distil the unsaturated acids in steam before vacuum distillation.

Attempted Separation of the Mixture (A).—A typical sample of the liquid mixture had $d_{4^\circ}^{18\cdot7^\circ}$ 0·9608, $n_{\mathrm{D}}^{18\cdot7^\circ}$ 1·4435, whence $[R_L]_{\mathrm{D}}$ 31·52 (calc., 30·98), iodine addition (Linstead and May, J., 1927, 2573; ten-minute reaction) 30·4%. Practically no separation of βγ-acid was effected by distillation, the acid boiling steadily at 117—118°/23 mm., and having $d_{4^\circ}^{18^\circ}$ 0·9614, $n_{\mathrm{D}}^{18^\circ}$ 1·4440, iodine addition, 32·7%.

The mixture (A) (33 g.) was treated with half the theoretical amount of sodium hydroxide and the solution distilled in steam. The acid in the distillate was isolated in the usual way [(i), 15 g.]. The residue was treated with one-third of the theoretical amount of acid and again distilled in steam. The distillate gave 5 g. of acid (ii). The residue was acidified and extracted, giving 10 g. of acid (iii). These acids had the following properties :

	B. p.	$n_{\mathrm{D}}^{18\cdot7^\circ}$.	$d_{4^\circ}^{18\cdot7^\circ}$.	$[R_L]_{\mathrm{D}}$.
(i)	110—112°/12 mm.	1·4452	0·9623	31·58
(ii)	—	1·4457	0·9635	31·56
(iii)	—	1·4432	0·9632	31·39

The iodine addition of (iii) was 35·9% (about 70% βγ-acid). Separation was therefore incomplete and the method was not further investigated.

Separation by Partial Esterification.—As the principal object of this process is the preparation of pure βγ-acid, we have used shorter times of reaction than Sudborough (*loc. cit.*). There are also other differences in the methods of working. The mixture (A) (80 g.) was added to a solution of 208 c.c. of *N*/1-alcoholic hydrogen chloride in 625 c.c. of absolute alcohol, and the whole allowed to stand for 3 hours at room temperature. The product was poured into 3 volumes of water, made alkaline with sodium carbonate, and allowed to separate. The layer of ester was dissolved in a little ether and the aqueous solution run off without thorough extraction, which at this stage only results in the removal of alcohol, which has to be removed by fractionation through a column later. The alcohol was then removed from the aqueous layer at a temperature of 50° at the pump and the residue twice thoroughly extracted with ether. The extracts and the layer originally separated were combined, washed twice with saturated brine, and dried with calcium chloride. After removal of the ether, the residue was fractionated under reduced pressure. The unesterified acid was obtained from the aqueous solution after complete removal of the ester, acidification and exhaustive extraction. (This process has now been used with minor modifications in seven or eight separations; convenient quantities appear to be: acid mixture, 1 g.-mol.; *N*/1-alcoholic hydrogen chloride, 300 c.c.; alcohol 900 c.c. The most convenient time of esterification is found by preliminary experiments.) In the present example the acid fraction yielded 30 g. (37·5%) of nearly pure αβ-acid, crystallising readily at room temperature. The neutral fraction gave 44 g. (45%) of an ester (a) boiling constantly at 70°/15 mm., and having $d_{4^\circ}^{21^\circ}$ 0·8970, $n_D^{21^\circ}$ 1·4267, $[R_L]_D$ 40·63 (calc., 40·33). This was hydrolysed with 2 equivs. of 10% potassium hydroxide and sufficient alcohol to secure miscibility for 48 hours at room temperature. The product was diluted to twice its volume with water, and the alcohol removed at the pump with as little warming as possible. The solution was then acidified and extracted with ether. The solvent was removed and the acid freed from traces of ester by extraction with 10% potassium carbonate solution. From the alkaline layer, after extraction with ether, the acid was recovered in the usual way; 26 g. were obtained, b. p. 108°/15 mm. (B). In another experiment 77 g. of the mixture (A) gave after one 3-hour esterification an ester yielding 25 g. of acid on hydrolysis. This may be compared with the following experiment with the αβ-acid.

10 G. of the pure solid acid were treated under exactly the same conditions for 4 hours. After removal of the solvent from the neutral fraction there was a faint smell of ester but no detectable residue. The acid fraction yielded 7·5 g. of unchanged solid αβ-acid.

The acid (B) has $d_{4^\circ}^{18^\circ}$ 0·9611, $n_D^{18^\circ}$ 1·4403, $[R_L]_D$ 31·3, and an iodine addition of 43·6%. It readily solidifies in ice and melts at about 4°. To test its purity it was submitted to further partial esterifications.

After 4 hours' treatment 10 g. of acid (B) yielded 10 g. (80%) of ester, and 0·8 g. (8%) of acid. The acid (B′) had b. p. 116°/15 mm., $n_D^{19^\circ}$ 1·4457, iodine addition 23·4%, and slowly deposited a solid (presumably the αβ-acid) in a freezing mixture. The ester (b) had b. p. 66°/14 mm., $d_{4^\circ}^{18\cdot5^\circ}$ 0·8973, $n_D^{18\cdot5^\circ}$ 1·4264, $[R_L]_D$ 40·57, and on hydrolysis gave 7 g. of an acid (C). This had b. p. 110—111°/15 mm., $d_{4^\circ}^{17^\circ}$ 0·9638, $n_D^{17^\circ}$ 1·4405, $[R_L]_D$ 31·24, iodine addition 45·5%.

The acid (C) (7 g.) was then partially esterified for a shorter time ($2\frac{1}{2}$ hours) and yielded 7 g. of ester and 0·5 g. of acid. The acid (C′) had b. p. 108°/15 mm., $n_D^{16\cdot2^\circ}$ 1·4407, and iodine addition 37%. It readily solidified in a freezing mixture and was obviously mainly βγ-acid. The ester (c) had b. p. 67°/15 mm., $d_{4^\circ}^{17^\circ}$ 0·8983, $n_D^{17^\circ}$

1·4272, $[R_L]_D$ 40·60, and may be taken to be the pure βγ-compound for its properties are almost exactly those of (b). On hydrolysis (c) gave 4 g. of an acid (D). This had b. p. 105°/13 mm., $d_{4°}^{14°}$ 0·9626, $n_D^{14°}$ 1·4397, $[R_L]_D$ 31·23, iodine addition 46·7%, and is taken to be the pure βγ-acid.

Δ^β-n-*Hexenoic acid* (Found : C, 63·3 ; H, 8·8. $C_6H_{10}O_2$ requires C, 63·1 ; H, 8·9%) forms colourless plates, m. p. 4—5°. A mixture with equal parts of the αβ-acid does not solidify in a freezing mixture. The liquid acid has a smell of the general unsaturated acid type but less unpleasant than that of the γδ-isomeride. 4 G. of the acid were oxidised by the method previously used for hydrosorbic acid. 3·0 G. of total oxidation products were isolated in which propionic acid (*p*-toluidide) and oxalic acid (m. p. 102°, titration) were identified as before (Goldberg and Linstead, *loc. cit.*). No trace of succinic acid could be detected.

The acid chloride was obtained in 90% yield by use of thionyl chloride, and from this the anilide and *p*-toluidide were prepared in the usual manner. The *anilide* forms felted needles from light petroleum, m. p. 75° (Found : N, 7·5. $C_{12}H_{15}ON$ requires N, 7·4%). The p-*toluidide* crystallises from benzene and petroleum ether in needle clusters, m. p. 95° (Found : C, 76·7 ; H, 8·3. $C_{13}H_{17}ON$ requires C, 76·8 ; H, 8·4%).

Reference curve. Δ^β-Hexenoic acid has given the least satisfactory results by the iodine method of any unsaturated acid yet examined. The same sample of the acid may give iodine additions varying by 2% (or even more in one or two cases). It has not been possible to correlate this with any variation in the experimental procedure, and it is certainly not due to impurity in the acid. It seems probable that the variable results are due to an unusual instability of the iodo-lactone which is the product of the action of iodine on the βγ-acid. The figures given below for synthetic mixtures, although concordant among themselves, are therefore subject to an error of about ± 2%. That they are reasonably correct is suggested by the close agreement between them and those for similar mixtures of the *n*-pentenoic acids which are added for comparison (Goldberg and Linstead, *loc. cit.*) :

% αβ-Acid in mixture	100	80	75	66·7	50
Iodine addition to *n*-Hexenoic acids	0·8	12·4	15·3	19·4	27·2
Iodine addition to *n*-Pentenoic acids	4·4	13·7	—	19·8	26·6

% αβ-Acid in mixture	33·3	20	10	0 (βγ-)
Iodine addition to *n*-Hexenoic acids	34·2	40·0	43·8	46·7
Iodine addition to *n*-Pentenoic acids	34·8	41·4	—	46·8

Equilibration. The βγ-acid (4·5 g.) was equilibrated with 10 equivs. of 30% caustic potash at 100° in a copper flask fitted with a reflux condenser, the heat being regulated by means of a salt bath. The equilibrated acid was isolated (3·5 g.) in the usual way (Goldberg and Linstead, *loc. cit.*). The product had $d_{4^\circ}^{19^\circ}$ 0·9483, $n_D^{19^\circ}$ 1·4442, $[R_L]_D$ 31·81, iodine addition 17·04% (equivalent to 71% αβ-acid). 1·14 G. of this were dissolved in bicarbonate solution and treated with 24 c.c. of a solution of iodine (25 g.) and potassium iodide (40 g.) in water (125 c.c.) (Linstead and May, *loc. cit.*, p. 2573). After two hours, an excess of saturated sodium carbonate solution was added and the unchanged acid and iodolactone were separated in the usual manner. The acid fraction yielded 0·80 g. of αβ-acid (m. p. 32°, mixed m. p.) and the neutral fraction gave 0·47 g. of the liquid β-iodo-γ-lactone corresponding with 0·223 g. of βγ-acid (compare Bougault, *Ann. Chim. Phys.*, 1908, **14**, 167). The solid αβ-acid was also isolated from the equilibrated material by a partial esterification experiment.

β-*Form of* Δ^γ-n-*Hexenoic Acid*.—Crotyl alcohol (V) (Charon, *Ann. Chim. Phys.*, 1899, **17**, 215) was converted by the method of Hibbert and Birt (*J. Amer. Chem. Soc.*, 1928, **50**, 1413) into the bromide (VI), b. p. 101—105°/760 mm.; yield 25 g. from 400 g. of crotonaldehyde.

Sodium (4·3 g.) was dissolved in 100 c.c. of alcohol which had previously been boiled under reflux with $\frac{1}{20}$th of its weight of sodium and redistilled. To the cold solution, 30 g. of redistilled ethyl malonate were added and then crotyl bromide (25 g.) drop by drop. The mixture was heated on the steam-bath until neutral to litmus, the alcohol was allowed to evaporate, and the solution diluted with water and extracted thoroughly with ether. The ethereal solution was dried over calcium chloride and the residue after removal of the solvent was fractionated under reduced pressure. *Ethyl* Δ^β-*butenylmalonate* was thus obtained as a colourless, almost odourless liquid (18 g.), b. p. 132°/20 mm., $d_{4^\circ}^{20^\circ}$ 0·9953, $n_D^{20^\circ}$ 1·4372, $[R_L]_D$ 56·35 (calc., 55·93) (Found: C, 62·0; H, 8·2. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·5%).

The ester (16 g.) was added slowly to a solution of 32 g. of caustic potash in its own weight of water, left over-night, and finally warmed for $\frac{1}{2}$ hour on the steam-bath. After removal of the neutral portion with ether, the alkaline liquid was acidified and extracted thoroughly with ether. The aqueous portion was considerably evaporated and again extracted. The united extracts were dried and freed from the bulk of the ether under a column. The residue was left in a vacuum desiccator and gradually solidified to a hard white cake (11 g.), m. p. (crude) 112°. Δ^β-*Butenylmalonic acid* forms needles from benzene, m. p. 115° (Found: C, 53·4; H, 6·5. $C_7H_{10}O_4$ requires C, 53·1; H, 6·4%).

The malonic acid (11 g.) was heated in a glycerol-bath at 140°

under atmospheric pressure until evolution of carbon dioxide had almost ceased, and the resulting acid was then twice distilled under reduced pressure. The β-*form* of Δ^{γ}-n-*hexenoic acid* (6 g.), b. p. 111—112°/20 mm., thus obtained (Found: C, 63·1; H, 9·0. $C_6H_{10}O_2$ requires C, 63·1; H, 8·9%) is a colourless liquid with a strong unpleasant smell, resembling that of "hydrosorbic acid"; it has $d_{4^\circ}^{18\cdot7^\circ}$ 0·9584, $n_D^{18\cdot7^\circ}$ 1·4367, $[R_L]_D$ 31·17, and does not solidify in a freezing mixture either alone or when seeded with the α-acid. The iodine addition is 91·4%.

The oxidation products were prepared and separated in the manner previously used, acetic acid (usual tests) and succinic acid (m. p. 186°, mixed m. p., titration) being identified.

The cadmium salt, prepared by Fichter's method (*loc. cit.*) crystallised immediately in glistening white plates. The acid chloride, b. p. 55—57°/20 mm., yielded the *anilide* which crystallised from light petroleum in felted needles, m. p. 87° (Found: C, 75·9; H, 8·3. $C_{12}H_{15}ON$ requires C, 76·2; H, 8·0%), and also the *p*-toluidide, crystallising from the same solvent in glistening plates, m. p. 103° (Found: C, 76·6; H, 8·7. Calc. for $C_{13}H_{17}ON$: C, 76·8; H, 8·4%).

The acid (2·5 g.) was heated for 24 hours with 12·3 g. of caustic potash in 40 c.c. of water. The product was worked up in the usual way and gave 2 g. of an acid, b. p. 115°/17 mm., $d_{4^\circ}^{20^\circ}$ 0·9599, $n_D^{20^\circ}$ 1·4364, iodine addition 93·9%, which was therefore the unchanged β-form. The *p*-toluidide melted at 103° and did not depress the m. p. of the derivative prepared from the pure acid.

The α-*form* of Δ^{γ}-*n*-hexenoic acid was prepared in 12% yield by Fichter's method (*loc. cit.*) from α-acetylglutaric ester (Perkin and Simonsen, J., 1907, **91**, 1740). It had b. p. 106—108°/8 mm., $d_{4^\circ}^{17\cdot2^\circ}$ 0·9715, $n_D^{17\cdot2^\circ}$ 1·4413, $[R_L]_D$ 31·13. It solidified immediately in a freezing mixture and melted at 0° (Found: C, 63·1; H, 9·0. Calc.: C, 63·1; H, 8·9%). The iodine addition was 80·1%.

The acid chloride boiled at 48—50°/7 mm., and yielded an anilide, m. p. 88°, and a *p*-toluidide, m. p. 103°, which did not depress the m.p.'s of the corresponding derivatives previously obtained from the α-form. The cadmium salt had the identical crystalline form. Mixtures of the anilide and *p*-toluidide of "hydrosorbic acid" (Goldberg and Linstead, *loc. cit.*) with approximately equal weights of the corresponding derivatives of the pure βγ- and γδ-acids melted as follows:

Mixture.	M. p.
Hydrosorbic anilide (55°) + βγ-anilide (76°)	66—67°
,, ,, + γδ-anilide (86—87°)	69—70
Hydrosorbic *p*-toluidide (74°) + βγ-*p*-toluidide (96°)	91
,, ,, + γδ-*p*-toluidide (103°)	89—90

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