226. *Reactions of Olefinic Compounds. Part III. The Orienting Influence of the Phenyl Group.*

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THE orientations assumed by the components of hypochlorous acid when this reagent is added to the Δ^{α}- and Δ^{β}-forms of δ-phenylpentenoic acid follow very exactly those found for the analogous Δ^{α}- and Δ^{β}-hexenoic acids (Part I; Bloomfield and Farmer, J., 1932, 2062). Thus the orienting influence of a phenylalkyl group is of a similar nature to that of the corresponding alkyl group in which methyl replaces phenyl. But when the orienting influence of the phenyl group in cinnamic acid is compared with that of the methyl group in crotonic acid (cf. Part II; Bloomfield, Farmer, and Hose, this vol., p. 800), it is

	$CH_2R\cdot CH{=}CH\cdot CH_2\cdot CO_2H$		$CH_2R\cdot CH_2\cdot CH_2\cdot CH{=}CH\cdot CO_2H$	
R=Ph	OH···Cl	86%	OH···Cl	100%
	Cl···OH	14%	OH···Cl	100%
R=Me	OH···Cl	80%		
	Cl···OH	20%		

seen that the former group has the more powerful influence in leading to *effective* polarisation in the sense $R{\cdot}CH{=}\overset{\delta-}{C}H{\cdot}CO_2H$:

$CHPh{=}CH{\cdot}CO_2H$		$CHMe{=}CH{\cdot}CO_2H$	
$OH \cdots Cl$	100%	$OH \cdots Cl$	74%
		$Cl \cdots OH$	26%

This result does not necessarily mean, however, that the electron-releasing influence of the phenyl group is here overwhelmingly greater than that of methyl: the complete production of an α-chloro-β-hydroxy-addition product may result from the absorption by the nucleus (in the manner suggested by Ingold, *Ann. Reports*, 1928, **25**, 147) of any negative charge which might be conferred on the β-carbon atom by the substituents attached to the α-carbon atom, thus suppressing the polarisation $Ph\overset{\delta-}{C}H{=}CH{\cdot}CO_2H$ on which the production of a β-chloro-α-hydroxy-compound depends. This latter view is strongly supported by experiments with α-methylcinnamic acid, which reveal that orientation in the case of the α-methylated acid is precisely similar to that which holds for cinnamic acid itself—a surprising result in view of the wide difference in orienting tendency between α-methylacrylic and crotonic acid (cf. Bloomfield, Farmer, and Hose, *loc. cit.*). But whatever the mechanism by which the influence of the phenyl group is rendered effective, there is no doubt that its orienting influence is extremely powerful.

An example of great importance in this connexion is that afforded by δ-phenyl-Δ^{γ}-pentenoic acid, $Ph{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, to which hypochlorous acid adds very readily. Here, however, the resulting two lactonic chlorohydrins are readily decomposable substances, and a prolonged examination of both has failed to yield decisive evidence as to their structure; they are in all probability stereoisomeric forms of γ-chloro-δ-phenyl-δ-valerolactone, $Ph{\cdot}\underline{CH{\cdot}CHCl{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}O}$, and in this case the evidence is strengthened in favour of the view that the δ-phenyl group owes its powerful orienting influence mainly to a capacity to render ineffective all polarisation induced by the group $\cdot CH_2{\cdot}CH_2{\cdot}CO_2H$ in the direction $Ph{\cdot}\overset{\delta-}{C}H{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, rather than by directly and overwhelmingly activating (100% negative activation) the γ-carbon atom.

A point of interest in connexion with the examples described above concerns the speed of reaction, which varies with change in the groups attached to the ethylenic centre no less than does the additive mode. Now, although the type of reaction here studied does not lend itself to facile measurement of comparative speeds of addition, yet certain broad distinctions are readily observable. The Δ^{β}- and Δ^{γ}-acids of the δ-phenylpentenoic series, like those of the δ-methylpentenoic series, react very much more rapidly with the reagent than does the corresponding Δ^{α}-compound. Again, the slowness of reaction which distinguishes cinnamic acid becomes more marked still in the case of α-methylcinnamic acid; also the latter acid reacts more slowly than tiglic acid. It thus appears that the low degree of reactivity which characterises the ethylenic centre in the Δ^{α}-acids examined, although mainly attributable to the carboxyl group (see Part II), is accentuated when a phenyl group is directly attached to the unsaturated centre; moreover, the deactivating influence of the phenyl group is apparently further increased when it occurs in combination with certain other types of substitution.*

EXPERIMENTAL.

Preparation of Hypochlorous Acid.—A 2% solution of the reagent was in all cases prepared as described by Bloomfield and Farmer (*loc. cit.*, p. 2067).

Addition to Cinnamic Acid.—To an ice-cold solution of the acid (25 g.) in ether (400 c.c.), the requisite quantity of hypochlorous acid solution was gradually added. After standing

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* (Added in proof.) Since this paper was written, Kharasch and his collaborators (*J. Amer. Chem. Soc.*, 1933, **55**, 2468, 2521, 2531) have shown that the presence of peroxidic impurities may affect both the speed of reaction and the additive mode in certain olefinic additions in which hydrogen bromide is the addendum. The possibility that a similar catalytic influence may affect the additivity of hypochlorous acid under the conditions here employed is being tested by us.

at 0° for 72 hours, the aqueous layer was separated and extracted with more ether. The united extracts, on removal of solvent, gave an oil which was thoroughly agitated with cold water. The chlorohydrin dissolved in the water and was subsequently re-extracted with ether; the residual material consisted partly of cinnamic acid (8 g.), which was filtered off, and partly of a colourless oil which was taken up in petroleum ether, dried, and distilled. The oil, b. p. 83—84°/11 mm., had all the characteristics of ω-chlorostyrene (Found: Cl, 25·6. Calc. for C_8H_7Cl: Cl, 25·7%).

The chlorohydrin was obtained from the ethereal extract as a viscous oil which soon solidified. The solid so obtained was homogeneous and yielded, after thrice recrystallising from dry benzene, colourless prisms, m. p. 94·5° (Found: Cl, 17·7; *M*, monobasic, 199. Calc. for $C_9H_9O_3Cl$: Cl, 17·7%; *M*, 200·5). On crystallising the chlorohydrin from water a hydrate, $C_9H_9O_3Cl,H_2O$, was obtained in the form of colourless prisms, m. p. 55·5° (Found: M, 217. Calc.: *M*, 218·5). The crude chlorohydrin invariably possessed a m. p. between that of the anhydrous form and its hydrate, but the most careful examination of many samples of the addition product failed to show the presence therein of any appreciable quantity of an isomeric chlorohydrin. Both the anhydrous compound and its hydrate have previously been described by Smith (*Z. physikal. Chem.*, 1913, **81**, 371), but all other workers appear to have had in their hands mixtures of the two forms.

Since Read and Andrews (J., 1921, **119**, 1774) record the m. p. of cinnamic acid chlorohydrin as 78—80°, a quantity of cinnamic acid was converted into its chlorohydrin by their method, *i.e.*, dropping sodium cinnamate solution into cold acidified chlorine water; although this method differs considerably from ours, the two products were identical. The second crude product (m. p. 74—77°) yielded the hydrate (m. p. 55·5°) when crystallised from water: this hydrate gradually reverted to the anhydrous substance (m. p. 94·5°) on heating above its m. p. By the kindness of Professor Read, we were able to compare his original specimen with our products: the low m. p. of Read and Andrews's specimen was found to be due to partial hydration. No other observation in the literature affords any indication that cinnamic acid can yield by direct addition a second (positionally isomeric) chlorohydrin.

Constitution of Cinnamic Acid Chlorohydrin.—Although it has been generally assumed that the chlorohydrin has the constitution $Ph\cdot CH(OH)\cdot CHCl\cdot CO_2H$, we can find no record of a satisfactory proof of structure. The correctness of the α-chloro-β-hydroxy-orientation was accordingly demonstrated.

The pure chlorohydrin (3 g.) was dissolved in water, neutralised with sodium bicarbonate and reduced with sodium amalgam at 0° in the presence of excess of carbon dioxide. The reduction liquor yielded on extraction with ether a solid acid which, after recrystallisation from water, melted at 93°; this acid was found by direct comparison with an authentic specimen synthesised for the purpose (see below) to be β-hydroxy-β-phenylpropionic acid.

The chlorohydrin (1 g.) suffered dehydration when refluxed with acetic anhydride (5 c.c.) for 2 hours. The product, worked up in the usual way, partly solidified, yielding an acid crystallising from water in needles, m. p. 138·5°. This was α-chlorocinnamic acid (Found: Cl, 19·5; *M*, 182. Calc. for $C_9H_7O_2Cl$: Cl, 19·4%; *M*, 182·5) (cf. Forrer, *Ber.*, 1883, **16**, 854).

Frequently preparations of the chlorohydrin yielded, on recrystallisation, a small gummy residue which failed to crystallise on long keeping. This residue did not, however, contain an isomeric chlorohydrin, but consisted partly of a neutral substance, partly of cinnamic acid, and partly of a viscous acidic oil which was insoluble in water and did not display the properties of a chlorohydrin.

Synthesis of β-*Hydroxy*-β-*phenylpropionic Acid.*—Andriewsky's synthesis of this acid (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1635) was found to be much improved by modifying the conditions of reaction. Redistilled benzaldehyde (30 g.), bromoacetic ester (41 g.), and zinc shavings (17 g.) were mixed with benzene and heated on a steam-bath. The brisk reaction which set in was complete in 1 hour, and the reaction product yielded, when worked up in the usual way, *ethyl* β-*hydroxy*-β-*phenylpropionate* (23·5 g.) as a viscous liquid, b. p. 154—156°/13 mm. (Found: C, 68·3; H, 8·7. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%). The hydrolysis of this ester was best accomplished by mixing it (1 pt.) with 20% potassium hydroxide solution (2·2 pts.) and sufficient alcohol to cause dissolution, and allowing the mixture to stand for 48 hours. The hydroxyphenylpropionic acid was isolated by removing the alcohol from the product and extracting the acidified aqueous residue with ether. It crystallised from water in colourless needles, m. p. 93° (Found: C, 64·7; H, 6·0; *M*, monobasic, 166. Calc. for $C_9H_{10}O_3$: C, 65·0; H, 6·0%; *M*, 166).

Addition to α-*Methylcinnamic Acid.*—The α-methylcinnamic acid was conveniently prepared by the Reformatski reaction. A mixture of redistilled benzaldehyde (122 g.), α-bromopropionic ester (208 g.), zinc shavings (74 g.), and dry benzene (500 c.c.) was heated on a steam-bath. The reaction which set in was complete in 45 mins., and the product, *ethyl* β-*hydroxy*-β-*phenyl*-α-*methylpropionate*, b. p. 157—158°/11 mm., isolated in the usual way (Found : C, 69·0; H, 7·5. $C_{12}H_{16}O_3$ requires C, 69·0; H, 7·6%). Yield 187 g. This ester (8 g.) yielded on hydrolysis at room temperature with 20% potassium hydroxide (20 c.c.), sufficient alcohol being added to give a homogeneous solution, the corresponding hydroxy-acid, β-*hydroxy*-β-*phenyl*-α-*methylpropionic acid*. This was first obtained as an oil, which partly solidified on cooling; the solid portion crystallised from light petroleum in stout prisms, m. p. 77° (Found : C, 66·4; H, 6·4; *M*, monobasic, 180. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·6%; *M*, 180). This solid acid would seem to be different from a compound, m. p. 95°, reported in the literature as " α-methyl-β-phenyläthylenmilchsäure " (*Centr.*, 1897, ii, 349; 1898, i, 668) and derived by the interaction of benzaldehyde and α-bromopropionic ester. For the purpose, however, of preparing α-methylcinnamic acid, the hydroxy-ester (20 g.) was dissolved in pyridine (15 g.), and mixed, while cooling in ice, with thionyl chloride (6·9 c.c.). The mixture, after standing at room temperature for 4 hours, was poured into dilute hydrochloric acid and worked up in the usual way. The ethyl α-methylcinnamate so obtained was hydrolysed by mixing with 3 times its bulk of 10% potassium hydroxide solution and sufficient alcohol to give a clear solution, and allowing the mixture to stand for 48 hours. The α-methylcinnamic acid crystallised from light petroleum in colourless prisms, m. p. 74—75°.

To a solution of α-methylcinnamic acid (12·1 g.) in ether (200 c.c.), cooled to 0°, the requisite quantity of hypochlorous acid solution was gradually added. After 72 hours, the product was worked up as in the case of cinnamic acid.* The crude oily addition product was agitated with water, wherein the chlorohydrin dissolved, and a quantity of unchanged acid remained suspended in the aqueous solution. The filtered liquor was extracted twice with light petroleum (extract A) and then several times with ether (extract B). The extract A was separated into a neutral and an acidic portion by means of sodium bicarbonate solution; the acidic portion consisted mainly of crystals of unchanged acid but contained a little oily chlorohydrin, whereas the neutral portion consisted of a sweet-smelling mobile liquid, b. p. 118—123°/28 mm., which, owing to its spontaneous formation in the reaction by a process of combined dehydration and decarboxylation, could not be other than β-*chloro*-α-*phenyl*-Δ^{α}-*propylene* (Found : Cl, 23·6. C_9H_9Cl requires Cl, 23·3%), derived from the α-chloro-β-hydroxy-form of the chlorohydrin of α-methylcinnamic acid. The extract B contained almost pure chlorohydrin and this, as also the purified chlorohydrin from extract A, soon partly solidified. The solid portion, representing about 60% of the total chlorohydrin, crystallised from water as a white crystalline powder, m. p. 156° (Found : Cl, 16·4; *M*, monobasic, 213. $C_{10}H_{11}O_3Cl$ requires Cl, 16·5%; *M*, 214).

This solid chlorohydrin suffered facile and complete reduction on treatment of a solution of its sodium salt with sodium amalgam at room temperature, in the presence of excess of carbon dioxide. The chlorohydrin was consequently an α-chloro-acid, *viz.*, α-*chloro*-β-*hydroxy*-β-*phenyl*-α-*methylpropionic acid*, and the reduced acid, obtained from the reduction liquor as an unsolidifiable colourless oil, gave benzoic acid in good yield when warmed with chromic acid mixture.

The crude liquid chlorohydrin which was drained from the above-described solid form still contained a little methylcinnamic acid (Found : Cl, 14·5%). On treatment of its sodium salt with sodium amalgam at 0°, in the presence of excess carbon dioxide, a chlorine-free syrupy hydroxy-acid was obtained : this gave on oxidation with hot chromic acid mixture a good yield of benzoic acid. There was no indication, therefore, that the liquid chlorohydrin contained any of the β-chloro-α-hydroxy-form.

Addition to α-*Phenyl*-Δ^{α}-*pentenoic Acid*.—The phenylpentenoic acid was prepared by the Doebner method. A mixture of β-phenylpropionic aldehyde (28 g.), dry pyridine (20 g.), and malonic acid (21·6 g.) was kept for ½ hour, and then heated on a steam-bath until evolution of carbon dioxide ceased (3—4 hours). The product was cooled and acidified; the precipitated acid was filtered off, and the filtrate extracted with ether. The combined acidic products thus

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* Good results were also obtained by adding the hypochlorous acid solution to a cold aqueous suspension of α-methylcinnamic acid. In this case the reaction product was treated *in the cold* with bicarbonate solution until effervescence ceased. The unchanged (un-neutralised) methylcinnamic acid could then be filtered off, and the neutral product of reaction extracted from the alkaline liquor by light petroleum. Acidification of the alkaline liquor, and extraction with ether, yielded the chlorohydrin in almost pure condition.

obtained were freed from neutral products by treatment with sodium bicarbonate; the purified acid, which contained a little oily acid (probably the Δ^{β}-isomeride), was crystallised from aqueous acetone. The pure *δ-phenyl-Δ^{α}-pentenoic acid* separated in colourless needles, m. p. 103° (Found: C, 75·0; H, 6·6; *M*, monobasic, 176. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%; *M*, 176); the barium salt crystallised in characteristic long silky needles. The Δ^{α}-constitution was verified by oxidising the acid at 0° with alkaline permanganate, whereby good yields of β-phenylpropionic acid, m. p. 46° (mixed m. p. with authentic specimen, 46°), and oxalic acid were obtained.

To a solution of the acid (17·6 g.) in ether (400 c.c.) cooled to 0°, the requisite quantity of hypochlorous acid solution was added. Reaction took place only slowly, but after 80 hours the product was worked up. The aqueous was separated from the ethereal layer and extracted with more ether. The crude product isolated from the combined ethereal liquors was agitated with water; the undissolved phenylpentenoic acid was removed by filtration, and the aqueous filtrate extracted twice with light petroleum and twice with ether. The petroleum extract yielded mainly phenylpentenoic acid, and the ethereal extract a yellow oily chlorohydrin (4·6 g.) which began to solidify only after many months. About 80% of the phenylpentenoic acid was recovered unchanged. The chlorohydrin (*α-chloro-β-hydroxy-δ-phenylvaleric acid*) was only sparingly soluble in water and still contained a little phenylpentenoic acid as impurity (Found: Cl, 14·3. $C_{11}H_{13}O_3Cl$ requires Cl, 15·5%); it could not be further purified by distillation, owing to its strong tendency to lose hydrogen chloride on heating. An attempt to prepare the chlorohydrin in better yield by using chlorine water as the reagent (cf. Read and Andrews's method for cinnamic acid, p. 964) yielded a very impure product containing much αβ-dichlorocinnamic acid (Found: Cl, 22%).

When reduced in aqueous alcohol with sodium amalgam at 0°, the solution being kept slightly acid throughout the operation, the chlorohydrin yielded an oily acid which, after precipitation from chloroform by addition of light petroleum, soon solidified. The solid was chlorine-free and crystallised from water in colourless prisms, m. p. 130°. Its identity as β-hydroxy-δ-phenylvaleric acid was fully established by synthesis of the latter acid for the purpose of comparison.

Synthesis of β-Hydroxy-δ-phenylvaleric Acid.—This acid (m. p. 131°) was isolated by Fittig as a by-product during the interconversion of the Δ^{α}- and the Δ^{β}-form of δ-phenylpentenoic acid with boiling caustic alkali. No satisfactory method of synthesis has hitherto been described.

β-Phenylpropionaldehyde (30 g.) and bromoacetic ester (33·5 g.), dissolved in dry benzene (100 c.c.), were heated with zinc shavings (14·5 g.) on a steam-bath. The reaction product, on being worked up in the usual way, yielded an oily hydroxy-ester, b. p. 178—182°/12 mm. (ethyl β-hydroxy-δ-phenylvalerate), which was immediately hydrolysed by allowing it to stand for 48 hours with excess of 20% potassium hydroxide solution and sufficient alcohol to produce a homogeneous solution. The solid β-hydroxy-δ-phenylvaleric acid thus obtained crystallised from water in colourless prisms, m. p. 130° (Found: C, 68·0; H, 7·0; *M*, monobasic, 193. Calc. for $C_{11}H_{14}O_3$: C, 68·0; H, 7·2%; *M*, 194).

Addition to δ-Phenyl-Δ^{β}-pentenoic Acid.—Three methods of preparing the phenylpentenoic acid were tried: (*a*) Malonic acid (10·8 g.) was added to a mixture of redistilled β-phenylpropionaldehyde (14 g.) and redistilled triethanolamine (12 g.) and, after ½ hour, heated on a steam-bath until evolution of carbon dioxide ceased. The product, isolated and freed from neutral material in the usual way, was oily, but on distillation gave a fraction (b. p. 160—185°/11 mm.) which mainly solidified (crystals, m. p. 30°) when cooled in a freezing mixture; yield, 3 g. (*b*) To a mixture of β-phenylpropionaldehyde (34 g.) and malonic acid (25 g.) in absolute alcohol (65 c.c.) a little redistilled diethylamine (5 drops) was added and the whole refluxed for 6 hours. The product, when isolated and freed from neutral material, gave on distillation a small fraction, b. p. 165—175°/11 mm., which partly solidified (crystals, m. p. 30°); yield, 1·5 g. (*c*) Owing to the low yields obtained by the foregoing methods, the acid was obtained in quantity by the reduction of cinnamylideneacetic acid. The latter compound was prepared according to the Doebner method (cf. *Ber.*, 1902, **35**, 2137) but in working up the product it was convenient to add the crude acid to sodium carbonate solution and to filter off, wash, and finally acidify the precipitated sodium salt (a second crop of sodium salt was obtained by concentrating the mother-liquor). The acid so obtained was washed with water and crystallised once from alcohol, whereupon it melted at 165°; yield, 50 g. (40%).

By the reduction of this acid, Perkin had obtained only an oily product (J., 1877, **31**, 403). By treating a suspension of the sodium salt of the acid (17·4 g. acid) with 3% sodium amalgam (1800 g.) at 0° in the presence of excess carbon dioxide, a reduction product was obtained which boiled at 178—181°/10 mm., leaving a small residue of unreduced acid. The distillate, on cooling, set to a mass of crystals, m. p. 24—28°, from which pure δ-phenyl-Δ^{β}-pentenoic acid, m. p. 30°, could be obtained by crystallisation from light petroleum; the distillate, however, contained, as would be expected, some δ-phenyl-Δ^{γ}-pentenoic acid (cf. Evans and Farmer, J., 1928, 1644) and the oxidation products of both acids (*i.e.*, phenylacetic, benzoic, oxalic and acetic acids) were readily obtained when the distillate was oxidised with dilute alkaline permanganate. From a consideration of the percentage loss of hydrogen chloride sustained on distilling the mixed chlorohydrins produced from the acid mixture (see below), it appeared that the Δ^{γ}-acid was formed during the reduction of the conjugated acid to the extent of about 13% (αβ, αδ-ratio = 13 : 87).*

When the requisite quantity of hypochlorous acid solution was added to a solution of pure δ-phenyl-Δ^{β}-pentenoic acid (28 g.) in ether (500 c.c.), reaction was rapid. The product, worked up after 24 hours, yielded a yellow oil which turned brown on keeping for a few days. This oil was mainly lactonic in character and could be separated by means of sodium bicarbonate into a liquid chloro-lactone and a small amount of liquid chloro-acid. The former was a slightly impure lactone derived from chlorohydroxy-δ-phenylvaleric acid (Found : Cl, 15·4. $C_{11}H_{11}O_2Cl$ requires Cl, 16·6%) and since it lost all its chlorine as hydrogen chloride on distillation at reduced pressure, it was undoubtedly *β-chloro-γ-hydroxy-δ-phenylvalerolactone*. The dehydrochlorination product was a liquid lactone which was readily oxidised by dilute alkaline permanganate to yield oxalic acid and a neutral substance (apparently a polymeride or derivative of α-hydroxy-β-phenylpropionaldehyde); moreover, on heating the unsaturated lactone on a steam-bath with an excess of aqueous-alcoholic potash it yielded an unsaturated acid (after acidification), which when crystallised, first from light petroleum and then by slow evaporation of its aqueous solution, formed long colourless needles, m. p. 57°. This latter acid was a hydroxy-δ-phenylpentenoic acid (Found : C, 69·0; H, 6·1; *M*, monobasic, 194. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·25%; *M*, 192), which, owing to its relationship to the preceding unsaturated lactone, and, in turn, to the original saturated lactone, cannot be other than *γ-hydroxy-δ-phenyl-Δ^{α}-pentenoic acid*, formed by ring-opening, under the action of caustic alkali, of the corresponding lactone. The total amount of the saturated β-chloro-δ-phenylvalerolactone present in the original reaction mixture amounted to at least 86% of the addition product.

The original liquid chloro-acid was not homogeneous and contained some unsaturated material. On long standing, a few crystals of a chloro-acid, m. p. 113°, separated, which probably represent the γ-chloro-β-hydroxy-form of the chlorohydrin, *i.e.*, γ-chloro-β-hydroxy-δ-phenylvaleric acid; owing to the extremely small yield, however, an investigation of the acid could not be carried out.

Addition to δ-Phenyl-Δ^{γ}-pentenoic Acid.—Erlenmeyer, jun., and Kreutz report the production of δ-phenyl-Δ^{γ}-pentenoic acid from cinnamyl chloride and malonic ester (*Ber.*, 1905, **38**, 3503). The preparation of the acid in considerable quantities may be conveniently carried out by employing cinnamyl bromide (cf. Braun and Köhler, *Ber.*, 1918, **51**, 79) in place of the corresponding chloride. It is important, however, to fractionate the crude oily condensation product first obtained, selecting the fraction, b. p. 180—200°/13 mm., consisting of pure ethyl cinnamylmalonate (Found : C, 69·2; H, 7·0. Calc. for $C_{16}H_{20}O_4$: C, 69·5; H, 7·2), and subsequently to hydrolyse it with aqueous-alcoholic potash at room temperature (48 hours). The cinnamylmalonic acid thus produced, when freed from neutral material and crystallised from benzene, formed colourless prisms, m. p. 131° (Found : *M*, monobasic, 258. Calc. for $C_{12}H_{12}O_4,2H_2O$: *M*, 256). This acid, when decarboxylated by heating in an oil-bath at 140°, gave crude phenylpentenoic acid; the latter, after being freed from neutral material and crystallised from petroleum, melted at 90° (Found : C, 74·9; H, 6·8; *M*, monobasic, 177. Calc. for $C_{11}H_{12}O_2$: C, 75·0; H, 6·8%; *M*, 176); total yield (based on quantity of original reactants taken), 61%. On oxidation with alkaline permanganate at 0°, the pure acid gave benzoic acid and succinic acid in good yield.

A solution of the acid (16 g.) in ether (250 c.c.) was treated at 0° with the requisite quantity of hypochlorous acid solution. Reaction was rapid, and after 12 hours a crop of crystals had separated at the liquid interface. The crystals were filtered off, and the remaining portion of the reaction product isolated from solution in the usual way. The latter was a viscous yellow oil which deposited more of the crystalline material on standing. The crystalline

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* At the time this work was carried out the authors were not aware that Karrer, Yen, and Reichstein (*Helv. Chim. Acta*, 1930, **13**, 1308) had obtained evidence of the production of a mixture of Δ^{β}- and Δ^{γ}-dihydro-acids by the reduction of cinnamylideneacetic acid with titanous chloride.

material, which constituted 40% of the addition product, was lactonic in character and obviously represented the *lactone* of a *chlorohydroxy-δ-phenylvaleric acid* (Found : Cl, 16·8; *M*, monobasic, 209·5. $C_{11}H_{11}O_2Cl$ requires Cl, 16·6%; *M*, 210·5); the liquid residue possessed all the characteristics of a chloro-lactone in equilibrium with a small proportion of the corresponding chlorohydroxy-acid. Attempted separation of the latter acid by means of bicarbonate invariably yielded mixtures of acid and lactone, reversion to the lactonic form occurring extensively on acidifying the salt of the acid. The liquid lactone proved to be unsolidifiable; it distilled at 180—190°/6 mm. (Found : Cl, 14·5%), and on heating with alkali suffered complete loss of hydrogen halide. By repeated treatment of the acidic fraction of the liquid lactone with bicarbonate and rejection of the successively obtained non-acidic portions, there was ultimately left about 3% of the total material, and this still contained a lactonic fraction and some of the original phenylpentenoic acid. Consequently any acidic component of non-lactonic character (*i.e.*, of an entirely different structural constitution from the above-described solid and liquid chloro-lactones) must have been present in very small amount, and there is no reason to believe that any such substance was present.

The ready loss of hydrogen chloride by both the solid and the liquid form of the lactone on treatment with reagents, coupled with the fact that both lactones invariably suffered oxidation to benzoic acid and succinic acid with permanganate and with chromic acid (no matter what the conditions of reaction), quite precluded the definite ascertainment of the orientation of the addendum in the respective lactones. The two lactones, however, resembled one another so closely in chemical behaviour that they are most probably to be regarded as stereoisomerides; moreover, the invariable failure which attended long-continued efforts to obtain even a small proportion of chlorophenylacetic acid from either lactone indicates that the lactones are to be regarded as stereoisomeric forms of γ-chloro-δ-hydroxy-δ-phenylvalerolactone. On submission to the action of sodium amalgam in the presence of carbon dioxide and to the action of aluminium amalgam, some reduction and partial opening of the lactone ring occurred, but no pure specimen of hydroxyvaleric acid could in this way be obtained.

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