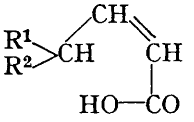
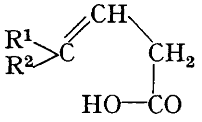
145. *Investigations of the Olefinic Acids. Part X. The Formation of Lactones from Δ^{α}- and Δ^{β}-*n*-Butenoic and -Pentenoic Acids.*

By E. J. Boorman and R. P. Linstead.

In Part VI (J., 1932, **115**) it was suggested that in the series *trans*-crotonic acid–vinylacetic acid–γ-butyrolactone (I, II, and III; $R^1, R^2 = H,H$) tautomeric change in the direction


(I.)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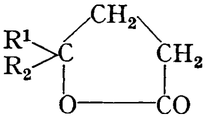
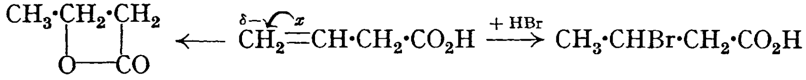

(III.)

(II) ⟶ (I) would occur to the exclusion of lactonisation. This was indicated by the work of Fichter and Sonneborn (*Ber.*, 1902, **35**, 938) and by the fact that the Δ^{β}-acid could be prepared by the hydrolysis of its nitrile (Bruylants, *Bull. Soc. chim. Belg.*, 1922, **31**, 228; 1924, **33**, 334) under conditions normally favourable to lactonisation.

The addition of hydrogen bromide to vinylacetic acid in active solvents (preceding paper) is entirely in the direction shown below:

(IV.)


$$CH_3{\cdot}CH_2{\cdot}CH_2(O\text{—}CO) \longleftarrow \overset{\delta-\curvearrowright x}{CH_2{=}CH{\cdot}CH_2{\cdot}CO_2H} \xrightarrow{+\,HBr} CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CO_2H$$

This result was correlated with the tendency of the double bond to polarise preferentially in the manner indicated by the arrow *x*. Applied to the self-addition of the carboxyl group in the same substance, this tendency would lead to the formation of β-butyrolactone (IV) and would oppose the formation of γ-butyrolactone. If it be assumed, however, that the carbon chain in the phase most favourable for ring closure is coiled with tetrahedral angles at the corners, the oxygen of the carboxyl group does not normally approach the β-carbon atom as closely as is necessary for the formation of β-butyrolactone. Moreover, no β-lactone would be stable under the conditions of reaction normally employed.

Theory thus suggests that the lactonisation of vinylacetic acid in either sense (β or γ) will be inhibited by constitutional factors and that the principal reaction will be tautomeric change into the stable Δ^{α}-form. A re-examination of this acid and its isomerides under the conditions described in Part VI verified these anticipations. On being boiled with 50% sulphuric acid under Fittig's conditions, vinylacetic acid yielded crotonic acid but no γ-butyrolactone, in agreement with Fichter and Sonneborn (*loc. cit.*), and the same result was obtained when the acid was boiled alone or in decalin for a considerable time. The non-formation of γ-lactone cannot be attributed solely to the irreversible change of the Δ^{β}- into the Δ^{α}-acid, because when the former acid is left at room temperature with 60% sulphuric acid, no lactone is produced but there is no appreciable tautomeric change. In its inertia in these circumstances vinylacetic acid is unique among the Δ^{β}-acids so far examined. As anticipated, crotonic acid showed no tendency to tautomerise or lactonise, and γ-butyrolactone was also found by independent experiments to be stable under all these conditions.

n-*Pentenoic Acids.*—If the reactivity of unsaturated acids is determined by the order but not by the nature of the alkyl substitution, the *n*-pentenoic acids (I and II; $R^1 = Me$, $R^2 = H$) should differ sharply from the butenoic acids discussed above, but should resemble the *n*-hexenoic acids previously investigated. Experiment completely verified this deduction: Δ^{β}-*n*-pentenoic acid gave γ-valerolactone (III; $R^1 = Me$, $R^2 = H$) readily with hot 50% sulphuric acid, slowly with the 60% acid in the cold, and not at all on being boiled alone. Δ^{α}-*n*-Pentenoic acid, on the other hand, was unaffected by the cold 60% acid, but was rapidly tautomerised and lactonised by hot 50% sulphuric acid. As indicated in Part VI, Fittig and McKenzie's statement (*Annalen*, 1894, **283**, 86) that this Δ^{α}-acid is stable to boiling 50% sulphuric acid is incorrect: we find that there is an appreciable change under their experimental conditions and that lactonisation is practically complete in an hour.

Hydrolysis of the Lactones.—The reversible hydrolysis of γ-*n*-butyro-, -*n*-valero-, -*n*-hexo-, and -*iso*hexo-lactones into the corresponding hydroxy-acids in boiling water has now been measured by a new method with the object of collecting comparative data for future examination. For the same reason, the rates of formation of the first two lactones from their hydroxy-acids in neutral solution have also been determined. These results are on p. 580; consideration of them is deferred.

EXPERIMENTAL.

The equivs. (*M*) of acids and lactones and the proportions of mixtures of isomeric acids and lactones were determined by titration with $Ba(OH)_2$ (Linstead, *loc. cit.*, p. 121). M.p.'s at low temps. are corrected for stem exposure. Densities and refractive indices are for $d_{4^\circ}^{20^\circ}$ and $n_D^{20^\circ}$ throughout.

Materials.—The four unsat. acids were prepared and purified by the methods described in the preceding papers, and had the properties there given.

γ-Butyrolactone (cf. Frühling, *Monatsh.*, 1882, **3**, 700). A mixture of 53 g. of trimethylene chlorohydrin (b.p. 64°/14 mm. to 68°/12 mm.) and 200 c.c. of rectified spirit was boiled while KCN (41 g. of 95% salt in 60 c.c. H_2O) was run in, then for 22 hr., and finally, after addition of 41 g. KOH in 45 c.c. H_2O, until no more NH_3 came off (12 hr.). The EtOH was boiled off, and the aq. residue extracted twice with Et_2O to remove neutral products and acidified (Congo-red) with HCl aq. Continuous extraction with Et_2O (48 hr.) removed a liquid which on distillation gave first H_2O and then the crude lactone at 200—210°. This fraction was left in contact with K_2CO_3 in a desiccator for 24 hr. and then fractionated (b. p. 84—86°/12 mm.): repetition of this treatment gave γ-butyrolactone (free from acid), b. p. 83·5°/12 mm., *n* 1·4354, *d* 1·1299; whence $[R_L]_D$ 19·88; *M* 86·2 (calc., 86·1). The lactone solidified in solid CO_2–Et_2O to a mass of leaflets, m. p. — 48°. The yield was 30%, calc. on the chlorohydrin. The lactone, treated with HBr, gave a γ-bromobutyric acid having the same properties as that described by Henry (*Compt. rend.*, 1886, **102**, 369; this vol., p. 572).

γ-Valerolactone. This was prepared by the reduction of lævulic acid (Wohlgemuth, *Ann. Chim.*, 1914, **2**, 298) and purified in the same manner as the γ-butyrolactone. The lævulic acid was conveniently prepared as follows (cf. Wolff, *Annalen*, 1881, **208**, 104): Sucrose (900 g.; starch was less satisfactory) was dissolved in warm H_2O (2 l.), and 600 c.c. of conc. HCl added. The mixture was heated on a steam-bath for 48 hr., filtered, and evaporated to a syrup, which was diluted with an equal vol. of H_2O and again filtered; Et_2O then extracted lævulic acid (138 g.), b. p. 161°/24 mm., which solidified readily. The γ-valerolactone obtained by its reduction in 46% yield had b. p. 102—103°/28 mm., *n* 1·4322, *d* 1·0529, whence $[R_L]_D$ 24·67; *M*, 100·1 (calc., 100·1). It solidified readily in solid CO_2–Et_2O to a mass of leaflets, m. p. — 36°. It was characterised by conversion into the hydroxy-amide, which, although not formed as readily as those from the lactones previously studied (J., 1932, 122), was produced in 92% yield under the following conditions: A solution of the lactone in ½ vol. of aq. NH_3 (*d* 0·880) was saturated with NH_3 gas, and again after 24 hr. The viscous liquid was kept over H_2SO_4 in a vac. desiccator until it solidified (2—3 days); the deliquescent product was triturated and washed with Et_2O, dried on a porous tile in the desiccator, and crystallised by slow evapn. of the solvent from a sat. solution in $CHCl_3$. After being dried as before, γ-hydroxy-*n*-valeramide had m. p. 51·5—52°. Neugebauer (*Annalen*, 1885, **227**, 104) gives m. p. 50°.

Lactonisation Experiments.—(1) *Butenoic acids.* The acids were treated by the methods described in Part VI. The products were distilled in vac. to eliminate polymeric impurity, but were not distilled in steam.

(i) Vinylacetic acid, after being boiled with 50% H_2SO_4 for 5 min. under Fittig's conditions, gave a product, b. p. 85—90°/12 mm., m. p. 69—70°; acid 98%, lactone 1·5%.

(ii) Treated similarly for 1 hr., the acid yielded an almost identical product, b. p. 80°/9 mm., m. p. 68—69°; acid 97·5%, lactone 2%.

The crotonic acid obtained was shown by a bromometric method to contain not more than 2% of vinylacetic acid.

(iii) Separate quantities of vinylacetic acid were left with 60% H_2SO_4 at room temp. for 4 hr., 2 days, and 7 days:

			Properties of distilled product.			
Time.	% Recovery.	% Residue on distillation.	B. p.	% Acid.	% Lactone.	% Crotonic acid.
4 Hr.	92	1	66—67°/8 mm.	98	2	5
2 Days	89	19	68/5 mm.	98	2	4
7 Days	78	35	—	97·5	1·5	10

All three distilled products had the general properties of vinylacetic acid and deposited no solid at room temp. Their approx. content of crotonic acid (last col.) was determined by bromometric titration.

(iv) Two quantities of crotonic acid, m. p. 72°, were boiled with 50% H_2SO_4 for 5 min. and 1 hr. The products, after distillation as before (b. p. 85°/9 mm.), contained 99% acid, 1% lactone, and 97·5% acid, 1·5% lactone respectively and melted at 71° and 69°. A similar expt. was carried out for 3 hr.: there was considerable polymerisation, but the distilled product was almost unchanged (m. p. 70—71°) and had an only slightly increased affinity for bromine.

(v) Finely powdered crotonic acid was left for 7 days with cold 60% H_2SO_4. Solution was complete in about 20 min. with a slight fall of temp. 94% of the unchanged acid was recovered with m. p. 72°; acid 99%, lactone 0·5%.

(vi) γ-Butyrolactone after similar treatment with cold 60% H_2SO_4 for 7 days was recovered unchanged (b. p. 69—70°/6 mm.; 96% lactone, 1·5% acid).

(vii) The lactone was boiled for 3 hr. with 50% H_2SO_4. Some charring occurred, but 70% was recovered with b. p. 77°/3·5 mm.; 98·5% lactone, 1·5% acid, m. p. and mixed m. p. − 49·5°.

(2) n-*Pentenoic acids.* The same methods were used, but the products from the expts. with boiling H_2SO_4 were distilled in steam before isolation. If *x* g. of unsat. acid were used, 50*x* c.c. of steam distillate were collected and saturated with $(NH_4)_2SO_4$; the product was extracted continuously in Et_2O (24 hr.), dried and distilled in vac. before examination.

(i) Δ^{β}-*n*-Pentenoic acid was boiled with 50% H_2SO_4 for 5 min. under Fittig's conditions. The distilled product contained 94·5% lactone, 4·5% acid. The lactone was identified as γ-valerolactone by its general properties (b. p. 94°/15 mm.; *n* 1·4326; *M*, 100·4; m. p. − 34·5°) and by conversion into the γ-hydroxy-amide of m. p. 51·5° (mixed m. p.).

(ii) Δ^{β}-*n*-Pentenoic acid, treated with cold 60% H_2SO_4 for various times, gave the products described below:

Time.	% Recovery.	B. p.	% Acid.	% Lactone.
1 Hr.	81	92—97°/14 mm.	84·5	15
5 ,,	79	90—93/16 mm.	41	57·5
5 ,,	—	—	40·5	56·5
8 ,,	60	94—95/16 mm.	19·5	79·5
2 Days	—	90—93/17 mm.	5·5	95

The products were mixed and separated into lactone and acid. The acid was almost pure Δ^{β}-*n*-pentenoic acid from its general properties (b. p. 90°/12 mm., *n* 1·4346, *d* 0·9869, m. p. 0·5°) and iodine addition. The lactone was identified as γ-valerolactone as before (*n* 1·4326, *d* 1·0546, m. p. − 36·5°, m. p. and mixed m. p. of hydroxy-amide 51·5°).

(iii) Δ^{α}-*n*-Pentenoic acid was boiled with 50% H_2SO_4 for various times. There was only very slight charring during the reaction.

Time.	% Recovery.	% Acid.	% Lactone.
5 Min.	73	63·5	35
30 ,,	60	6·5	93
60 ,,	58	1·5	97

The acid and lactone were separated from the products in the usual manner. The acid was the practically pure Δ^{α}-isomeride, indicating that the Δ^{β}-acid was lactonised as fast as formed. It had *M* 101·0, *n* 1·4513, *d* 0·9903, m. p. 8·0—8·5° and was almost without affinity for iodine. The lactone was pure γ-valerolactone with *M* 100·9, b. p. 96—97°/19 mm., *n* 1·4320, *d* 1·0528, m. p. − 37°; and yielded the γ-hydroxy-amide of m. p. and mixed m. p. 51—52°.

(iv) The Δ^{α}-acid was allowed to stand with 60% H_2SO_4 for 2 days. The product, obtained in good yield, contained 95% acid and 4% lactone. The presence of this small amount of ψ-acid appears to be fortuitous, because duplicate expts. for 7 days gave products containing more acid (96·5, 97% of acid and 4, 2·5% of lactone). The recovered acid was the pure Δ^{α}-isomeride; an insufficient amount of the ψ-acid was available for its identification.

(v) γ-*n*-Valerolactone was completely unchanged after 7 days' treatment with cold 60% H_2SO_4, and then contained no acidic material.

(vi) The lactone was boiled for 1 hr. with 50% H_2SO_4. The product contained 99% lactone, 1% acid, and had the general properties of the initial material.

Lactonisation of γ-Hydroxy-acids.—These expts. were carried out by the modification of Hjelt's method (*Ber.*, 1891, **24**, 1236) previously described (J., 1932, 127), with the following results:

Time of heating (hr.)	¼	½	¾	1	1½	2	2½	4	7	14
% Formation of γ-valerolactone	17	29	—	44	53	57	—	—	—	—
„ „ γ-butyrolactone	6	—	18	—	31	—	40	49	61	69

The times for half change by interpolation are 80 min. and 4¼ hr. respectively.

Hydrolysis of Lactones by Water.—About $M/500$ g. of the lactone were weighed into a dry flask and treated with enough H_2O to make an exactly $N/25$-solution. The flask was fitted with a ground-in condenser and soda–lime tube and heated at 100° for 24 hr. A further series of expts. was also carried out for 48 hr. to ensure that equilibria had been attained. The composition of the product was determined by titration of the cooled solution with $N/10$-$Ba(OH)_2$ and, in the case of the 48-hr. expts., the amount of unchanged lactone was checked in the usual manner.

Lactone.	% Hydroxy-acid formed. In 24 hr.	In 48 hr.	% Lactone unchanged in 48 hr.
γ-*n*-Butyro-	25·2	25·1	75·1
γ-*n*-Valero-	7·1	7·0	92·7
γ-*n*-Hexo-	6·6	6·8	92·3
γ-*iso*Hexo-	3·5	3·5	95·1

Fittig and Chanlaroff (*Annalen*, 1884, **226**, 334) found that the equilibrium in the case of γ-*n*-butyrolactone corresponded with a 20·8% hydrolysis, and Fittig and Rühlmann (*ibid.*, pp. 344, 345) found 6·6% and 9·3% hydrolysis for γ-*n*-valerolactone and γ-*n*-hexolactone respectively. It seems probable that the method of direct titration here used is more likely to lead to correct results than that used in this earlier work, which involved the isolation and weighing of the hydroxy-acid as a salt. The results are nevertheless of the same order.

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