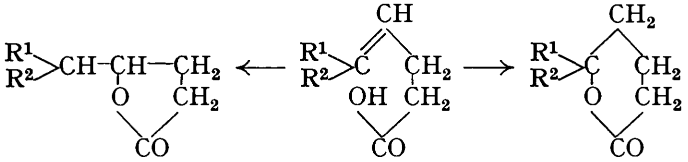
146. *Investigations of the Olefinic Acids. Part XI. The Formation of Lactones from some Δ^γ-Unsaturated Acids, and an Example of Ring-Chain (Lacto-Enoic) Tautomerism.*

By R. P. Linstead and H. N. Rydon.

The lactonisation of Δ^{γ}-unsaturated acids is in some respects more interesting than that of acids with the double bond nearer the carboxyl group, because it is possible for the self-addition to occur in two directions with the formation of a γ- or a δ-lactone :



(I.) (II.) (III.)

Both modes of addition are stereochemically possible and both types of product are stable under the conditions usually employed in lactonising unsaturated acids. The theory developed in this series of papers requires that the direction of lactonisation of any particular Δ^{γ}-acid shall be determined by the order of the alkyl substitution about the double bond.

The two types of polarisation of the double bond concerned are precisely those operative in orienting the addition of hydrogen halide to Δ^{γ}-unsaturated acids in "active" solvents (Boorman, Linstead, and Rydon, this vol., p. 569). Of these, the polarisation $R^1R^2{\cdot}\overset{\curvearrowleft}{C}{=}CH{\cdot}[CH_2]_2{\cdot}CO_2H$ which leads to the formation of a γ-lactone should be favoured if the double bond is terminal (R^1R^2 = H,H), whereas the reverse, $R^1R^2{\cdot}C\overset{\curvearrowright}{=}CH{\cdot}[CH_2]_2{\cdot}CO_2H$, leading to δ-lactone formation should be favoured if R^1R^2 are alkyl groups.

The present paper describes the study of allylacetic acid (II; $R^1R^2 = H,H$) and Δ^{γ}-*iso*heptenoic acid (II; $R^1R^2 = Me,Me$) from this point of view. In each case, the lactone actually formed from the unsaturated acid, by the action of heat or mineral acid, has been compared with the appropriate lactones of the γ- and δ-series, which have been independently synthesised. The sharp contrast between the general properties of γ- and δ-lactones made the identification of the products both simple and definite. The results were in complete accordance with the theoretical requirements.

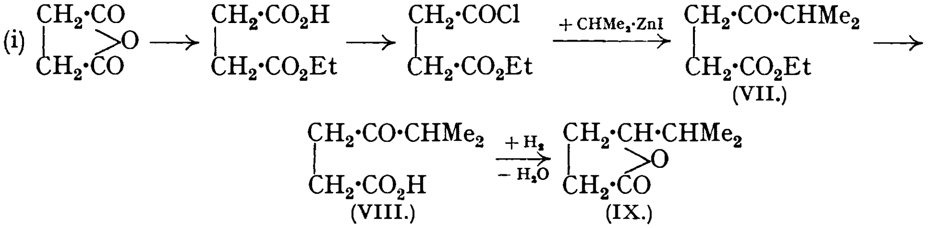
The action of dilute sulphuric acid, cold or boiling, on allylacetic acid readily gave γ-valerolactone free from the δ-isomeride. The lactonisation at room temperature was actually considerably faster than that of the isomeric Δ^{β}-acid under the same conditions (Boorman and Linstead, this vol., p. 579), being nearly complete in 2 hours with a half-change period of about 25 minutes. Allylacetic acid showed little tendency to lactonise on being boiled alone, but a small amount of what appeared to be the γ-lactone was very slowly formed.

An improved method for the preparation of δ-valerolactone was developed in the course of this work.

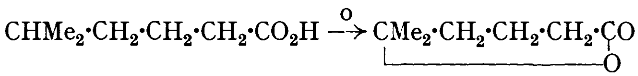
The Δ^{γ}-*iso*heptenoic acid required for the next group of experiments had been synthesised from isoprene as follows (Staudinger, Kreis, and Schilt, *Helv. Chim. Acta*, 1922, **5**, 743): $CH_2{:}CMe{\cdot}CH{:}CH_2 \longrightarrow CMe_2{:}CH{\cdot}CH_2Br$ (IV) $\longrightarrow CMe_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2Et)_2$ (V) $\longrightarrow CMe_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2H)_2$ (VI) $\longrightarrow CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$. The work of Staudinger and his collaborators proved that the double bond was in the $\gamma\delta$-position. In view, however, of the structural resemblance to pyroterebic acid it appeared probable that the acid would yield a lactone with great facility and that the synthetic product formed by decarboxylating the malonic acid (VI) might contain this as an impurity.

A repetition of the synthesis of Staudinger, Kreis, and Schilt yielded the required acid contaminated with some 12% of lactonic material. The acid could only be separated from this with difficulty by a method similar to that used for the purification of pyroterebic acid (Linstead, J., 1932, 124), and was then obtained as a crystallisable liquid.

The δ-lactone required for reference (δ-*iso*heptolactone, $\delta\delta$-dimethyl-δ-valerolactone; XIII) was unknown, and the γ-lactone (γ-*iso*propyl-γ-butyrolactone, IX) imperfectly characterised. They were therefore synthesised by the two unambiguous methods outlined below:



(ii) $CHMe_2{\cdot}CH_2{\cdot}CH_2Br \rightarrow CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2$ (X.) $\rightarrow CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2H)_2$ (XI.) $\rightarrow$


(XII.) $CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \xrightarrow{O} CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO$ (XIII.)

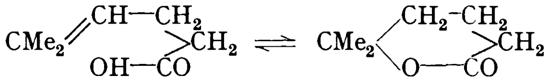
The two lactones differed widely in physical properties and in the ease with which they were hydrolysed to the corresponding hydroxy-acids. On treatment with hydrogen bromide, they yielded isomeric bromo*iso*heptoic acids.

In its ease of lactonisation, Δ^{γ}-*iso*heptenoic acid was comparable with the corresponding Δ^{β}-acid containing the *iso*propylidene group (pyroterebic acid). On treatment with cold dilute sulphuric acid it became warm, dissolved rapidly, and was almost completely lactonised within 15 minutes. In contrast to allylacetic acid, the product was the pure δ-lactone.

Δ^{β}-Unsaturated acids containing two γ-alkyl groups are converted into γ-lactones on being boiled alone (Fittig and Geisler, *Annalen*, 1881, **208**, 37; von Braun and Münch, *ibid.*, 1928, **465**, 52) and, as far as is known, the reaction is irreversible. It was therefore not surprising to find that Δ^{γ}-*iso*heptenoic acid, after being boiled alone for 6 hours, yielded a product containing some 60% of δ-*iso*heptolactone. Heating for a longer period gave an unexpected and most interesting result; the amount of lactone was not appreciably increased, and it appeared that the reaction was reversible. The pure δ-lactone was accordingly boiled for 12 hours; the product then contained 40% of Δ^{γ}-*iso*heptenoic acid, identical with the acid prepared from isoprene. The approach to equilibrium from both sides was followed quantitatively (p. 585).

In view of these results, the occurrence of lactone in the original product obtained by decarboxylating the malonic acid (VI) is not surprising. This was separated and proved to be the δ-lactone.

There is therefore no doubt that the lactone and the acid become directly interconvertible above 200° in the sense :



No appreciable change occurs at room temperature and both isomerides have been kept for a considerable period without alteration.

This reaction not only exemplifies a new structural type of tautomeric change—which may be termed "*lacto-enoic*"—but provides what appears to be the "purest" example of ring-chain tautomerism, previous examples of which have depended upon the presence of reagents. In the present case, there is no apparent side reaction and an equilibrium mixture containing, as indicated, some 40% of acid is produced. As the lactone is cheaply and readily prepared, the acid is actually best obtained from it by equilibration. Further quantitative work on the change is in progress.

The reversal of the lactonisation of a simple unsaturated acid, thus realised, was anticipated in Part VI, where it was pointed out that a similar process accounted for the formation of teraconic acid in the pyrolysis of terebic acid.

The lactonisation of Δ^{γ}-*iso*heptenoic acid involves the preferential formation of a six-membered rather than a five-membered lactone ring and is thus analogous to the recent observations of Haworth and his school in the sugar group, although the reaction here studied is an addition and not an esterification. As the work is being extended to the field of larger rings, discussion of the implications of the results on the ease of formation and the stability of ring systems may be postponed.

Other general reactions of these acids and lactones have been examined. Both Δ^{γ}-acids were unchanged by treatment with caustic alkali at 100° (cf. Fittig and Spenzer, *Annalen*, 1894, **283**, 80). The extent of hydrolysis of the four lactones to the corresponding hydroxy-acids and the ease of lactonisation of the latter presented no unexpected features.

EXPERIMENTAL.

Equivs. (*M*) of acids and lactones were determined by the method previously used (J., 1932, 121). Recorded densities and refractive indices are for $d_{4^\circ}^{20^\circ}$ and $n_{\mathrm{D}}^{20^\circ}$ throughout. Recorded m. p.'s below room temp. are corrected for stem exposure.

1. *Allylacetic Acid.*

The acid (II; R^1R^2 = H,H) was prepared as follows (cf. Conrad and Bischoff, *Annalen*, 1880, **204**, 168). Allylmalonic ester was prepared from 43·5 g. of Na in 435 g. of pure EtOH, 300 g. of ethyl malonate, and 234 g. of allyl bromide at 90°. The product, diluted with H_2O, extracted with Et_2O, washed with brine, and dried over $CaCl_2$, distilled at 116—124°/20 mm. Yield, 305 g., 80%. The ester (325 g.) was hydrolysed with 375 g. of KOH in 500 c.c. of H_2O for 2—3 hr. at room temp. EtOH was removed by means of a pump, and the solution acidified and extracted with Et_2O. From the dried extract, allylmalonic acid separated on removal of the solvent (85% yield). It was most economically crystallised from C_6H_6 and light petroleum (b. p. 60—80°), the cryst. mass being washed with a little light petroleum before being drained on tiles (loss, about 5%). The purified acid (90 g.), m. p. 102° (lit., 103°), was decarboxylated at 180°, 44 g. (70%) of allylacetic acid being obtained, b. p. 91—92°/17—18 mm. After two more distillations the acid had b. p. 90°/16 mm., *d* 0·9798, *n* 1·4283, $[R_L]_D$ 26·29 (calc., 26·36), *M* 100·6 (calc., 100·1). It solidified in solid CO_2–Et_2O and melted sharply at − 22·5°. The iodine addition (Linstead and May, J., 1927, 2565) was 92·0% in 10 min. at 20°.

γ-*n*-Valerolactone, prepared from lævulic acid (preceding paper), had b. p. 93°/21 mm., m. p. − 37°, *d* 1·0524, *n* 1·4320, $[R_L]_D$ 24·65 (calc., 24·74), *M* 100·8.

δ-n-*Valerolactone*.—In agreement with Hollo (*Ber*., 1928, **61**, 895) we find that many of the recorded methods for the prepn. of this substance give uncertain results. Poor yields of impure lactone were obtained by the methods of Cloves (*Annalen*, 1901, **319**, 357), Wieland and Fischer (*ibid*., 1925, **446**, 74), and Sircar (J., 1928, 898). Condensation of trimethylene chlorohydrin with sodioacetoacetic ester, followed by hydrolysis and decarboxylation with baryta, yielded 6% of impure lactone, b. p. 108—114°/17 mm. A similar condensation and hydrolysis using sodiomalonic ester in place of the acetoacetate gave an unidentified unsaturated *product*, forming long needles from EtOH, m. p. 148° (Found : C, 73·3; H, 9·0; equiv., monobasic, 182·5. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%; equiv., 180). The method finally adopted was as follows :

ω-Phenoxypropylmalonic ester (Gabriel, *Ber*., 1892, **25**, 415; Carter, *J. Amer. Chem. Soc*., 1928, **50**, 1967) was converted directly into δ-iodovaleric acid by the following process (cf. Merchant, Wickert, and Marvel, *J. Amer. Chem. Soc*., 1927, **49**, 1828). The phenoxy-ester (128 g.) was heated with 90 c.c. of aq. HI (*d* 1·7) in a 500 c.c. flask fitted with a fractionating column, so that the temp. of the distillate did not exceed 110°. When the initial frothing subsided, more HI (120 c.c.) was added, and the heating continued for 6 hr. The residue was cooled and diluted, the separated oil extracted with Et_2O, the extract washed with 10% aq. Na_2CO_3, the washings acidified, and the separated solid filtered and dried on porous earthenware. Yield, 85 g. (86%); m. p. 53° (crude), 56° after one crystn. from light petroleum. This process is more economical than that involving the intermediate preparation of phenoxyvaleric acid by ordinary hydrolysis and decarboxylation (Carter, *loc. cit*.). A repetition of the latter process showed that δ-phenoxyvaleric acid has the m. p. (65—66°) reported by Gabriel and not that (55—56°) given by Carter (*loc. cit*.).

For the last stage Hollo's procedure was followed (*loc. cit*.). Dry sodium δ-iodovalerate (45 g.) was heated to 150°/4 mm., and a distillate of the δ-lactone and its polymerides collected (11 g., 61%). On redistillation, 5·3 g. of the pure lactone were obtained as a mobile liquid, b. p. 88°/4 mm., m. p. — 12·5°, *d* 1·1081, *n* 1·4568, $[R_L]_D$ 24·64 (calc., 24·74), *M* 100·2 (calc., 100·1). Solid polymerides were obtained from the higher-boiling fractions. The lactone yielded δ-bromovaleric acid, m. p. 40°, with aq. HBr (Boorman, Linstead, and Rydon, *loc. cit*.). When dissolved in a little H_2O or EtOH and titrated with $N/10$-$Ba(OH)_2$ in the presence of phenolphthalein it gave no definite end-point, as the red colour first formed rapidly faded. The equiv. can only be determined by addition of an excess of alkali and back-titration.

Lactonisation of Allylacetic Acid.—The methods for carrying out the reactions and isolating and analysing the products were those described in previous papers of this series. Percentages of lactone and acid are given, as usual, to the nearest $\frac{1}{2}$%.

(i) *Boiling* 50% H_2SO_4 in 10 min. yielded a product containing acid 1%, lactone 96·5%. The end-point in the direct titration of the free acid with $Ba(OH)_2$ was sharp, which is an excellent indication of the absence of δ-lactone. The product was left over anhyd. K_2CO_3 and redistilled; it then had b. p. 90—91°/18 mm., m. p. − 37°, *d* 1·0524, *n* 1·4317, *M* 100·6 (see above). It was very similar to authentic γ-valerolactone in its velocity of hydrolysis in aq. solution and in the velocity of lactonisation of the derived hydroxy-acid (p. 586).

(ii) *Cold* 60% H_2SO_4 produced no appreciable evolution of heat. The mixture became homogeneous within 1 min. and, after being left for various times, had the compositions indicated below :

Time (min.)	15	30	30	60	480	1440
Acid %	69	40·5	41	16·5	2·5	2
Lactone %	33·5	61	57·5	83·5	99·5	99

These figures correspond with a unimolecular vel. const. of 0·0275 (*t* in min.) and a half-change period of 25 min.

The mixed products were kept over-night in an excess of aq. $NaHCO_3$ and the lactone was extracted with Et_2O and distilled. It had b. p. 88°/15 mm., m. p. − 36·5°, *d* 1·0519, *n* 1·4315, *M* 100·6, and was further identified as γ-valerolactone by the methods given on p. 586.

(iii) The acid was *boiled alone* under reflux for 8 hr. in an atmosphere of CO_2, and, after distillation, contained 99% of free acid. Another sample, boiled for 52 hr., contained 94·5% acid, 5·5% lactone; and a sample heated for 96 hr. at 200° in a sealed tube contained 93·5% acid, 5·5% lactone. Insufficient lactone was formed for its identification but, as the end-point of the acid titration was sharp, it was presumably the γ-isomeride.

2. Δ^γ-iso*Heptenoic Acid.*

ω-Dimethylallyl bromide (IV), b. p. 30—35°/13 mm. (Staudinger, Kreis, and Schilt, *loc. cit.*), was prepared from isoprene (Harries and Gottlob, *Annalen*, **1911**, **383**, 228) immediately after the final distillation of the freshly prepared hydrocarbon. From the high fraction obtained in its prepn., αα-dimethyltrimethylene dibromide, b. p. 68—72°/12 mm., was isolated. 62 G. of the monobromide in 64 c.c. of Ca-dried EtOH were added to sodiomalonic ester (from 9·5 g. Na, 157 c.c. Ca-dried EtOH, and 67 g. malonic ester), and the reaction completed over-night on the steam-bath. Dimethylallylmalonic ester (V) (Staudinger, Kreis, and Schilt, *loc. cit.*) was isolated in the usual way in 55% yield, b. p. 125—130°/11 mm. The same substance was obtained in 73% yield from the dimethyltrimethylene dibromide by Ipatieff's method (*J. pr. Chem.*, 1899, **59**, 542).

The malonic acid (VI) was obtained by the following improvement of Staudinger's process : 72 g. of the ester, dissolved in 75 c.c. of EtOH, were refluxed over-night with 56 g. of KOH in 112 c.c. of EtOH and 100 c.c. of H_2O, the EtOH was removed, and the residue acidified with HCl aq. Et_2O then extracted the acid (VI) (46 g., 85%), m. p. 96°, after recrystn. from C_6H_6–light petroleum, in agreement with Staudinger, Kreis, and Schilt (Ssolonina, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 734, gives m. p. 83°).

The product obtained by decarboxylating this malonic acid and distilling the residue contained lactone which could not be removed by the usual method of extracting a solution in aq. $NaHCO_3$ with Et_2O, because subsequent acidification of the $NaHCO_3$ solution and extraction with Et_2O to regain the acid caused further lactonisation. The following process, in which advantage is taken of the immiscibility of petroleum and HCl aq., the unsat. acid being extracted and protected as fast as it is formed, was satisfactory. 35 G. of the recryst. malonic acid (VI) were heated under reflux at 150° for 1 hr. The product was extracted over-night with 350 c.c. of 10% aq. $NaHCO_3$ and then thoroughly with Et_2O. Removal of the solvent from the dried extract and distillation of the residue yielded 6·7 g. (25%) of a lactone, b. p. 94°/6 mm., m. p. 28°, identified as δ-*iso*heptolactone (mixed m. p. 27·5°). The $NaHCO_3$ solution was cooled in ice and covered with a layer of petroleum (b. p. 40—50°), and an ice-cold solution of 48 c.c. of conc. HCl and 52 c.c. of H_2O (95% of the theo. quantity) slowly added with vigorous shaking. The lower layer was run off and extracted with further quantities of light petroleum. The combined extracts were dried and the residue, after removal of the solvent, was distilled under low press. It boiled at 95°/1 mm. and was free from lactone (Found : *M*, 128·2. Calc., 128·1). Yield, 13 g. (52%).

Pure Δ^γ-*iso*heptenoic acid has b. p. 105°/5 mm., m. p. — 33°, *d* 0·9541, *n* 1·4461, $[R_L]_D$ 35·72 (calc., 35·60), and an iodine addition of 97·4% in 5 min. at 20° (Found : C, 65·7; H, 9·4. Calc. for $C_7H_{12}O_2$: C, 65·6; H, 9·4%). The high density and refractivity given by Ssolonina for this acid ($d_{0^\circ}^{0^\circ}$ 0·9864, *n* 1·4504; *loc. cit.*) indicate the presence of lactone in his material.

γ-iso*Propyl-γ-butyrolactone* (IX) (cf. Fittig and Zanner, *Annalen*, 1889, **255**, 90).—*iso*Propyl zinc iodide, prepared from 29 g. of Zn–Cu couple and 68 g. of *iso*propyl iodide in petroleum with EtOAc as catalyst (Blaise, *Bull. Soc. chim.*, 1911, **9**, xi), was diluted with an equal vol. of toluene, and cooled in a freezing mixture, and 33 g. of succinic half-ester half-chloride (Blaise and Koehler, *ibid.*, 1910, **7**, 226), dissolved in an equal vol. of toluene, were added slowly with continuous shaking. The mixture was kept for ½ hr. in the freezing mixture and for ½ hr. at room temp. and was worked up in the usual way. Removal of the toluene from the product left ethyl γ-keto*iso*heptoate (VII), b. p. 113—114°/21 mm., in 38% yield. The corresponding acid (VIII) (Tiemann and Semmler, *Ber.*, 1897, **30**, 434), obtained by hydrolysis with KOH in EtOH–H_2O at 90°, had m. p. 39°. 11 G. of it were dissolved in 110 c.c. of H_2O, and 350 g. of 5% Na–Hg added during a week. The Hg was run off and the aq. layer was acidified with excess of HCl aq., heated under reflux for 15 min., cooled, and saturated with $(NH_4)_2SO_4$. The solution was then extracted with Et_2O, the extract dried, and the solvent removed. The residue, which deposited some solid, probably succinic acid, was treated with aq. $NaHCO_3$, and the γ-*iso*propyl-γ-butyrolactone (IX) extracted with Et_2O. Yield, 1·8 g. It is a mobile liquid, b. p. 98°/15 mm., *d* 1·0023, *n* 1·4410, $[R_L]_D$ 33·83 (calc., 33·98), *M* 127·9 (calc., 128·1). These properties were practically unchanged when the lactone was left over K_2CO_3 and redistilled. Both samples became viscous without solidifying at − 68°. With HBr the lactone yielded γ-bromo*iso*heptoic acid, m. p. 41° (Boorman, Linstead, and Rydon, *loc. cit.*).

δ-iso*Heptolactone* (cf. Bredt and Fittig, *Annalen*, 1881, **208**, 55; Noyes, *J. Amer. Chem. Soc.*, 1901, **23**, 394).—Ordinary (fusel-oil) amyl alcohol was converted through the bromide into crude *iso*amylmalonic ester (X) (Paal and Hoffmann, *Ber.*, 1890, **23**, 1495), which was hydrolysed to the crude malonic acid. From this, *iso*amylmalonic acid (XI) was readily separated by crystn. from a dil. solution in C_6H_6–light petroleum : 172 g. of crude *iso*amyl bromide gave 100 g. of the pure malonic acid, m. p. 94° (Paal and Hoffmann, *loc. cit.*, give m. p. 93°). The complete removal of the isomeric acid was shown by the fact that solutions of the acid of m. p. 94° were optically inactive. Heated at 140°, the recryst. malonic acid gave a 94% yield of *iso*heptoic acid (XII) (Paal and Hoffmann, *loc. cit.*), b. p. 110°/10 mm., m. p. − 7°. *iso*Heptoic acid (25 g. in 1 l. H_2O and 24 g. KOH at 70—80°) was oxidised with a solution of $KMnO_4$ (30 g., 50% excess, added dropwise with mechanical stirring), the filtrate and washings evaporated on the steam-bath, and the residue acidified with HCl aq. and refluxed for 15 min. From the cooled solution, sat. with $(NH_4)_2SO_4$, Et_2O extracted the crude lactone, which was taken up in excess of aq. NaOH, freed from neutral impurities by Et_2O extraction, recovered, and kept in $NaHCO_3$ aq. over-night to remove unchanged acid. The lactone was then isolated by Et_2O extraction, dried, and distilled. Yield, 12·5 g. boiling over 2° (50%); 6 g. of *iso*heptoic acid were recovered from the $NaHCO_3$ extract, making the overall yield of lactone 67%.

Redistillation of the lactonic fraction gave pure δ-iso*heptolactone* (XIII), b. p. 90°/3 mm., 119°/19 mm., *d* 1·0111, *n* 1·4497, $[R_L]_D$ 34·03 (calc., 33·98) (Found : C, 65·5; H, 9·4; *M*, 128·2. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%; *M*, 128·1). It solidified in flattened needles, m. p. 28°. The first prepn. of the lactone was a liquid which solidified in solid CO_2–Et_2O to give a second form, m. p. 8°; this suggests that the lactone is dimorphous. After being kept at room temp. for some time, the second form suddenly solidified to the 28°-form and was not obtained again. On oxidation with $K_2Cr_2O_7$ and $2N$-H_2SO_4 the lactone yielded acetone and succinic acid. Treated with HBr, it gave δ-bromo*iso*heptoic acid, m. p. 45° (Boorman, Linstead, and Rydon, *loc. cit.*).

Lactonisation of Δ^{γ}-iso*Heptenoic Acid.*—The usual methods of lactonisation and isolation were employed, but the composition of mixtures of acid and δ-lactone could not be determined by the method of double titration owing to the fugitiveness of the direct end-point. For such mixtures, a weighed quantity was shaken for 10 min. with an excess of an aq. suspension of pptd. $BaCO_3$, which reacted with the acid but not with the lactone. After filtration the lactone in the filtrate and washings was estimated in the usual manner [heating with excess of $N/10$-$Ba(OH)_2$ for 15 min., cooling, and titrating the excess with $N/10$-H_2SO_4 and phenolphthalein]. The acid was determined by difference. Tests with the pure acid and δ-lactone showed this method to be accurate to 2%.

Δ^{γ}-*iso*Heptenoic acid (2·9 g.) was mixed with 14·5 c.c. of 60% H_2SO_4. The temp. rose to *ca.* 30° and the second layer disappeared in 1 min. After 15 min. the product was isolated and distilled, 2·6 g. being recovered containing acid 4%, lactone 96%. This solidified on being cooled in ice and seeded with δ-*iso*heptolactone and after being drained on a tile had m. p. 28·5°, alone or mixed with δ-*iso*heptolactone.

Ring-chain Tautomerism of Δ^{γ}-iso*Heptenoic Acid.*—The acid was heated under reflux at the b. p. (*ca.* 216°) for various times and yielded products of the following compositions :

Time (hr.)	0 (control)	1	6	18
% Lactone	0	26	60	63·5

The solid lactone on similar treatment gave :

Time (hr.)	0 (control)	1	4	6	8	10	12	12
% Lactone	100	94	75·5	63	59·5	57	58	58

The mixture formed from the acid was treated over-night with aq. $NaHCO_3$, and the lactone extracted in the usual manner. The distilled product solidified to pure δ-*iso*heptolactone, m. p. and mixed m. p. 27·5°.

The mixture produced from the lactone was similarly treated. The lactone, isolated by the same method, was identified as unchanged material. The acid was recovered from the $NaHCO_3$ solution by acidification under light petroleum (p. 584). The distilled acid had b. p. 98°/5 mm., *n* 1·4462, *M* 127·7, and an iodine addition of 98·1% in 5 min. at 20°. It solidified in solid CO_2–Et_2O and then melted at − 34·5°, alone or mixed with authentic Δ^{γ}-*iso*heptenoic acid.

Its solution in aq. $NaHCO_3$ decolorised cold $KMnO_4$ solution. After filtration the product was treated with I in KI and NaOH. A ppt. of CHI_3 was obtained in the cold, indicating the presence of acetone in the oxidation product and of the *iso*propylidene group in the acid. A sample of the acid prepared from the lactone was saturated with HBr; the solid bromo-acid obtained had m. p. 44°, alone or mixed with authentic δ-bromo*iso*heptoic acid.

Action of Alkali at 100° *on the* Δ^γ*-Acids.*—Allylacetic acid was heated with 25% aq. KOH for 6 hr. under the general conditions used for equilibrating Δ^α- and Δ^β-acids (J., 1927, 2579). The product after distillation had m. p. − 24°, *n* 1·4285, *M* 100·7, and an iodine addition of 92·2% in 10 min. at 20°. These properties are almost exactly those of the pure acid.

Δ^γ-*iso*Heptenoic acid was similarly treated for 6 hr. The product was isolated, with the special precautions to avoid lactonisation which are described above. After distillation, the unchanged Δ^γ-acid was recovered with *n* 1·4462, *M* 128·3, and an iodine addition of 97·3% in 5 min. at 20°.

Hydrolysis of the Lactones.—For expts. with the γ-lactones, the methods described in the preceding paper were employed. For the δ-lactones the hydrolysis was carried out by the same method, and the estimation by the method described on p. 585 for the analysis of δ-*iso*heptolactone in the presence of Δ^γ-*iso*heptenoic acid.

	% Hydrolysis in		
Lactone.	10 min.	24 hr.	48 hr.
γ-*n*-Valerolactone from (*a*) lævulic acid	0·4	7·0	—
,, ,, (*b*) hot H_2SO_4 and allylacetic acid	0·4	7·0	—
,, ,, (*c*) cold ,, ,, ,, ,,	0·4	7·3	—
δ-*n*-Valerolactone	—	82·8	—
γ-*iso*Propylbutyrolactone	—	3·8	—
δ-*iso*Heptolactone	—	55·4	54·8

Lactonisation of Hydroxy-acids.—These expts. were carried out by the standard method previously used. The modified method of analysis was again employed for the estimation of δ-lactones in the presence of hydroxy-acids, *N*/100-$Ba(OH)_2$ being used for the titrations.

	% Formed from hydroxy-acid in (min.).									
Lactone.	5.	10.	20.	30.	40.	60.	90.	120.	180.	240.
γ-*n*-Valerolactone (*a*)	4·0	—	—	27·4	—	41·7	49·0	54·6	—	—
,, (*b*)	8·1	—	—	24·0	—	40·8	49·3	56·9	—	—
,, (*c*)	8·4	—	—	29·5	—	43·1	50·1	56·1	—	—
δ-*n*-Valerolactone	—	15·0	18·1	19·2	—	19·8	—	—	21·5	21·9
γ-*iso*Propylbutyrolactone	17·9	—	48·8	—	68·1	74·1	—	83·9	—	—
δ-*iso*Heptolactone	43·6	—	50·4	50·8	—	52·7	54·6	—	—	—

The samples of valerolactone were prepared (*a*) from lævulic acid, (*b*) by the action of hot H_2SO_4 on allylacetic acid, (*c*) by the action of cold H_2SO_4 on allylacetic acid.

The results obtained for γ-*n*-valerolactone are close to those recorded in the preceding paper for an independent prepn.

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