441. *Investigations of the Olefinic Acids. Part XIV. Preparation and Additive Reactions of* Δ^{δ}-n-*Hexenoic Acid. An Unusual Isomeric Change in the Three-carbon System.*

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THE examination of the additive reactions of unsaturated acids (Boorman, Linstead, and Rydon, J., 1933, 568) has now been extended to the simplest acid of the Δ^{δ}-series in the hope that further light would be thrown on the effect on additive properties of the recession of the double bond from the carboxyl group. The main results were inconclusive, but certain incidental observations of interest were made.

The known methods for the preparation of Δ^{δ}-*n*-hexenoic acid (I) (Wallach, *Annalen*, 1900, **312**, 189; 1905, **343**, 48; Helferich and Malkomes, *Ber.*, 1922, **55**, 702; Fichter and Langguth, *Annalen*, 1900, **313**, 375; *Ber.*, 1897, **30**, 2051) failed to give an acid of sufficient purity for the purpose in view, but it was eventually prepared in good yield through Δ^{γ}-n-*butenylmalonic acid* (V) as follows:

$$CH_2{:}CH{\cdot}CH_2Br \longrightarrow \underset{(II.)}{CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH} \longrightarrow \underset{(III.)}{CH_2{:}CH{\cdot}CH_2{\cdot}CH_2Br} \longrightarrow$$

$$\underset{(IV.)}{CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2} \longrightarrow \underset{(V.)}{CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2H)_2} \longrightarrow$$

$$(I.)\ CH_2{:}CH{\cdot}[CH_2]_3{\cdot}CO_2H$$

The *p*-toluidide of the acid so prepared and also, though less readily, by the methods of Wallach and Fichter, melted at 58°. The figure (75°) given by Fichter and Pfister (*Ber.*, 1904, **37**, 2000) is possibly a misprint. From this crystalline derivative the acid could be regenerated through the *ethyl* ester (p. 1999). This process is convenient for the purification of liquid acids, even those containing comparatively labile double bonds, and has been successfully applied to Δ^{β}-*n*-hexenoic acid. The regenerated Δ^{δ}-acid was similar to the other preparations in general properties, but, unlike them, it could be frozen to a crystalline solid with a sharp melting point.*

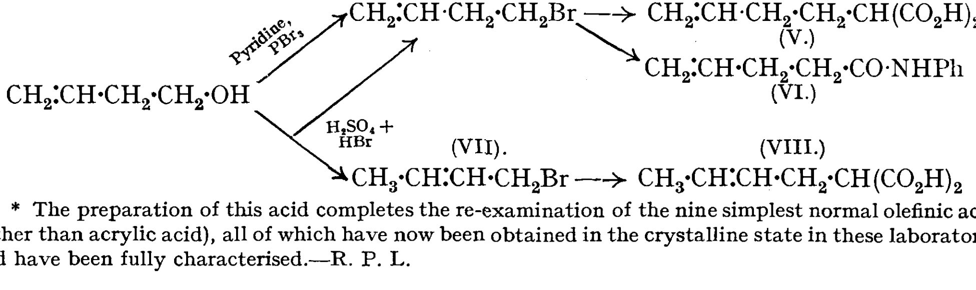
Preparative method.	M. p.	B. p.	$d_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.
Fichter and Langguth †	—	101—102°/8 mm.	0·9648	1·4358
Wallach †	*ca.* −60°	108/13 mm.	0·9635	1·4349
From Δ^{γ}-butenylmalonic acid	*ca.* −56	103/12 mm.	0·9607	1·4337
Regenerated from toluidide	−37	107/17 mm.	0·9610	1·4343

† Present authors' figures.

The purity of the various samples of the acid was also assessed by oxidation with permanganate. The regenerated acid gave glutaric acid as required for a Δ^{δ}-double bond, together with a small amount (6%) of succinic acid, possibly formed from a little Δ^{γ}-acid or by secondary oxidation. The material prepared from Δ^{γ}-butenylmalonic acid yielded 8% of succinic acid, but the Fichter and the Wallach acid gave 51% and 36% respectively and the presence of substantial amounts of the Δ^{γ}-acid in these can hardly be doubted.

The material of m. p. − 37° was used as pure Δ^{δ}-hexenoic acid in this work. Like all Δ^{γ}-acids and unlike all Δ^{β}-, the acid was not isomerised by a large excess of potash at 100°.

Isomeric Change of Δ^{γ}-Butenyl Bromide or Δ^{γ}-Butenol.—The conversion of Δ^{γ}-butenol (II) into the bromide (III) was smoothly effected by phosphorus tribromide and pyridine, following Juvala (*Ber.*, 1930, **63**, 1989). The magnesium compound of this bromide reacted with phenyl *iso*cyanate (Schwartz and Johnson, *J. Amer. Chem. Soc.*, 1931, **53**, 1063) to yield the pure anilide of Δ^{γ}-*n*-pentenoic acid (VI), which established its homogeneity and the position of the double bond. Moreover, the derived malonic acid (V) was readily obtained in the pure condition (m. p. 92°). When, however, the same butenol was treated with hydrobromic and sulphuric acids, it yielded a *mixture* of the Δ^{γ}- and the Δ^{β}-bromide (III and VII). The presence of the former was shown by the fact that the action of phenyl *iso*cyanate on the Grignard compound yielded a mixture of anilides from which a small amount of the Δ^{γ}-*n*-pentenoic derivative could be separated. On the other hand, the bromide gave a mixture of malonic acids from which Δ^{β}-butenylmalonic acid (VIII), m. p. 113°, could be isolated, and this on decarboxylation yielded pure Δ^{γ}-*n*-hexenoic acid of m. p. 1° (compare preceding paper).



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* The preparation of this acid completes the re-examination of the nine simplest normal olefinic acids (other than acrylic acid), all of which have now been obtained in the crystalline state in these laboratories and have been fully characterised.—R. P. L.

The migration of a double bond during the conversion of an unsaturated alcohol into a bromide has already been observed in the case of substituted allyl alcohols, which isomerise thus:

$$R{\cdot}CH(OH){\cdot}CH{:}CH_2 \longrightarrow R{\cdot}CHBr{\cdot}CH{:}CH_2 \longrightarrow R{\cdot}CH{:}CH{\cdot}CH_2Br$$

(Baudrenghien, *Bull Soc. chim. Belg.*, 1922, **31**, 160; Lépingle, *Bull. Soc. chim.*, 1926, **39**, 864; Bouis, *ibid.*, 1927, **41**, 1160). In these substances the migrating atom is bromine, whereas Δ^{γ}-butenyl bromide is novel in that it is hydrogen which appears to migrate. The change is also noteworthy for the fact that the three-carbon system is separated from the only polar atom by a methylene group.

Additive Reactions of Δ^{δ}-*Hexenoic Acid.*—(1) *Lactonisation.* Theory suggests that Δ^{δ}-*n*-hexenoic acid should yield δ- and not ε-*n*-hexolactone on treatment with sulphuric acid (Linstead, J., 1932, 115; Linstead and Rydon, J., 1933, 580). Unfortunately the lactonisation was accompanied to an unusual extent by side reactions, particularly when the acid was kept with cold dilute sulphuric acid. The lactonic product undoubtedly contained δ-hexolactone, but differed from the pure material, which was independently synthesised (m. p. 18°), in that it could not be crystallised. No trustworthy method could be devised for the estimation of the amount of ε-lactone present. Pure δ-*n*-hexolactone, like other δ-lactones, was formed comparatively quickly when solutions of the salts of the corresponding δ-hydroxy-acid were acidified, and was readily hydrolysed by boiling water to yield an equilibrium mixture containing 52% of the hydroxy-acid. The terminal methyl group stabilised the ring to some extent, for δ-valerolactone is hydrolysed to the extent of 83% under the same conditions (Linstead and Rydon, *loc. cit.*).

This stabilisation of the lactone ring by alkyl substitution is also shown by a comparison of the tendency of various δ-lactones to polymerise. Carothers, Dorough, and van Natta (*J. Amer. Chem. Soc.*, 1932, **54**, 761) have observed that the spontaneous polymerisation of δ-lactones is inhibited by α-alkyl substitution and we find that δ-alkylation produces a striking effect in the same direction. For instance, of the lactones described in this and our previous paper, δ-valerolactone polymerised completely in a month, δ-methyl-δ-valerolactone (δ-hexolactone) partly in six months, and δδ-dimethyl-δ-valerolactone has now been kept for two years without appreciable change. On the basis of Carothers's view that polymerisation is due to the formation of ester linkages between the lactone molecules, the new facts indicate that the ease of esterification of various types of *potential* hydroxyl groups in this way is the same as that of *real* hydroxyl groups, namely, primary OH > secondary OH > tertiary OH (compare Menschutkin, *Ann. Chim. Phys.*, 1880, **20**, 229; 1881, **23**, 14; 1883, **30**, 81). Monomeric δ-hexolactone can be regenerated from partly polymerised material by vacuum distillation, whereas the polymerisation of δ-valerolactone cannot be reversed in this way.

(2) During preliminary experiments on the addition of hydrogen bromide to Δ^{δ}-*n*-hexenoic acid the possible importance of peroxides on the orientation of the addition was not realised. The acid is, however, not particularly suitable for work of this kind, as neither of the possible addition products, δ- and ε-bromohexoic acids, could be obtained crystalline for direct comparison. The ethyl ester of the ε-bromo-acid reacted slowly with ethyl sodiomalonate to yield a product hydrolysing to suberic acid, but the δ-bromo-esters could not be characterised in this way and the analysis of the addition products was therefore incomplete.

EXPERIMENTAL.

[Recorded densities and refractive indices are for $d_{4^\circ}^{20^\circ}$ and $n_D^{20^\circ}$ throughout. Iodine additions, *J*, were determined for 10 minutes at 20°. Equivalents of lactones were obtained by back titration.]

Preparation of Δ^{δ}-n-*Hexenoic Acid.*—(i) *Fichter and Langguth's method.* The original procedure was modified as follows: A paste of 115 g. of potassium cyanide (95%) and 40 c.c. of water was treated dropwise with stirring with 198 g. of γ-acetobutyric acid (Fittig and Wolff, *Annalen*, 1882, **216**, 127). The product was acidified after 12 hours, left for 24 hours, and extracted with ether. The crude cyanohydrin (225 g.) was hydrolysed with concentrated hydrochloric acid (3 hours on the steam-bath), and the α-hydroxy-α-methyladipic acid isolated by continuous extraction with ether for 48 hours. The semi-solid product was boiled for 5 hours with 10% caustic soda solution (400 c.c.), freed from neutral material, acidified, extracted as before, and left in a vacuum; it then readily solidified. Yield, 50 g. of the pure acid, m. p. 91° (crystallised from ether and light petroleum). The acid was pyrolysed at 190° for 3 hours and the product purified through the barium salts, following Fichter and Langguth. The barium salt insoluble in alcohol yielded pure Δ^{γ}-*n*-hexenoic acid (5 g., b. p. 107°/16 mm., m. p. 0°). The soluble barium salt, freed from the Δ^{γ}-salt by two evaporations and extractions with alcohol, was converted into the crude Δ^{δ}-acid, which was purified through sodium bicarbonate; 8·85 g. were obtained with the physical properties given on p. 1996 (Found : equiv., by titration, 114·5. Calc., 114·1). The *p*-toluidide crystallised from petroleum in flattened needles, m. p. 56°, alone or mixed with the derivative prepared by method (iii).

(ii) *Wallach's method.* Mixtures of 10 g. (not more) of pure *cyclo*hexanoneoxime, m. p. 89° (Osterberg and Kendall, *J. Amer. Chem. Soc.*, 1920, **42**, 2618), and 20 c.c. of sulphuric acid (80% by volume) were heated over a small flame until violent reaction set in. The product of a number of such experiments was diluted with an equal volume of ice and *very carefully* neutralised with 30% caustic soda solution (mechanical stirring) at 0—10°, and the ε-hexolactam isolated by extraction of the filtrate from the precipitated sodium sulphate with chloroform. The lactam, b. p. 138—140°/8 mm., m. p. 70—71°, formed plates from light petroleum. The yield (45% in 65 experiments) was much lower if excess of alkali was added before extraction (compare Ruzicka, *Helv. Chim. Acta*, 1921, **4**, 477). The lactam (230 g.) was refluxed for 30 minutes with 210 c.c. of concentrated hydrochloric acid and 1 l. of water, and the solution evaporated to dryness. The residue of ε-aminohexoic acid hydrochloride was dissolved in a little water and treated with 146 g. of sodium nitrite in 250 c.c. of water, added during 2 hours (ice-cooling and mechanical stirring). After 4 hours, the product was distilled in steam, leaving a large residue (207 g.). The mixture of acid and lactone in the distillate was extracted and separated in the usual manner. The ε-hexolactone (9 g.) after treatment with anhydrous potassium carbonate had b. p. 103°/13 mm., *d* 1·0188, *n* 1·4423, $[R_L]_D$ 29·65 (calc., 29·36), equiv. 114·6 (calc., 114·1). The unsaturated acid (30 g., 12%) had the properties already given (Found : equiv., 115·1) and solidified slowly in solid carbon dioxide–ether (compare Helferich and Malkomes, *loc. cit.*). The acid yielded an acid chloride, b. p. 54—56°/15 mm., and a *p*-toluidide, m. p. 49—51° (crude), 56° after crystallisation, mixed m. p. 56°.

(iii) *From allyl bromide.* Δ^{γ}-*n*-Buten-α-ol (II) was prepared by the following improvement of the method of Pariselle (*Ann. Chim.*, 1911, **24**, 318; compare Grischkevitsch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 901). To a gently boiling mixture of magnesium turnings (24 g.), trioxymethylene (30 g.), and ether (250 c.c.), a mixture of 120 g. of allyl bromide, 200 c.c. of ether, and a little iodine was added during 6 hours (mechanical stirring). Stirring and boiling were continued for 2—3 hours and the mixture was then left over-night at room temperature, poured on 500 g. of ice, and decomposed with a slight excess of dilute sulphuric acid. The aqueous layer was distilled in steam and the first 500 c.c. of distillate were saturated with potassium carbonate and extracted with ether. The extract and the original ethereal layer were dried and fractionated. Four such runs gave 136 g. of pure butenol, b. p. 112—114°. The yield (47%) is lower if the stirring is inefficient, if boiling is not maintained, or (in agreement with Juvala, *loc. cit.*) if the addition of allyl bromide is hurried.

α-Bromo-Δ^{γ}-*n*-butene (III) was obtained in 50% yield by Juvala's method, or better as follows : A mixture of the butenol (115 g.) and pyridine (35 g.) was added dropwise with mechanical stirring during 6 hours to 172 g. of phosphorus tribromide at 0°. The mixture was then distilled until the residue frothed and gave off nauseous fumes. The distillate was washed with alkali and water, dried over calcium chloride, and distilled. Yield, 144 g. (78%); b. p. 97—102°. The bromide (1·5 g.) yielded Δ^{γ}-*n*-pentenoanilide (0·7 g.) by Schwartz and Johnson's procedure (*loc. cit.*). This had m. p. 88—89° (crude), 91° after being crystallised from benzene–petroleum, and 92° in admixture with an authentic specimen.

153 G. of the bromide were added to a mixture of 26 g. of sodium, 380 c.c. of alcohol, and 180 g. of malonic ester. The reaction was at first moderated by cooling and was finished on the steam-bath over-night. Δ^{γ}-Butenylmalonic ester, isolated in the usual way, boiled at 116—121°/12 mm. (yield, 178 g.; 74%). This was hydrolysed over-night at room temperature with 200 g. of caustic potash in 280 c.c. of water to *Δ^{γ}-n-butenylmalonic acid*, m. p. 87—89° (crude), 92° after crystallisation from benzene and a little light petroleum (unchanged on further crystallisation). Yield, 114 g. (88%) (Found : C, 53·1; H, 6·3. $C_7H_{10}O_4$ requires C, 53·2; H, 6·3%).

75 G. of this acid were decarboxylated at 160° for 3 hours (wax-bath); distillation then yielded

53 g. of an acid, b. p. 101—104°/12 mm. This was purified through sodium bicarbonate in the usual way, 47 g. of Δ^{δ}-*n*-hexenoic acid being obtained with the physical properties given on p. 1996 (Found : equiv., 113·0. Calc., 114·1).

Regeneration. 34 G. of this acid were converted through the acid chloride, b. p. 59—60°/24 mm., into the *p*-toluidide (52 g., m. p. 55—58°), which formed flattened needles, m. p. 58°, from light petroleum. The m. p. was sharp and unaffected by further crystallisation (Found : C, 76·6; H, 8·4. Calc. for $C_{13}H_{17}ON$: C, 76·8; H, 8·4%). 78 G. of the recrystallised *p*-toluidide were refluxed for 24 hours with 85 g. (2 equivs.) of sulphuric acid in 850 c.c. of absolute alcohol. The product was poured into water (3 l.) and extracted with ether; the extract was washed with brine, dried, and freed from solvent. The residue yielded 45 g. (83%) of *ethyl* Δ^{δ}-n-*hexenoate*, b. p. 65—66°/15 mm., *n* 1·4212, *d* 0·8960, $[R_L]_D$ 40·23 (calc., 40·33) (Found : C, 67·3; H, 9·8. $C_8H_{14}O_2$ requires C, 67·6; H, 9·8%). This ester (43 g.) was hydrolysed overnight at room temperature with 250 c.c. of 10% aqueous sodium hydroxide and sufficient alcohol for miscibility. Δ^{δ}-*n*-Hexenoic acid was isolated in the usual way, purified through sodium bicarbonate, and distilled. In addition to the properties already recorded it had : $[R_L]_D$ 30·94 (calc., 30·98), equiv., 114·8, and *J* 72·9% (Found : C, 63·4; H, 8·8. Calc. for $C_6H_{10}O_2$: C, 63·2; H, 8·8%).

The acid was heated for 72 hours at 100° with 25% potash solution (10 equivs.). The recovered acid (88%) was practically unchanged (b. p. 111—112°/21 mm., *d* 0·9592, *n* 1·4338, equiv. 113·9, *J* 74·3%).

Oxidation of the Various Samples of Δ^{δ}-*Hexenoic Acid.*—The acid (about 1·5 g.) in an excess of 10% aqueous sodium bicarbonate was treated at 0° with a slight excess of 3% potassium permanganate solution, and the oxidation completed at room temperature. The solution was filtered, acidified, and extracted continuously with ether for 24 hours. The solvent was removed from the dried extract, and the residue weighed and crystallised from 25 volumes of benzene. The insoluble succinic acid was weighed and identified by mixed m. p. The soluble glutaric acid was freed from dihydroxy-acid on a porous tile, crystallised, and identified similarly. The Δ^{γ}-*n*-hexenoic acid, m. p. 1°, described on p. 2000 gave a 78% yield of oxidation product which was pure succinic acid, m. p. and mixed m. p. 184°, and the various preparations of the Δ^{δ}-acid gave the following results :

		Oxidation product.				
			Succinic acid.		Glutaric acid.	
Δ^{δ}-Acid.	Total yield, %.	Mol. %.	M. p.	Mixed m. p.	M. p.	Mixed m. p.
Regenerated	81	6	182°	184°	96°	97°
From butenylmalonic acid ...	66	8	180	182	95	97
Wallach's method	66	36	183	185	96	98
Fichter's method	76	51	183	185	85	92

Other Attempted Preparations of Δ^{δ}-n-*Hexenoic Acid.*—(i) *Oxidation of* cyclo*hexanone with Caro's acid.* The procedure of Ruzicka and Stoll (*Helv. Chim. Acta*, 1928, **11**, 1159) left the ketone unattacked, and by the method used by Baeyer and Villiger (*Ber.*, 1899, **32**, 3625) for the oxidation of suberone, *cyclo*hexanone was oxidised and esterified to a high-boiling oil which could neither be distilled without decomposition nor dehydrated to a hexenoic ester. ε-Hexolactone also could not be prepared by these methods.

(ii) *Through* Δ^{δ}-*pentenol.* Allylacetoacetic ester was prepared in 85% yield by Brühl's method (*J. pr. Chem.*, 1894, **50**, 133), but on reduction by Bouveault and Blanc's method it gave so poor a yield (12%) of the desired alcohol that the conversion through the bromide and nitrile into the acid was not attempted.

Isomeric Change of Δ^{γ}-*Butenyl Bromide.*—The product obtained from 93 g. of bromine, 120 g. of ice, and sufficient sulphur dioxide was treated with 65 g. of Δ^{γ}-butenol. The mixture was heated to 100° with mechanical stirring and 59 g. of concentrated sulphuric acid were added dropwise, stirring and heating being continued as long as an oil distilled over. The lower layer of the distillate was washed with sodium carbonate solution, dried, and distilled, 47 g. (39%) of butenyl bromide, b. p. 95—100°, and 54 g. (28%) of dibromobutane, b. p. 171—176°, being obtained. The Grignard compound prepared from the monobromide yielded with phenyl *iso*cyanate, a pasty solid, m. p. 50—60° after having been pressed on a porous tile. After a number of slow crystallisations from dilute solutions in light petroleum, a little pure Δ^{γ}-*n*-pentenoanilide was isolated, m. p. 90°, mixed m. p. 91°.

47 G. of butenyl bromide were treated with ethyl sodiomalonate (from 8 g. of sodium, 100 c.c. of absolute alcohol, and 47 g. of malonic ester). The malonic ester formed (48 g., 70%, b. p. 127—135°/21 mm.) was hydrolysed in the usual manner to an acid which slowly solidified (20 g.,

60%). After three crystallisations from benzene and light petroleum, 10 g. were obtained of m. p. 113°, not depressed by admixture with a sample of Δ^{β}-butenylmalonic acid, m. p. 114°, prepared by Eccott and Linstead's method (J., 1929, 2153) [Found : C, 52·9; H, 6·3; equiv. (dibasic), 158·6. Calc. : C, 53·2; H, 6·3%; equiv. (dibasic), 158·2].

8·3 G. of this acid were decarboxylated in the usual manner. The Δ^{γ}-*n*-hexenoic acid obtained (5·2 g., 85%) had b. p. 102°/12 mm., m. p. and mixed m. p. 1°, *d* 0·9658, *n* 1·4367, $[R_L]_D$ 30·93 (calc., 30·98) (Found : C, 63·2; H, 8·7; equiv. 113·8 Calc. : C, 63·2; H, 8·7%; equiv. 114·1). This acid yielded a *p*-toluidide, m. p. 100° (Eccott and Linstead give 103°), and a dibromide, m. p. 84° (Letch and Linstead, preceding paper), which did not depress the m. p.'s of authentic samples.

Additive Reactions.—Preparation of reference substances. δ-Hexolactone was made essentially by the method of Fittig and Wolff, who give only scanty details (*loc. cit.*). Ethyl γ-acetoglutarate was obtained by condensing 60 g. of ethyl β-chloropropionate, 57 g. of ethyl acetoacetate, and 10·7 g. of sodium in 130 c.c. of ethyl alcohol. Yield, 79%; b. p. 158—163°/15 mm. Hydrolysis (*loc. cit.*) yielded 90% of γ-acetobutyric acid (b. p. 146—148°/7 mm.). 35 G. of this acid were treated with 11 g. of caustic soda in 125 c.c. of water, and 900 g. of 5% sodium amalgam were added during 4 days. The solution was acidified, boiled under reflux for 30 minutes, cooled, saturated with sodium bicarbonate, and extracted with ether. The residue from the extract was freed from acid by treatment with potassium carbonate and distilled, a 21% yield of δ-hexolactone being obtained, b. p. 107°/14 mm., *n* 1·4451, *d* 1·0443, $[R_L]_D$ 29·12 (calc., 29·36) equiv. 114·4 (calc., 114·1). This solidified in ice to long flattened needles, m. p. 18°. When the lactone was warmed with caustic soda and iodine, iodoform was liberated (distinction from γ-hexolactone). The pure lactone became thick after 6 months and deposited a white polymerised material, by slow distillation of which under reduced pressure the pure lactone was regenerated, b. p. 113°/20 mm., m. p. 17°.

The amount of hydroxy-acid formed from the lactone in *N*/25-aqueous solution at 100° during 24 hours (Linstead and Rydon, *loc. cit.*, p. 585) was 50·7, 53·7%. The rate of lactonisation of this hydroxy-acid under the standard conditions (J., 1932, 127) was as follows :

Time (mins.)	0	15	30	60	90	120
% Lactone formed	25·9	32·3	40·8	45·7	47·6	48·2

Hydrogen bromide was passed into the moist lactone at 100° for 10 minutes, the excess then being removed over potash in a vacuum. The δ-bromohexoic acid formed failed to solidify even when the above treatment was repeated. It was converted into the ester, b. p. 122—125°/22 mm., in 75% yield by the usual method (Wohlgemuth, *Ann. Chim.*, 1914, 2, 298). The same ester could be more readily obtained by saturating a solution of the lactone (1·13 g.) in 5 c.c. of alcohol with hydrogen bromide at 0° (4 hours). After standing over-night, the product was poured into 250 c.c. of water, the ester extracted with ether and washed with aqueous sodium carbonate, and the solvent removed from the dried extract. The residue yielded 1·74 g. (94%) of *ethyl δ-bromohexoate*, b. p. 121—122°/21 mm. (Found : Br, 35·8. $C_8H_{15}O_2Br$ requires Br, 35·9%). The ester obtained by both methods reacted very slowly with ethyl sodiomalonate under the conditions previously used (Boorman, Linstead, and Rydon, *loc. cit.*). After 5 days' refluxing, reaction was complete and on hydrolysis a yield of about 50% of an intractable oil was obtained.

Δ^{γ}-*n*-Hexenoic acid in light petroleum solution was treated with hydrogen bromide in the usual way. The bromo-acid failed to solidify and was converted into an ester (71% yield), b. p. 118—123°/22 mm., which exactly resembled the above in its behaviour towards ethyl sodiomalonate.

Addition of Hydrogen Bromide to Δ^{δ}-n-*Hexenoic Acid.*—The general methods previously described were followed. (i) Addition to the *acid alone* was complete in 15 minutes. The product failed to solidify and was converted into the bromo-ester in 79% yield, b. p. 128—131°/24 mm. Condensation of this with ethyl sodiomalonate was complete in 22 hours and the product on hydrolysis readily yielded almost pure suberic acid, m. p. (crude) 141°, mixed m. p. 142°. (ii) Addition to the *acid dissolved in light petroleum* was rapid. The liquid bromo-acid gave an ester (86%, b. p. 122—128°/21 mm.) which reacted completely with ethyl sodiomalonate in 28 hours. After hydrolysis a 40% yield of an acid was obtained, m. p. (crude) 130—134°, which formed prismatic needles from water, m. p. 142°, unchanged by admixture with suberic acid. (iii) Addition to the *acid moistened with* ½% *of water* was complete in 15 minutes. The liquid bromo-acid yielded 80% of an ester, b. p. 129—135°/25 mm., which reacted slowly with ethyl sodiomalonate (5 days) to yield a product hydrolysing to an intractable oil. This product closely resembled that obtained from authentic δ-bromohexoic ester.

Lactonisations.—After 15 minutes' boiling of Δ^{δ}-*n*-hexenoic acid with 50% sulphuric acid, a product was isolated in 85% yield, b. p. 104—105°/16 mm., d 1·0130, n 1·4397, $[R_L]_D$ 29·57 (calc., 29·36), equiv. 114·6 (calc., 114·1). This contained no residual acid, as shown by its behaviour with baryta and lack of affinity for iodine (J 0·5%), but did not solidify in a freezing mixture and was therefore not pure δ-hexolactone. It liberated iodoform when warmed with caustic soda and iodine and did not polymerise on long standing.

The acid dissolved almost immediately in cold 60% sulphuric acid with a slight rise in temperature. After 1 hour, four extractions with ether removed only 43% of a lactonic product, b. p. 103—105°/16 mm., n 1·4387, equiv. 114·7, J 0·4%, which did not solidify in a freezing mixture but gave a positive iodoform reaction. Another sample of acid after similar treatment was extracted continuously for 24 hours with ether; 49% of a product was isolated, b. p. 105—108°/15 mm., d 1·0387, n 1·4500, $[R_L]_D$ 29·52, equiv. 120·7, which failed to solidify in a freezing mixture. These experiments show that the lactonisation is masked by the formation of nearly 60% of some very soluble or volatile material. Both these lactonic products polymerised on long standing in a similar manner to pure δ-hexolactone.

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