CCVIII.—*Investigations of the Olefinic Acids. Part II.** *Preliminary Observations on the Occurrence of Spontaneous Tautomeric Change at Temperatures near the Boiling Point.*

By Reginald Patrick Linstead.

αβ- and βγ-Unsaturated acids have been found to undergo reversible isomeric change in the neighbourhood of their temperatures of ebullition or decomposition. This change occurs in the pure acids in the absence of added catalyst and, with certain limitations in the case of acids of exceptional stability, appears to be a general reaction. The first evidence of its occurrence was met with during the preparation of methylene*cyclo*hexane (III) by heating pure dry

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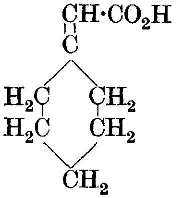
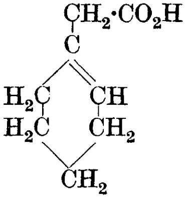
* This paper continues the series "Investigations of the Lower Olefinic Acids" (J., 1929, 2153).

*cyclo*hexylideneacetic acid (I) in a stream of dry hydrogen according to the method of Wallach (*Annalen*, 1908, **359**, 287). At the conclusion of one such preparation the small quantity of solid residual acid was found to be not the original substance (I) of m. p. 91° but its βγ-isomeride, m. p. 38° (II). It had a considerable affinity for iodine and gave the anilide, dibromide, and iodolactone of the acid (II).



(I.)



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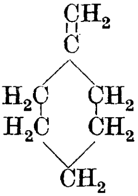

(III.)

Quantitative investigation of the change by iodometric methods showed that at the temperature of free decomposition into hydrocarbon (240°) the formation of βγ- from αβ-acid did not increase above some 83%. In agreement with this, unchanged αβ-acid could be separated from a fully equilibrated product by partial esterification (Eccott and Linstead, J., 1929, 2153) and, further, the pure βγ-acid, heated under the same conditions, gave a product from which the αβ-acid could be isolated.

Experiments at lower temperatures showed that the change could occur independently of decarboxylation. The same equilibrium was obtained at all temperatures and could be approached from either side.

Equilibrium values at	240°	200°	182°	
From αβ-acid	85, 80, 83	83, 84	81	% βγ-acid
From βγ-acid	—	84	86	

Interconversion was inappreciable below 100° and slow below 200°, the approximate times (by interpolation from the figures in Table II) for the half-change of αβ-acid into equilibrium mixture being :

Temperature	240°	220°	200°	182°
Half-change period ...	6 mins.	35 mins.	4 hrs.	20 hrs.

Apart from the formation of olefin above 200°, no appreciable side reaction can be observed and there is no evidence of the formation of γ-lactone from the βγ-acid, the observation of von Braun and Münch (*Annalen*, 1928, **465**, 52) being confirmed in this respect.*

* These authors' figures (60% αβ $\rightleftharpoons$ 40% βγ) for the equilibrium between the acids in boiling alkali were obtained by approach from the αβ-side only, and represent incomplete reaction, since they differ largely from the present author's data (12% αβ $\rightleftharpoons$ 88% βγ), which were obtained by approach from both sides and under a variety of conditions (J., 1927, 362, 2579).

Other acids showed a similar change: for instance, Δ^{α}- and Δ^{β}-*n*-hexenoic acids were slowly isomerised at their boiling points, and *cyclo*pentylideneacetic acid also passed into its βγ-isomeride, about a third being converted in 4 hours at 200°. On the other hand, two acids known to resist interconversion by alkali were found to be stable to heat. These were dimethylacrylic acid (αβ-) (Kon and Linstead, J., 1925, **127**, 616) and styrylacetic acid (βγ-) (Linstead and Williams, J., 1926, 2735).

No special study of the catalytic side of the phenomenon has yet been made, although certain incidental observations will be found in the experimental section. Whatever its ultimate cause, this type of interconversion represents the most facile class of three-carbon tautomeric change yet observed and in many ways, although not necessarily in mechanism, resembles the "spontaneous" changes which have been found in fused tautomerides of other types (compare, *e.g.*, Baker, J., 1928, 1583).

EXPERIMENTAL.

I. cyclo*Hexane Series.—Materials.* The acids (I) and (II), prepared by the usual methods, the βγ-acid being conveniently purified by partial esterification and hydrolysis, were recrystallised two or three times, the αβ-acid from light petroleum and benzene, and the βγ-acid from alcohol and water. In each case the final crystallisation was conducted rapidly in order to obtain the solid in fine crystals. These were dried for several weeks in a vacuum desiccator. The αβ-acid had m. p. 91° and *M* (titration with *N*/20-baryta) 140·1, and the βγ-acid m. p. 37—38° and *M* 140·2 (Calc. for $C_8H_{12}O_2$: *M*, 140·1).

Iodometric reference data. Two sets of figures for the addition of iodine to mixtures of the acids were available, namely, those obtained by the normal method when the mixture is acidified before back-titration, and those obtained when the acidification is omitted (Linstead and May, J., 1927, 2565; Kon and Linstead, J., 1929, 1269). The first method was generally adopted in the present work, but the results were checked in many cases by parallel analyses by the second method. In the figures given below, the additions obtained by the second method and the percentage compositions calculated from them are italicised. The reference data of both methods were checked, the results being given in Table I.

General procedure. Unless otherwise stated, heating of the acids was carried out in a stream of dry carbon dioxide in Pyrex vessels previously cleaned with chromic and sulphuric acids. In experiments above 200°, heating was effected with a free flame and maintained at the required temperature by hand adjustment. For

TABLE I.

Mean Percentage Iodine Addition to Mixtures containing βγ-Acid.

	0 (100% αβ-).	75%.	80%.	83·3%.	90%.	100%.
Normal method, old figure	1·0	48·2	—	—	54·0	55·6
,, ,, new ,,	0·2	—	—	—	55·8	58·6
Without acidification, old figure	*5·7*	*56·5*	—	*60·4*	—	*65·8*
Without acidification, new figure	*5·1*	—	*59·6*	—	*63·9*	*65·8*

experiments at 200° (± 2°) the source of heat was a hand-regulated oil-bath maintained at 208—210°. At 182° (± 1°) the acid was heated in a tube by means of an outer jacket containing the vapour of boiling aniline. The experiment at 150° was carried out in a sealed tube heated in an air oven, no pressure being developed. At 240°, samples of the product were removed at the required times with a hot pipette, but at the lower temperatures separate experiments were carried out on small amounts of acid. In all the experiments the product was rapidly cooled and left over-night with an excess of saturated sodium bicarbonate solution. The alkaline solution, after being freed from neutral material by extraction with ether, was acidified with dilute sulphuric acid and thoroughly extracted with ether. The dried extract was freed from solvent, the last traces being removed in a vacuum desiccator. The residue was weighed and analysed iodometrically and by titration with baryta. The results for the *cyclo*hexane acids are summarised in Table II.

In the experiments given with zero time (2, 11) the samples were worked up as soon as they had reached the desired temperature, and the results therefore indicate the extent of the change during the period of heating. In experiments 1 and 2—5 the inert gas was hydrogen. The physical condition of the various samples need not be detailed but was in each case in agreement with the composition as determined iodometrically.

Isolation of βγ-acid. The product in experiment (1) slowly deposited leaflets, which were separated by suction; they melted at 35—38° alone and at 36—38° in admixture with the authentic βγ-acid. A mixture with an equal part of the αβ-acid was liquid at room temperature. The dibromide (Wallach, *Annalen*, 1905, **343**, 52), prepared in carbon disulphide solution, melted at 120° alone or when mixed with an authentic sample. The anilide (Kon and Narayanan, J., 1927, 1548), prepared through the acid chloride, crystallised well from dilute alcohol and had m. p. and mixed m. p. 115°. This product (0·5 g.) was left at room temperature for 4 hours with *N*-alcoholic hydrogen chloride (1 c.c.) and absolute

TABLE II.

No.	Initial material.	Temp.	Time.	Acid product.			
				Yield %.	Mol. wt.	% Iodine addition.	% $\beta\gamma$-Acid.
1	$\alpha\beta$-	240°	60 (mins.)	12	141·1	53·9	85
2	,,	,,	0	—	140·6	20·6	24
3	,,	,,	15	—	139·8	37·5	52
4	,,	,,	30	—	139·8	47·4	71
5	,,	,,	40	—	140·8	51·5	80
6	,,	,,	5	—	140·1	30·1	38
7	,,	,,	15	—	139·8	38·2	53
8	,,	,,	30	—	140·9	49·1	75
9	,,	,,	40	—	141·2	52·5	83
10	,,	220	30	85	142·5	28·2	35
11	,,	200	0	—	139·9	1·3	1
12	,,	,,	30	90	138·4	13·2	14
13	,,	,,	3 hrs.	83	140·0	25·0	30
14	,,	,,	6	63	—	39·0	55
15	,,	,,	7·5	50	140·7	53·9 *59·3*	85 *81*
16	,,	,,	10·5	37	140·9	54·1 *59·7*	85 *82*
17	$\beta\gamma$-	,,	6	25	141·2	53·7 *60·7*	85 *84*
18	$\alpha\beta$-	182	28·5	57	140·3	35·9 *42·9*	49 *48*
19	,,	,,	49	55	139·7	48·9 *55·9*	74 *73*
20	$\beta\gamma$-	,,	53	50	141·2	54·4 *61·7*	86 *86*
21	$\alpha\beta$-	150	117	74	140·5	25·2 *29·4*	30 *26*

alcohol (3 c.c.). The unesterified acid was separated through sodium bicarbonate and recrystallised from light petroleum; it then had m. p. and mixed m. p. 90—91°. Similar results were obtained with some of the later products.

Isolation of $\alpha\beta$-*acid.* The $\beta\gamma$-acid (9·5 g.) was heated at 240° for 25 minutes under the usual conditions. Free evolution of carbon dioxide began at 220° and appeared to be more vigorous than in the case of the isomeride. The acid product was treated with iodine under Bougault's conditions (*Ann. Chim. Phys.*, 1908, **14**, 145), and the iodolactone removed (equivalent to 66% of $\beta\gamma$-acid). The $\alpha\beta$-acid was separated in the usual way and purified by extraction with bicarbonate and crystallisation from light petroleum. It then had m. p. and mixed m. p. 90—91°.

For the examination of the products from the equilibration of the $\beta\gamma$-acid at lower temperatures (experiments 17 and 20) the following modification was developed which can be used on very small quantities of material. The acid product (0·25 g.) was dissolved in sodium bicarbonate solution (25 c.c.) (the ordinary solutions used in iodine titrations were actually used). In each case the solution was treated with 20% iodine in aqueous potassium iodide for 5 minutes. The product was extracted twice with ether, which removed all the iodolactone and most of the iodine. The aqueous solution was evaporated to half-bulk; it was then colourless and was cooled in ice and made faintly acid. The solid αβ-acid was thus obtained almost pure (m. p.'s 90° and 88°, mixed m. p.'s).

*Methylene*cyclo*hexane* (III). This was isolated, following Wallach's procedure (*loc. cit.*), in about 60% yield in experiments 1, 2—5, and 6—9, the products showing a close agreement in physical properties. The hydrocarbon obtained in experiments 6—9 may be taken as typical. It had b. p. 102—103°, $n_D^{23\cdot2^\circ}$ 1·4481, $d_{4^\circ}^{23\cdot2^\circ}$ 0·7979, $[R_L]_D$ 32·25 and yielded the nitrosochloride and nitrolpiperidide of Wallach. The lower boiling point, which was common to all these preparations, agrees with the figures of Faworski and Borgmann (102—103°; *Ber.*, 1907, **40**, 4863) rather than that of Wallach (106°; *loc. cit.*).

The following additional experiments were carried out.

(22) The αβ-acid, kept at 182° for 20 hours in a silica tube, gave an acid product (74%) with molecular weight 139·5; iodine addition 32·0, *38·6*%, whence βγ-acid formed = 42, *40*%.

(23) The αβ-acid, intimately mixed with anhydrous sodium carbonate (2%), was heated at 182° for 19 hours, a vigorous reaction occurring during the first moments of heating. The acid product (49%) had iodine addition 51·6, *59·7*%; whence βγ-acid formed = 80, *82*%.

Sodium *cyclo*hexylideneacetate prepared from the acid and a slight deficiency of sodium ethoxide (J., 1927, 370) was freed from the excess of acid by washing with ether and dried for 15 minutes at 100° and in a vacuum desiccator. 1·5 G. of the salt were suspended in 100 c.c. of dry redistilled decalin and the suspension was kept at 192° for 6 hours. The solid was filtered off, washed with ether, and acidified. The acid was purified in the usual way, 89% being isolated with molecular weight 139·2, iodine addition 10·3, *16·4*%; whence βγ-acid = 10, *10*%.

The sodium salt (1 g.) was kept in an open tube at 200° for 4 hours. The acid, isolated as above (96%), had molecular weight 139·4, iodine addition 1·9, *5·1*%; whence βγ-acid = 1, *0*%.

II. *Other Acids.*—These were obtained by standard methods except Δ^β-*n*-hexenoic acid, which was prepared from *n*-butaldehyde and malonic acid in one stage with piperidine as a catalyst. The author is indebted to Mr. S. E. Boxer for this material and a fuller account of the method will appear shortly. The acid obtained was, if anything, slightly purer than the original solid Δ^β-*n*-hexenoic acid (m. p. 4—5°, iodine addition 46·7%) of Eccott and Linstead, the melting point of which it did not depress. It had m. p. 5°, iodine addition 49·8%, and yielded the pure βγ-derivatives. The *cyclo*pentylideneacetic acid was purified and dried in the same way as the higher homologue. The other solid acids were recrystallised twice from water, dried by suction, and dissolved in ether. The solutions were dried with calcium chloride, the solvent was removed, and the residue left in a vacuum desiccator.

The Δ^{α}-*n*-hexenoic acid had m. p. 33°, iodine addition 0%, molecular weight 114·1 (calc., 114·1). 10 G. of this acid, kept at the boiling point (217°), gave after 2 hours an acid product (1·09 g.) with molecular weight 115·2, iodine addition 7·6% (whence βγ- = 12%), which slowly deposited some crystalline αβ-acid. The remainder (7·83 g., 89% in all) was examined after 4 hours and had molecular weight 116·4, iodine addition 12·5% (20% βγ-), and yielded no solid at room temperature. The βγ-acid was kept at the boiling point (208°) for 7¼ hours: 88% was recovered as an acid fraction with iodine addition 37·7% (71% βγ-), which failed to solidify in a freezing mixture. 2·9 G. of this were treated for 3 hours with 8 c.c. of *N*-alcoholic hydrogen chloride and 20 c.c. of absolute alcohol. The unesterified acid gave an oil which on standing in ice (without extraction) gave bold flattened needles of the αβ-acid, m. p. and mixed m. p. 33°. 0·18 G. of the solid acid was so obtained together with 0·68 g. of an acid mixture liquid at room temperature and undoubtedly containing some βγ-acid.

*cyclo*Pentylideneacetic acid had m. p. 63°, molecular weight 125·3 (calc., 126·1), iodine addition *6·6*% (Goldberg and Linstead found *12·8*%). 5 G., kept at 200° for 4 hours, gave a liquid acid (50%) with molecular weight 126·4, iodine addition *45·6*% (34% βγ-acid), which slowly deposited large crystals of the αβ-acid.

ββ-Dimethylacrylic acid (m. p. 69°, iodine addition 0·2%) was kept at the boiling point (195°) for 9¼ hours. The product immediately solidified to the pure unchanged acid, m. p. and mixed m. p. 69°. Styrylacetic acid (m. p. 87°) was treated similarly at 200° for 7 hours. There was no formation of α-naphthol at this temperature, and the product immediately yielded a solid melting crude at 75—82°, and at 87° after one crystallisation from light petroleum (mixed m. p. 87°).

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.7.

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