128. *Catalytic Influences in Three-carbon Tautomerism. Part IV. The Tautomeric Changes of Unsaturated Acids at High Temperatures.*

By R. P. Linstead and E. G. Noble.

It has been shown (J., 1930, 1603) that certain Δ^{α}- and Δ^{β}-unsaturated acids are capable of interconversion at their b. p.'s, apparently in the absence of added catalyst. A detailed examination has now been made of the tautomerism of Δ^{α}- and Δ^{β}-*n*-hexenoic, -pentenoic, and -butenoic acids both in the pure state and dissolved in organic solvents, water, and

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* The physical properties and iodine additions of the various products isolated in this part of the work have been omitted for the sake of brevity. There was no significant difference between the composition of the tautomeride from the alcoholic layer and that from the *cyclo*hexane layer in any experiment.

alkalis. In this way it has been possible to connect the "spontaneous" tautomerism of these acids with that occurring in the alkaline solutions of their salts.

A. *Tautomerism in the Absence of Water.*—The preliminary evidence (*loc. cit.*) for the occurrence of tautomerism in pure Δ^{α}- and Δ^{β}-*n*-hexenoic acids at their b. p.'s (219° and 208°) was first confirmed qualitatively (see p. 618). At and below 200° there was very little side reaction in clean apparatus, although a small amount of neutral impurity, apparently a product of decarboxylation and polymerisation, was slowly formed. The reaction was thus suitable for quantitative study, which was easily controlled by iodometric analysis. The results (see Experimental) lead to the following generalisations :

(1) Purification of an acid beyond a certain point has no appreciable effect on the velocity of interconversion. Provided that all mineral impurity be eliminated, the change proceeds at a definite and reproducible rate.

(2) This rate is independent of the surface of the vessel.

(3) The velocity is very little affected by the medium, provided that no secondary decomposition occur; *e.g.*, Δ^{β}- is converted into Δ^{α}-*n*-hexenoic acid with the same ease whether heated alone or dissolved in its ethyl ester, xylene, decalin, tetralin, or chlorobenzene, and but little faster in water and diethyl ketone. The same is true of Δ^{β}-pentenoic acid, but the difference between the rate of change with and without water is greater in the case of Δ^{β}-butenoic acid. If much secondary decomposition or charring occurs, the change is accelerated.

(4) Most *added catalysts* cause secondary decomposition. Alkalis increase the rate of change enormously, neutral salts to a smaller extent.

(5) There is little change below 150°, and between this temperature and the b. p. the rate increases rapidly. The velocities of change of the three acids at 150° are related to the velocities of the same changes in aqueous alkali (see below); for instance, Δ^{β}-pentenoic acid is slightly, and Δ^{β}-butenoic acid considerably, more mobile than Δ^{β}-hexenoic acid under both sets of conditions.

(6) The position of equilibrium is independent of the conditions of interconversion (cf. J., 1927, 2579).

Mechanism of the "pure" change. The facts summarised under (1), (2), and (3) above are only consistent with the reaction's being of the first order. Moreover, as the solvent is without influence, it would appear that the change is *intramolecular*. When, however, bases, salts, or perhaps even water, are added, this comparatively inefficient process is superseded by one involving the surrounding molecules. It is remarkable that no evidence could be obtained of a similar change in ethyl Δ^{β}-*n*-hexenoate, suggesting that the hydrogen of the carboxyl group plays some specific part within its own molecule.

B. *Tautomerism in Aqueous Solutions.*—This has been studied in the presence of large amounts of free alkali by Fittig (*Annalen*, 1894, **283**, 47) and in these laboratories. We have now followed the equilibration of Δ^{β}-*n*-hexenoic acid and its homologues at temperatures from 100° to 200°, concentrations from $N/2$ to $4N$, and in the presence of 0—1½ equivs. of alkali. Observations were reproducible at and below 150°, but were rather uncertain at 200° owing to occasional charring. The results may be summarised as follows :

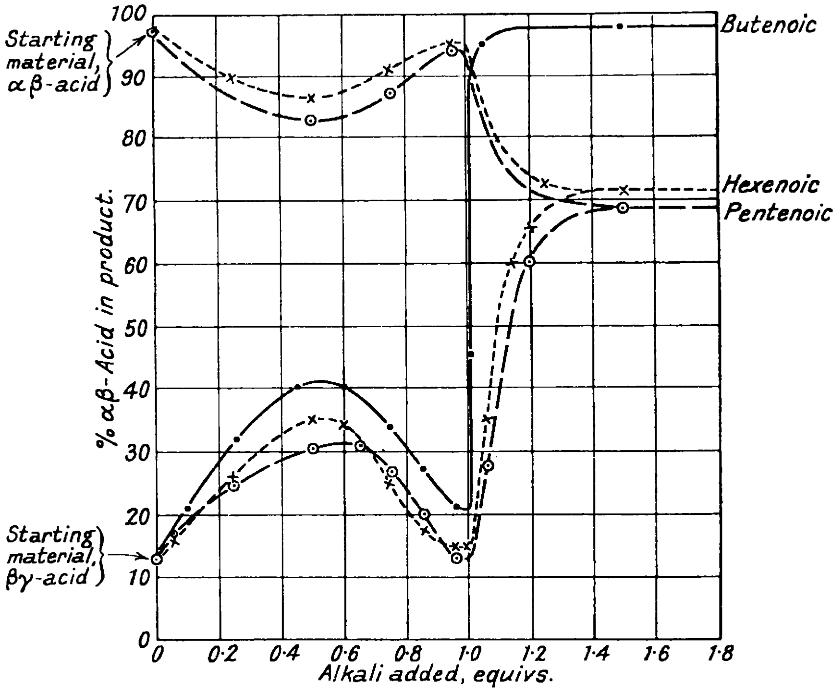
(1) The same equilibrium was reached in aqueous solutions of the acids, in neutral solutions of the sodium salts, or in the presence of free alkali [cf. (6) above].

(2) The interconversion of the acids follows a unimolecular course in aqueous solution or for any one concentration of alkali. The unimolecular constants (hrs.$^{-1}$) for the change of Δ^{β}-*n*-hexenoic acid are given below, the equilibrium position being taken as 26% Δ^{β}-.

Conditions of equilibration.	$k_1 + k_2$. Mean.	Max.	Min.	No. of detmtns.
Acid alone in $N/1$-aqueous solution at 150°	0·0042	0·0047	0·0038	6
Sodium salt in $N/2$-aqueous solution + 1 equiv. of $N/1$-NaOH at 100°	0·055	0·057	0·052	7
Acid + 10 equivs. of 25% aqueous KOH at 100°	0·60	0·61	0·59	4

The fraction of the acid and of the sodium salt isomerised in aqueous solution in a given time was independent of the initial concentration. A similar result was obtained in a constant concentration of free alkali (*N*/1-sodium hydroxide), the sodium salt of Δ^{β}-hexenoic acid attaining equilibrium with the same velocity coefficient when its initial concentration was varied between *N*/1 and *N*/10. Sodium Δ^{β}-*n*-pentenoate behaved similarly.

(3) Effect of the concentration of alkali. Comparisons were made of the extent of isomerisation of all six acids in aqueous solution at 150°; the concentration of the acid was maintained at *N*/1 and increasing amounts of alkali were added. These results are illustrated in the fig. To obtain convenient values, the more mobile butenoic acids were heated for one hour, the other acids for 24 hours. It will be seen that the amount of an acid isomerised under these conditions is increased by the addition of alkali until about half the initial acid has been neutralised. The proportion changed then decreases until, when the solution is almost neutral, it is very little greater than in the solution of the acid in water. As soon as the neutral point has been reached, the addition of more alkali causes an enormous increase in the change, affording a clear example in the three-carbon system of an effect well known in other tautomeric changes. The figures for the reaction at the neutral point were confirmed by experiments carried out on solutions of the isolated sodium salts.



The peak in the curves on the acid side of neutrality may be interpreted as follows : The increase in the rate of change of the acid caused by the addition of alkali may be attributed to catalysis of the change in the acid molecule by its own anion. As neutralisation proceeds, there is more salt to catalyse the change but less acid to be affected, and this finally leads to a fall in the effective change. As well as the isomerisation in the acid itself, a corresponding change occurs in the anion of the salt, which becomes more important as neutralisation proceeds and finally accounts for the whole of the change at the neutral point.

These two series of experiments show that in alkaline solution an unsaturated acid tautomerises at a rate determined by the concentration of free alkali. Hence, in equilibrations for preparative purposes, it is better to use a small excess of alkali at high concentration (*e.g.*, 2 equivs. in 40% solution) rather than the very large amounts (10 equivs.) originally used by Fittig.

For the sake of completeness we have re-examined the equilibration of the same acids under standard conditions (J., 1927, 2579), using more accurate reference data and purer materials, with the following results:

Acid.	Equilibrium, % Δ^{α}.	Mobility * (*t* in hours).
n-Hexenoic	74 (70) †	6·0 (*ca.* 7)
n-Pentenoic	68 (75)	10·0 (*ca.* 7)
n-Butenoic	98	Very high.

* Measured from Δ^{β}-side.

† Earlier data in parentheses (J., 1928, 2343; 1930, 2153).

The equilibrium value for the *n*-butenoic acids is that expected in the light of the work of Fichter and Sonneborn (*Ber.*, 1902, **35**, 938); they record a considerable addition of the elements of water in the action of alkali on the Δ^{β}-acid (*loc. cit.*, p. 941), but little evidence of this was obtained in our experiments.

C. *Attempted Equilibration of Neutral Substances.*—It has been shown by Letch and Linstead (J., 1932, 443) that typical Δ^{α}- and Δ^{β}-unsaturated nitriles undergo no tautomeric change at or above their b. p.'s in the absence of catalyst. This result is substantiated by the recent work of Bruylants and his school on the exhaustive fractionation of such nitriles under atmospheric pressure (see Baerts, *Bull. Soc. chim. Belg.*, 1932, **41**, 314). Similar negative results have now been obtained by heating ethyl Δ^{β}-*n*-hexenoate alone or admixed with its parent acid, and by heating allyl cyanide in the presence of Δ^{β}-*n*-butenoic acid.

EXPERIMENTAL.

For references to the preparative methods see J., 1933, 562.

Estimation of Mixed Δ^{α}- and Δ^{β}-Acids.—For hexenoic and pentenoic acids, iodine additions (*J*) (Linstead and May, J., 1927, 2565) were carried out at 20° for 10 minutes (hexenoic) and 1 hour (pentenoic). The addition of iodine to Δ^{β}-butenoic acid was too slow for convenience and a bromometric method was used (cf. J., 1927, 355): 10 C.c. of an *N*/15-solution of the acid in chloroform were treated with 1 mol. of bromine in a freshly standardised *N*/20-solution in chloroform and left in the dark for 30 minutes at 20°; potassium iodide and water were then added and the free iodine was titrated. It was found desirable to check the standardisation of the bromine solution every 30 minutes. The reference data for the pure acids and synthetic mixtures are given below:

Mean % Addition of Halogen (J) *to Unsaturated Acids at* 20° ± 0·25°.

Δ^{α}-Acid, %	100	90	80	60	40	20	10	0 (Δ^{β}-)
Addition of I to hexenoic acid	0	7·5	15	27	38	48	—	55·5
Addition of I to pentenoic acid ...	1·5	10·9	19·4	36	50·8	63·6	68·8	74
Addition of Br to butenoic acid ...	1·4	11	20·5	39·5	55	69	75·3	80

1. *Preliminary Equilibrations.*—Samples of Δ^{α}- and Δ^{β}-hexenoic acids were boiled under reflux in silica or soft-glass flasks in an atmosphere of carbon dioxide for various times. Three samples of the Δ^{α}-acid (A, B, and C) and two of the Δ^{β}-acid (D and E) were used. The temperature of the liquid was initially 219° (Δ^{α}-) and 208° (Δ^{β}-), but the latter rose considerably in the longer experiments. The product in each case was thoroughly shaken with sodium bicarbonate solution, traces of neutral material being removed with ether, and the acid isolated with sulphuric acid, extracted with ether, and dried over calcium chloride. The average recovery, from 10 g. samples, was 80—85%. The equivalents of the equilibrated acids were determined throughout by titration, but are not recorded; they were generally slightly high, indicating the presence of a trace of polymeride, unless the acids were first distilled in steam or under reduced pressure. The compositions, determined iodometrically, are given below to the nearest 0·5%, those representing complete equilibration being italicised. [In this and other tables each figure represents one complete experiment. When two figures are given in the first and subsequent columns, two separate experiments were carried out under the same conditions.

When two figures are given in the last two columns only, two separate analyses were performed on the same product. The figures under *J* are mean values.]

Expt.	Initial acid.	Vessel.	Time, hrs.	*J*, %.	Δ^α-Acid in product, %.
1	Δ^α-, A	Silica	3	7·5	90
2, 3	,,	,,	5, 5	8·5, 8·3	89, 89·5
4, 5	,,	,,	7, 7	8·6, 11·0	89, 86
6	,,	,,	48	18·0	*75*
7	,,	Glass	3	9·0	88·5
8	,,	,,	48	18·0	*75*
9	Δ^α-, B	Silica	3	11·0	86
10	,,	Glass	3	15·0	80
11	,,	,,	5	18·0, 14·0	*75·5*, 81·0
12	,,	,,	7	17·4	76·6
13	,,	,,	12	18·8	*75*
14	,,	,,	30	20·5	*72*
15	Δ^α-, C	Silica	1·5	4·1	94
16	,,	,,	15	9·5	87·5
17	Δ^β-, D	,,	5	45·5	24·5
18	,,	,,	7	44·0	28
19	Δ^β-, E	,,	48	18·5	*75*
20	,,	Glass	1·5	51·0	14
21	,,	,,	48	18·3	*75·5*
22	,,	,,	75	19·0	*74*
23	Δ^β-, D	,,	7	43·0	30
24	,,	,,	30	35·0	54·5

The results for samples A, B, and C of the Δ^α-acid show considerable differences, B being the most mobile. Ignition of this material showed it to contain about 0·3% of mineral material (Na, Ca) derived from the drying agents. This sample and sample A had been recrystallised (m. p. 33°) but not redistilled. Sample C, which was the most inert, had been redistilled. Subsequent results showed that redistilled material always gave reproducible velocity data (see below).

The reversibility of the change was confirmed as follows : (i) Equilibrated Δ^α-acid (from Expts. 6, 8, 11, 14, 15) was partially esterified (Eccott and Linstead, J., 1930, 2153) to yield a Δ^β-ester with b. p. 67°/16 mm., $d_{4^\circ}^{20^\circ}$ 0·8957, $n_D^{20^\circ}$ 1·4252, whereas the ester prepared from the silver salt of the pure Δ^β-acid had $d_{4^\circ}^{20^\circ}$ 0·8956, $n_D^{20^\circ}$ 1·4255. The ester from the equilibrated acid gave on hydrolysis almost pure Δ^β-acid, b. p. 98°/8 mm., m. p. 8—9°, *J* 54%, equiv. (by titration) 114·2 (Calc., 114·1). Another sample of equilibrated Δ^α-acid was treated for 24 hours with 5 vols. of 60% sulphuric acid at room temperature, and then separated into Δ^α-acid and lactone (J., 1932, 115). The lactone had b. p. 96°/15 mm., $n_D^{20^\circ}$ 1·4386 (lit., 1·4387), equiv. 114·2, and contained only 0·5% of acid. It was further identified as γ-*n*-hexolactone by the formation of the γ-hydroxy-amide, m. p. 73°. The Δ^α-acid yields no γ-lactone under these conditions.

(ii) Equilibrated Δ^β-acid (from Expts. 20, 24, 25) in aqueous sodium bicarbonate was treated with concentrated iodine in potassium iodide (Bougault, *Ann. Chim. Phys.*, 1908, **14**, 145), and the Δ^β-acid removed as iodo-lactone by extraction with ether. Acidification of the bicarbonate solution yielded the Δ^α-acid, m. p. 31—32°. Another sample was lactonised by the method given above, and the lactone removed by extraction with ether from a sodium bicarbonate solution. Acidification of the latter gave the Δ^α-acid, m. p. 30—31°, *J* 0·5%.

2. *Further Purification of the Acid, and Effect of Surfaces.*—Two flasks of the Claisen type were used ; one of quartz was fitted with a sealed-in pocket, in which the thermometer immersed in a little mercury was held, and with a ground quartz stopper for the side arm. The other was of soft glass, and was fitted with an ordinary thermometer and corks. The flasks were cleaned with chromic–sulphuric acid mixture and distilled water and dried. The redistilled acid was introduced, and the flasks evacuated and filled with dry carbon dioxide. The acid was boiled freely for a suitable time, and then isolated and analysed as before :

% *Change in Boiling Hexenoic Acids* (*Expts.* 25—32).

Initial material	Δ^α-.	Δ^α-.	Δ^β-.	Δ^β-.
Time (hrs.)	7	24	12	24
% Change in quartz	15	21·5	35	64·5
,, ,, glass	13·5	21	32	66·5

The use of quartz vessels, therefore, effects no alteration. To confirm this, samples of freshly distilled acid were redistilled into the quartz flask under reduced pressure from a Pyrex-glass apparatus. The air led into the bubbler in this distillation was freed from bases by scrubbing with sulphuric acid. After being boiled for 5 hrs., the Δ^{α}-acid yielded 10·5% of Δ^{β}-acid, and in 7 hrs. the latter acid gave 19·5% of Δ^{α}-acid. There was therefore no appreciable slowing of the reaction.

3. *Experiments at Lower Temperatures.*—The acid under study was distilled from a flask of Pyrex glass to a sealed-on vessel of the same glass in a current of air free from carbon dioxide, bases, and moisture. The apparatus was then evacuated, filled with pure carbon dioxide, and the receiving vessel sealed off from the distillation flask, after which the apparatus was again evacuated and filled with pure carbon dioxide. The receiving vessel was heated by an electric oven constant to ± 1° while a current of pure carbon dioxide was passed across the outlet tube. The product was allowed to cool in this gas, and analysed as before.

Any necessary catalysts were introduced before the equilibration through the outlet tube. These were treated as follows: Nitrobenzene (B.D.H. purified) was frozen, the liquid poured off at 3°, the residue washed with aqueous sodium carbonate and water, dried, and redistilled. Benzonitrile was distilled in steam, the distillate being treated with sodium carbonate and extracted with ether; the extracts were dried (calcium chloride), distilled under reduced pressure, again dried, and redistilled. Chlorobenzene, xylene, tetralin, and decalin were dried and redistilled, the hydrocarbons over sodium. The alkalis were of A.R. quality and the other materials were not specially purified.

When high-boiling solvents were used the procedure in working up the equilibrated acid was modified, the product being treated with sodium bicarbonate solution and then extracted four times with benzene and four times with ether before acidification. The loss in these experiments was about 15% and was largely mechanical except in equilibrations in nitrobenzene. The results are tabulated below:

*Equilibration of Δ^{β}-*n*-Hexenoic Acid in Pyrex Glass.*

(Temp.: In expts. 33 and 34, 210°; in all other expts., 200° ± 1°.)

Expt.	Catalyst or solvent.	Time (hrs.).	*J*, %.	Δ^{α}-Acid formed, %.
33, 34	None	7, 7	46·6, 48·6	25, 22
35, 36	,,	4, 4	53·6, 53·6	6, 6
37, 36	,,	8, 8	51·0, 52·1	10, 9
39	2 vols. Tetralin	4	53·5	6
40	,,	8	51·5	10
41, 42	1% Na_2CO_3	4, 4	48·0, 47·8	20, 20
43, 44	,,	8, 8	40·3, 42·0	34·5, 32·5
45, 46	20% ,,	4, 4	23·0, 22·2	67, 68
47, 48	2% Piperidine	4, 4	45·5, 45·0	25, 26
49	1% Na_2SO_4	8	49·7	15
50, 51	1% Phthalic anhydride	8, 8	50·9, 50·3	13, 14
52	1% Trichloroacetic acid	4	51·5	11
53	,,	8	47·5	20

Samples of the acid were also heated in 2, 5, and 10 vols. of boiling tetralin (204°) for 4 hours, 17, 17, and 17·5% respectively of the Δ^{α}-isomeride being formed (Expts. 54—56); these results, and a comparison of Expts. 35—40, indicate that this solvent is without influence on the change. Experiments in nitrobenzene gave the anomalous and non-reproducible results shown below:

Expt.	Apparatus.	Temp.	Time, hrs.	Amount of $PhNO_2$.	Δ^{α}-Acid formed, %.
57, 58	Pyrex	200°	4, 4	2 vols.	26, 35
59, 60	,,	200	8, 8	2 vols.	67·5, 50
61	Jena Geissler flask	b. p.	½	5 vols.	16
62	,,	,,	1	,,	35
63	,,	,,	2	,,	66·5

After these equilibrations only 60—65% of acid could be recovered, the equivalent of which was rather high (116·5—118), and a charred residue was formed. This was found to be an active catalyst, 1% of it increasing the change in boiling Δ^{β}-hexenoic acid from *ca.* 20% to 38% in 4 hours. Experiments in benzonitrile were rendered valueless by double decomposition leading to the formation of benzoic acid.

These catalysts were shown to yield the usual equilibrium by the following experiments, which were carried out at the b. p. in Jena glass :

Expt.	Initial acid.	Catalyst.	Time, hrs.	*J*, %.	Δ^{α}-Acid, %.
64	Δ^{β}-	2% Piperidine	15	19·3	*74*
65	Δ^{β}-	20% Na_2CO_3	4	20·1	*73*
66	Δ^{β}-	2 vols. $PhNO_2$	4	17·5	*77*
67	Δ^{α}-	2% Piperidine	4	18·4	*75*
68	Δ^{α}-	2 vols. $PhNO_2$	4	18·8	*75*

The following experiments, carried out on pure Δ^{β}-*n*-pentenoic acid at 190° in the special Pyrex apparatus (p. 619), show that the change is appreciably faster than in the higher homologue at 200° (cf. Expts. 35—38) :

Expt.	Time, hrs.	*J*, %.	% Δ^{α}-Pentenoic acid formed.
69, 70	4, 4	69·0, 69·1	9, 9
71, 72	8, 8	67·8, 67·5	13, 13·5

4. *Experiments at* 150° : *Effect of Solvents.*—Freshly distilled Δ^{β}-*n*-hexenoic acid and the solvent were delivered by a pipette into a heavy tube of Monax glass, which was then sealed and heated at 150° ± 1° in an electric furnace for 24 hours except in Expts. 73 and 74.

Expt.	Solvent.	*J*, %.	Δ^{α}-Acid formed, %.
73, 74	None (100 hrs.)	50·5, 50·5	12·5, 12·5
75, 76	None	52·2, 52·2	8, 8
77	Decalin, 1 vol.	52·0	9
78	,, 2½ vols.	52·2	8
79	,, 5 ,,	52·5	8
80	Xylene, 2½ ,,	52·5	8
81	,, 5 ,,	52·0	9
82	Ethyl Δ^{β}-*n*-hexenoate, 5 vols.	52·5	8
83	Chlorobenzene, 2½ vols.	53·0	7
84	,, 5 ,,	53·0	7
85	Water, to 4*N*	52·0	9
86	,, to 2*N*	51·0	11·5
87, 88	,, to *N*/1	50·8, 51·2	12, 11·5
89	,, to *N*/2	50·0	13

In view of the experimental error involved in the determination of small changes, similar experiments were carried out concurrently for 336 hours at 150°.

90, 91	None	48·5, 48·2	17, 18
92, 93	Water, 5 vols.	41, 41	35, 35
94, 95	Diethyl ketone, 5 vols.	41·5, 41·5	36, 36
96, 97	Chlorobenzene, 5 vols.	50, 49·5	14, 16
98, 99	Decalin, 5 vols.	48·5, 48·1	17, 18

With ethylene dibromide as solvent, secondary decomposition occurred.

Similar results were obtained with Δ^{β}-*n*-pentenoic acid at 150°.

Expt.	Solvent.	Time, hrs.	*J*, %.	Δ^{α}-Acid formed, %.
100, 101	None	24	69·0, 69·1	9, 9
102, 103	,,	100	67·0, 67·0	13, 13
104	Xylene, 5 vols.	60	68·8	10
105	Chlorobenzene, 5 vols.	60	69	9
106	Water, to 4*N*	24	69	9
107	,, to 2*N*	24	68·4	11
108	,, to *N*/1	24	67·4, 68·2	13, 11·5
109	,, to *N*/2	24	67·6	12·5

Δ^{α}-*n*-Pentenoic acid on being heated alone at 150° for 24 hours yielded 2% of Δ^{β}-acid, and 3·5% in *N*/1-aqueous solution under the same conditions.

5. *Action of Alkali* (*see Fig.*).—The results tabulated below were obtained in experiments carried out by heating the six unsaturated acids at 150° with various amounts of aqueous sodium hydroxide in sealed tubes of Monax glass. The alkali was added in the form of a standard solution (about 2·5*N*) and was then diluted with the requisite amount of water so that the final concentration of acid + salt was always *N*/1. The product was acidified and worked up in the usual manner, the average recovery being 85% for hexenoic acids and 80% for the lower homologues. The results for the pure aqueous solutions at the same dilution are added below for comparison.

Equilibration of Δ^{β}*-Hexenoic Acid by Aqueous* NaOH *at* 150°.

(Time : 24 hours except where stated.)

Expt.	NaOH, equivs.	*f*, %.	Δ^{α}-Acid, %.	Expt.	NaOH, equivs.	*f*, %.	Δ^{α}-Acid, %.
87, 88	0	50·8, 51·2	12, 11·5	124, 125	0·85	48·3, 48·3	18, 18
110, 111	0·05	49·0, 49·4	16·5, 16	126, 127	0·95	48·6, 49	17, 16·5
112, 113	0·25	45·6, 45	25, 26	128, 129	0·98	48·6, 49·1	16·5, 16·2
114—117	0·50	42·7, 41·2 41, 41	31, 34·5 35, 35	130	1·05	40·7	35·5
118, 119	0·60	42·6, 41·8	33, 34	131	1·20	24	66
120—123	0·75	45·2, 46 47, 45·8	26, 24, 22, 24·5	132, 133	1·50 *	20·9, 21·3	71, 70

* 8 hours.

Expts. 134—136. Sodium Δ^{β}-*n*-hexenoate was prepared by exact neutralisation of the acid, and precipitated by the addition of alcohol, ether, and acetone. At 150° the salt tautomerised in aqueous solution at concentrations *N*/1, 2*N*, and 4*N* to the extent of 15·5, 16·5, and 16% respectively (cf. Expts. 128, 129).

Δ^{α}-*n*-Hexenoic acid gave the following figures (150°, 24 hrs.) :

137	0	2·7	97	140	0·75	9·8	87
138	0·25	7·8	90	141	0·95	4·0	95
139	0·50	10·5	86	142	1·25	20·8	73

An artificial mixture of Δ^{α}- and Δ^{β}-*n*-hexenoic acids corresponding to the equilibrium (74% Δ^{α}-) was similarly treated but the composition was unchanged :

Expt.	Equilibrium mixture	Final compn.; Δ^{α}-, %.
143	+ Water to *N*/1	74
144	+ 0·5 equiv. NaOH in water to *N*/1	74
145	+ 0·95 equiv. NaOH in water to *N*/1	74

A number of parallel experiments with various amounts of aqueous sodium hydroxide were carried out on Δ^{β}-*n*-hexenoic acid at 100°. These are not recorded in detail, as, although the changes were small, they confirmed the results obtained at 150° in all respects. It is noteworthy that a slight change was observed in both the pure acid and the neutral sodium salt in aqueous solution at 100°, *i.e.*, conditions corresponding to those of the processes used in preparative work.

The *n*-pentenoic acids gave the following results in *N*/1-solution (150°, 24 hrs.) :

Expt.	Initial acid.	NaOH, equivs.	*f*, %.	Δ^{α}-Acid, %.
146, 147	Δ^{β}-	0	67·4, 68·2	13, 11·5
148	,,	0·05	64·9	17·5
149	,,	0·25	60·5	25
150	,,	0·50	57·6	30
151	,,	0·65	55·8	32·5
152	,,	0·75	59·5	26·5
153	,,	0·85	62·6	20·5
154	,,	0·95	67·2	13
155	,,	1·05	59	27·5
156	,,	1·20	36·5	60
157	,,	1·50	28·5	70
158	Δ^{α}-	0	4·8	96·5
159	,,	0·50	16·5	83·5
160	,,	0·75	15·2	85
161	,,	0·95	7·8	93·5
162	,,	1·50	27·5	71

Expts. 163—166. Sodium Δ^{β}-*n*-pentenoate, prepared in the same manner as the higher homologue, was heated at 150° for 24 hours in water at concentrations 4*N*, 2*N*, *N*/1, and *N*/2. The observed changes were 16, 14, 13, and 13·5% respectively (cf. Expt. 154).

Equilibrations of butenoic acids (cf. Bruylants, *Bull. Soc. chim. Belg.*, 1924, **33**, **334**). These show certain differences from the higher homologues and are therefore considered separately. The experiments were carried out in sealed tubes at 150° and 100° under the usual conditions. The acids showed a much greater tendency to polymerise and it was necessary to distil the acid products under reduced pressure before analysis.

Expts. 167, 168. Vinylacetic acid (Δ^{β}-) heated for 24 hours at 150° yielded 15·5% Δ^{α}-acid; in 100 hours, 38%.

Expt. 169. *trans*Crotonic acid (Δ^{α}-) heated for 100 hours at 150° yielded 30% of a non-volatile polymeric acid (possibly the dimeride; cf. Skau and Saxton, *J. Amer. Chem. Soc.*, 1930, **52**, 335) and a butenoic acid fraction, equiv. 85·8 (calc., 86·1), m. p. 69—70°, J 2%, corresponding to 99% Δ^{α}-acid.

Expt. 170. *trans*Crotonic acid, heated for 24 hours at 150° with 1½ equivs. of sodium hydroxide, gave after distillation a product with equiv. 86·1, m. p. 62—64°, J 3%, corresponding to 98% Δ^{α}-acid. The low m. p. is attributed to the presence of a little *iso*crotonic acid (cf. Morrell and Hanson, J., 1904, **85**, 1520; Skau and Saxton, *loc. cit.*).

The following results were obtained by the equilibration of the Δ^{β}-acid in $N/1$-aqueous solution with various amounts of alkali, 80% of butenoic acid free from hydroxy-acid being recovered :

Expt.	NaOH, equivs.	Temp.	Time, hrs.	J, %.	Δ^{α}-Acid, %.	Expt.	NaOH, equivs.	Temp.	Time, hrs.	J, %.	Δ^{α}-Acid, %.
171	0	150°	24	47·9	49	180	0·60	150°	1	55	40
172	0·25	,,	,,	4	*97*	181	0·75	,,	,,	60·8	32
173	0·5	,,	,,	4	*97*	182	0·85	,,	,,	62	30
174	0·75	,,	,,	5	*96*	183	0·95	,,	,,	68·9	21
175	0·95	,,	,,	8	93	184	1·005	,,	,,	51	25
176	1·5	,,	,,	5	*96*	185	1·05	,,	,,	6·6	94·5
177	0	,,	1	73·8	12·5	186	0·50	100°	,,	71·2	16·5
178	0·05	,,	,,	68·7	21	187	0·95	,,	,,	73·1	14
179	0·25	,,	,,	61·9	30	188	1·50	,,	,,	4	*97*

In Expts. 172—176 the change is so fast that the peak on the acid side of neutrality cannot clearly be seen, but it is obvious in the experiments (Nos. 177—184) for the shorter time. The sharp inflexion on the alkaline side of neutrality is particularly clearly shown (Expts. 183—185).

6. *Equilibrations under Standard Conditions* (J., 1927, 2579).—The six acids were treated with 10 equivs. of 25% potassium hydroxide at 100° in stout bulbs of Monax glass, the equilibrated products being distilled in steam.

Expt.	Initial acid.	Time, hrs.	J, %.	Δ^{α}-Acid, %.	Expt.	Initial acid.	Time, hrs.	J, %.	Δ^{α}-Acid, %.
189	Δ^{β}-*n*-Hexenoic	½	48·1	19	198	Δ^{β}-*n*-Pentenoic	½	58·2	28·5
190	,,	1	41·3	33	199	,,	1	49·8	41
191	,,	2	31·8	51·5	200	,,	2	38·9	56·5
192	,,	4	22·8	69	201	,,	4	33	64
193	,,	8	19·3	*73·5*	202	,,	8	31	*68*
194	Δ^{α}-*n*-Hexenoic	½	7·4	90	203	Δ^{α}-*n*-Pentenoic	½	13·4	87
195	,,	1	11·9	84	204	,,	1	19	80
196	,,	2	15·6	78·5	205	,,	2	24·2	74·5
197	,,	8	19·2	*73·5*	206	,,	8	31	*68*
					207	Δ^{α}-*n*-Butenoic	24	3	*98*
					208	Δ^{β}-*n*-Butenoic	10 mins.	(Solid crotonic acid, m. p. 70°.)	

These results have been used in compiling the table on p. 617. It is remarkable that the velocity of equilibration of Δ^{α}-hexenoic acid under these conditions seems to be greater than that of the Δ^{β}-acid (0·9 against 0·6) whereas the velocities of the two pentenoic acids are the same, as is required by theory.

7. *Effect of Concentration of Tautomeride.*—The experiments described below show that the concentration of tautomeride, unlike that of free alkali, is without influence on the velocity of equilibration in alkaline media. The solutions were made up so that, although the final concentration of sodium hydroxide was always $N/1$, that of the sodium salts varied over the following range :

Salt	Sodium Δ^{β}-*n*-hexenoate.				Sodium Δ^{β}-*n*-pentenoate.			
Solution	A	B	C	D	E	F	G	H
Concn., g./c.c.	0·136	0·068	0·027	0·0136	0·122	0·061	0·024	0·0122
Normality	1·0	0·5	0·2	0·1	1·0	0·5	0·2	0·1

The solutions were heated in sealed bulbs (Monax) at 100° with the results shown below. The experiments over similar times show almost exact agreement, and the other results also fall into line :

Expt.	Soln.	Time, hrs.	*J*, %.	Δ^{α}-Acid formed, %.	Expt.	Soln.	Time, hrs.	*J*, %.	Δ^{α}-Acid formed, %.
209	A	8	45·2	26	218	A	8½	44·5	28
210	B	8	45	26	219	C	8½	44	29
211	C	8	44·8	27	220, 221	B	10, 10	43·5, 43·5	31, 31
212	D	8	45	26	222	E	7	62·7	21·5
213, 214	B	2, 2	52·6, 52·5	8, 8	223	F	7	63	21
215, 216	B	5, 5	48, 48	18, 18	224	G	7	63·5	20
217	A	7½	46	24	225	H	7	63	21

8. *Attempted Equilibration of Neutral Substances.*—Ethyl Δ^{β}-*n*-hexenoate was prepared by partial esterification of the acid (Sample 1) and through the silver salt (Sample 2) (cf. Kon, Linstead, and Maclennan, J., 1932, 2454). *Expt.* 226. Sample 1 was heated for 7 days at 150° in a sealed tube and then distilled. The recovery of ester of constant b. p. was 95% and there was no residue (Sample 3). *Expt.* 227. Sample 2 was heated for 24 hours in a sealed tube at 150° with 0·2 vol. of Δ^{β}-*n*-hexenoic acid. The ester was recovered in 95% yield (after distillation) from the neutral extracts of the equilibration (Sample 4). These four specimens had the following almost identical properties :

Sample.	B. p./mm.	$d_{4^\circ}^{20^\circ}$.	$n_{D}^{20^\circ}$.	*J*, % (1 hr. at 18°).	Sample.	B. p./mm.	$d_{4^\circ}^{20^\circ}$.	$n_{D}^{20^\circ}$.	*J*, % (1 hr. at 18°).
1	58°/9	0·8955	1·4252	78	3	55°/7	0·8957	1·4252	77·5
2	57 /8	0·8956	1·4255	78·5	4	58 /9	0·8957	1·4255	78

A similar experiment was carried out with Δ^{β}-*n*-butenonitrile (allyl cyanide) and vinylacetic acid, but was vitiated by the fact that much high-boiling material was formed from the nitrile. The acid yielded 60% of the Δ^{α}-isomeride; the recovered nitrile was the practically pure Δ^{β}-isomeride.

IMPERIAL COLLEGE, LONDON, S.W. 7.

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