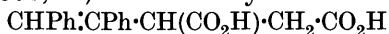


CCCLXIII.—*The Chemistry of the Three-carbon System.*
Part IX. The $\alpha\beta$ - $\beta\gamma$ -Change in β -Alkylcinnamic
Acids.

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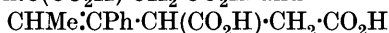
LINSTEAD and WILLIAMS (preceding paper) have shown that a terminal phenyl group, although capable of enhancing mobility when such is already present, cannot cause mobility in a three-carbon system, that is, cannot function as an activating group, because it is incapable of providing a point of attachment for a mobile hydrogen atom; it is, in fact, "non-polar." It has, however, a very powerful effect on the equilibrium of the system owing to the great tendency of double or triple linkings to become conjugated with its double linkings. For example, Stobbe (*Annalen*, 1902, **321**, 83; 1899, **308**, 67) obtained only the acid



by condensing deoxybenzoin with ethyl succinate, the acid $\text{CH}_2\text{Ph}\cdot\text{CPh:C}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ not being formed (compare also Fichter, *J. pr. Chem.*, 1906, **74**, 297).

A phenyl group in the β -position should not affect the *relative* stability of the $\alpha\beta$ - and $\beta\gamma$ -forms in a three-carbon system, because, being conjugated with the double bond in either form, it should exercise an equal stabilising influence on both forms. It is true that diphenylvinylacetic acid is said to be much less stable than its $\beta\gamma$ -isomeride (Fichter, *loc. cit.*), but we do not attach much importance to this observation, especially as no proofs are given of the structure of the two acids.

These considerations led us to extend the work of Kon and Linstead (*J.*, 1925, **127**, 616) on the $\alpha\beta$ - $\beta\gamma$ change to a series of β -phenyl compounds, including β -methyl-, ethyl-, propyl-, and *isopropyl*-cinnamic acids and their hitherto unknown $\beta\gamma$ -isomerides. The $\alpha\beta$ - and $\beta\gamma$ -forms of β -ethylcinnamic acid, $\text{CH}_2\text{Me}\cdot\text{CPh:CH}\cdot\text{CO}_2\text{H}$ and $\text{CHMe}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, are similar to the corresponding methyl-ethylacrylic acids, except that in the former the double bond is conjugated with the phenyl group in both forms. These acids, therefore, should behave similarly under the influence of agents such as strong alkali—a prediction which it is proposed to justify experimentally. The results obtained by Stobbe (*loc. cit.*) on the acids $\text{CH}_2\text{Me}\cdot\text{CPh:C}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and



are also in good agreement with this conception.

β -*Methylcinnamic acid*, $\text{CPhMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, the simplest member

of the series, is analogous to $\beta\beta$ -dimethylacrylic acid. The $\beta\gamma$ -isomere, $\text{CH}_2:\text{CPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is formed during the preparation of the $\alpha\beta$ -acid,* but its presence has hitherto been overlooked owing to the small quantity (2%) produced: the oily by-product which is always formed when the $\alpha\beta$ -acid is prepared by the hydrolysis of the ester (obtained by the dehydration of ethyl β -hydroxy- β -phenylbutyrate) is the $\beta\gamma$ -acid (*β -phenylvinylacetic acid*) contaminated with the eutectic mixture of *cis*- and *trans*- β -methylcinnamic acids. Its structure is apparent from the fact that its ester gives formaldehyde on oxidation with ozone. The formation of this acid can be accounted for by the stabilising effect of the phenyl group on the double linking with which it is conjugated. It is rapidly converted into the stable $\alpha\beta$ -acid by boiling concentrated alkali. Attempts have been made to prepare it from the $\alpha\beta$ -acid by means of alkali, on the assumption that the two forms exist in equilibrium in presence of this reagent, but so far without success.

β -Ethylcinnamic Acids.—A totally different relationship is met with in the higher homologues. β -Ethylcinnamic acid,



obtained by the hydrolysis of the corresponding unsaturated ester is always accompanied by a considerable quantity of an oil having the same composition. The two isomerides can be separated by the method used by Stoermer, Grimm, and Laage (*Ber.*, 1917, 50, 966) for the separation of stable and *allo*- $\alpha\beta$ -acids: the basic copper salt of the $\beta\gamma$ -acid is insoluble in ether, so that mixtures of stable $\alpha\beta$ - and $\beta\gamma$ -acids can be separated into their constituents and their composition determined with considerable accuracy (to about 2%). The pure $\alpha\beta$ -acid can be obtained by the action of acetic anhydride or cold concentrated sulphuric acid on the corresponding hydroxy-acid.

The oily acid is the $\beta\gamma$ -acid, $\text{CHMe}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$; it gives acetaldehyde on oxidation with ozone and forms characteristic derivatives.

The action of alkali on either of the two acids gives an equilibrium mixture of the two isomerides, the proportions of which can be determined by the copper salt method; the results obtained with 50% potassium hydroxide solution are as follows (the figures indicate the compositions of the mixtures and not the yields from a given amount of acid, because fission, producing propiophenone [5%], always takes place):

Initial material.	$\alpha\beta$ -Acid.			$\beta\gamma$ -Acid.		
Duration of heating (hrs.)	1	2	4	1	2	4
% $\alpha\beta$ -Acid formed	68	31	26	10	20	24

* Unless otherwise stated, the " $\alpha\beta$ -acid" is the stable form in all cases.

Boiling with 50% sulphuric acid produces a somewhat similar effect, but the action is complicated by the formation of a lactone and of α -ethylstyrene; *e.g.*, after 1 hour's boiling the following are isolated :

	$\alpha\beta$ -Acid.	$\beta\gamma$ -Acid.	Lactone.	Hydrocarbon
From $\alpha\beta$ -acid	60%	15%	5%	18%
From $\beta\gamma$ -acid	22	49	12	17

The acid chlorides also undergo interconversion: on heating either chloride at 140–160° for 3 hours a mixture is obtained containing about 21% of the $\alpha\beta$ -compound.

The mixture obtained by dehydrating ethyl β -hydroxy- β -phenylvalerate with phosphorus oxychloride or potassium hydrogen sulphate consists of the $\alpha\beta$ - and $\beta\gamma$ -esters.

β -Propylcinnamic Acids.—On hydrolysing the unsaturated ester produced by the dehydration of ethyl β -hydroxy- β -phenylhexoate a mixture of solid and liquid isomerides is again obtained. Schroeter (*Ber.*, 1908, **41**, 5) has suggested that the liquid may be the $\beta\gamma$ -isomeride, but Stoermer, Grimm, and Laage (*loc. cit.*) have isolated from it the “misch form” (mixture of stable and *allo*- $\alpha\beta$ -acids). This, however, forms only a very small proportion of the oil, from which we have isolated by the copper salt method a large quantity—about 50% of the original crude acid—of a liquid having the reactions of the $\beta\gamma$ -acid, $\text{CHEt}:\text{CPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. This was confirmed by oxidation of both the acid and its ester.

The two acids give the same amide, *m. p.* 100.5°, by Stoermer, Grimm, and Laage's method, and the same anilide, *m. p.* 108°, because the acid chloride produced by the action of phosphorus pentachloride on either acid is the $\beta\gamma$ -derivative. The *anilide* of the $\alpha\beta$ -acid has now been prepared and melts at 114°.

The interconversion of the two acids by different agents was investigated.

$\alpha\beta$ -Acid.						
% Potassium hydroxide	10	10	10	50	50	50
Duration of heating (hrs.)	2½	6	25½	2	4	6
% $\alpha\beta$ -Acid	60	53	53	54	52	53
$\beta\gamma$ -Acid.						
% Potassium hydroxide	10	10	10	50	50	50
Duration of heating (hrs.)	2	6	24½	2	4	6
% $\alpha\beta$ -Acid	40	50	52	50	51	52

The change of concentration of the alkali from 10 to 50% affects only the rate at which equilibrium is established and not the final composition of the mixture.

On boiling the acids with 50% sulphuric acid, the following mixtures were produced :

	$\alpha\beta$ -Acid.	$\beta\gamma$ -Acid.	Lactone.	α -Propylstyrene.
From $\alpha\beta$ -acid	53%	9%	5%	33%
From $\beta\gamma$ -acid	8	38	7	47

On heating, the acid chlorides gave a mixture consisting of 46% $\alpha\beta$ and 54% $\beta\gamma$. Attempts to produce isomerisation of the esters by the agency of sodium ethoxide were unsuccessful.

β -isoPropylcinnamic Acids.—These acids, neither of which had previously been prepared, have now been obtained from *isobutyrophenone* by the method employed in the preparation of the *n*-propyl acid and its $\beta\gamma$ -isomeride, to which they bear a great resemblance. They were separated from each other, although with some difficulty, by the copper salt method.

The interconversion of the two acids was carried out by means of 50% potassium hydroxide solution; at the end of 6 hours a mixture containing 54% of the $\alpha\beta$ -acid was obtained in each case. One hour's boiling with 50% sulphuric acid produced the following mixtures :

	$\alpha\beta$ -Acid.	$\beta\gamma$ -Acid.	Lactone.	α -isoPropylstyrene.
From $\alpha\beta$ -acid	58%	6%	5%	31%
From $\beta\gamma$ -acid	9	46	7	38

Reviewing the above results it will be seen that all the acids investigated have a degree of mobility greater than that of the corresponding aliphatic compounds. This increase in mobility is doubtless attributable to the influence of the phenyl group already discussed; nevertheless, none of the esters in this series could be alkylated. The second member of the series has a much greater tendency to pass into the $\beta\gamma$ -form than either the propyl or the *isopropyl* compound. A possible explanation of this may be forthcoming as the result of further work on the influence of comparatively large groups on the position of equilibrium. The views already put forward regarding the position of equilibrium in unsaturated acids containing a *gem*-group have been materially strengthened by the outcome of the present work.

The preparation of the methyl ketones corresponding to the preceding β -alkylcinnamic acids is a matter of considerable difficulty, because the chlorides of the acids from which they can be synthesised show a great tendency to form equilibrium mixtures and the yields of ketone obtainable from them are poor. The two *ketones* corresponding to the ethylcinnamic acids, namely, $\text{CH}_2\text{Me}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COMe}$ and $\text{CHMe}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{COMe}$, have been prepared. Although distinct, they readily form equilibrium mixtures in the presence of alcoholic alkalis, sodium ethoxide, or acids; they can also be ethylated, yielding the same ethyl derivative, which doubtless has

the structure $\text{CHMe}\cdot\text{CPh}\cdot\text{CHEt}\cdot\text{COMe}$. The ketones are thus analogous to the ketones studied by Kon and Linstead (J., 1925, 127, 814); but possess greater mobility, as they are readily alkylated. The ketone $\text{CMePh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_3$ was prepared, but it was not possible to prepare the $\beta\gamma$ -isomeride owing to the difficulty of obtaining the acid. The ketone has little tendency to pass into the $\beta\gamma$ -form and cannot be alkylated.

None of the ketones or esters of this series undergoes the Michael reaction, owing, no doubt, to the inhibiting effect of the β -phenyl group.

EXPERIMENTAL.

β -Methylcinnamic and β -Phenyl- Δ^{β} -butenoic Acids.—Acetophenone was condensed with ethyl bromoacetate and magnesium in the usual way. The crude benzene solution of the hydroxy-ester was boiled with phosphorus oxychloride ($\frac{1}{3}$ mol.) for $\frac{1}{2}$ hour, and the unsaturated ester isolated (Lindenbaum, *Ber.*, 1917, 50, 1270). It had b. p. 142—145°/16 mm., d_4^{20} 1.04036, $n_D^{19.5}$ 1.54510, $[\alpha]_D^{20}$ 57.78 (calc., 55.20); the yield was 55% (Found: C, 75.6; H, 7.5. Calc.: C, 75.8; H, 7.4%). The ester was hydrolysed with 50% aqueous potassium hydroxide, enough alcohol being added to effect solution; a little acetophenone was produced together with the acid. The latter was twice extracted with hot petroleum (b. p. 40—60°), which left the greater part unattacked; the extract was concentrated somewhat and cooled; a small quantity of solid then crystallised. This, and also the solid undissolved by the petroleum, consisted of β -methylcinnamic acid, m. p. 98.5° (Found: C, 73.9; H, 6.2. Calc.: C, 74.1; H, 6.2%). Its solution in sulphuric acid was yellow.

The petroleum mother-liquors contained a quantity of the "misch form" (compare Stoermer, Grimm, and Laage, *loc. cit.*), m. p. 76°. The violet solution of this in sulphuric acid gradually became yellow; addition of water at this stage precipitated the pure stable acid, m. p. 98.5°. The most soluble constituent of the acid mixture consisted of the oily $\beta\gamma$ -acid (*β -phenyl- Δ^{β} -butenoic acid*), which was still contaminated with a little of the "misch form" (Found: C, 73.8; H, 6.3. $\text{C}_{10}\text{H}_{10}\text{O}_2$ requires C, 74.1; H, 6.2%). The acids were present approximately in the following proportions: stable 89%, "misch form" 9%, $\beta\gamma$ - 2%.

The methyl ester of the new acid, obtained by the action of methyl sulphate on the sodium salt (Stoermer, Grimm, and Laage, *loc. cit.*), had b. p. 138°/16 mm. (Found: C, 74.9; H, 6.8. $\text{C}_{11}\text{H}_{12}\text{O}_2$ requires C, 75.0; H, 6.8%); the $\alpha\beta$ -ester has a somewhat higher b. p. The anilide was obtained in pearly plates, m. p. 127°; that of the stable $\alpha\beta$ -acid has m. p. 121°. On treatment of the new ester with ozone

and decomposition of the ozonide, formaldehyde (identified by means of β -naphthol) was obtained; the non-volatile portion of the product, which reacted with copper acetate and gave a coloration with ferric chloride, was presumably methyl benzoylacetate.

The new acid, on boiling with an excess of 50% potassium hydroxide solution for 1 hour, was completely converted into β -methylcinnamic acid. The $\alpha\beta$ -acid, subjected to the same treatment for 5 hours, was recovered unchanged.

The $\alpha\beta$ -acid (10 g.) was boiled under reflux for 20 minutes, cooled, and extracted once with 50 c.c. of petroleum (b. p. 40–60°). The extract on concentration deposited about 1 g. of the "misch form"; the filtrate contained about 1 g. of α -methylstyrene, b. p. 160° (Found: C, 91.5; H, 8.6. Calc.: C, 91.5; H, 8.5%).

The $\alpha\beta$ -acid (10 g.) was boiled for 1 hour with 50% sulphuric acid (100 c.c.), cooled, and extracted with ether. The extract was washed with sodium carbonate solution, which removed the $\alpha\beta$ -acid; from the neutral portion, 2.3 g. of α -methylstyrene were isolated.

The chloride of the stable $\alpha\beta$ -acid (b. p. 132°/18 mm.), prepared by means of thionyl chloride, remained unchanged on heating, and the pure acid could be regenerated from it.

β -Ethylcinnamic and β -Phenyl- Δ^{β} -pentenoic Acids.—The hydroxy-ester obtained from propiophenone by the Reformatski reaction in 35–40% yield had b. p. 152–154°/19 mm. It tended to lose water on distillation. The hydroxy-acid prepared from it had m. p. 123° after crystallisation from benzene; it was accompanied by small quantities of the unsaturated acids.

Stable β -ethylcinnamic acid was obtained from the hydroxy-acid by means of either cold concentrated sulphuric acid or boiling acetic anhydride and had m. p. 95° as found by previous authors.

allo- β -Ethylcinnamic acid was obtained from the above acid by the action of ultra-violet light, 62% being produced after 106 hours' exposure (Stoermer, Grimm, and Laage, *loc. cit.*). It was characterised by the formation of the anilide (needles, m. p. 122°).

β -Phenyl- Δ^{β} -pentenoic acid was produced when the hydroxy-ester was dehydrated by heating it for 3 hours with potassium hydrogen sulphate; the mixture of unsaturated esters obtained boiled at 152–159°/26 mm., and had d_4^{25} 1.0297 and n_D^{25} 1.52788. A more convenient method consists in treating the crude hydroxy-ester with phosphorus oxychloride as described on p. 2752. The products obtained by either of these processes gave propiophenone and acetaldehyde on oxidation with ozone and subsequent decomposition. On hydrolysis with potassium hydroxide, an oily mixture of acids was obtained which gave, on oxidation, products derived from

both the $\alpha\beta$ - and the $\beta\gamma$ -acid. By the basic copper salt method, the mixture was found to contain some 33% of the stable $\alpha\beta$ -acid; this was identical with the acid prepared from the hydroxy-acid and gave propiophenone and oxalic acid on oxidation with permanganate (Found: C, 74.8; H, 6.9. Calc.: C, 75.0; H, 6.8%). The isomeric acid was liquid; on treatment with permanganate, it gave acetaldehyde, acetic and benzoic acids, and a trace of propiophenone* (Found: C, 74.9; H, 6.9%).

The *anilide* of the $\beta\gamma$ -acid was obtained by heating the acid (1.96 g.) in dry ether with phosphorus pentachloride (2.48 g.) until the latter dissolved, cooling the mixture, and slowly adding an excess of aniline. The ethereal solution was shaken successively with dilute hydrochloric acid, alkali and water, dried, and evaporated; from the residue, crystallised from ether and light petroleum, rhombic plates were obtained, m. p. 127° (mixed m. p. with the *allo*-anilide, 94—99°) (Found: C, 81.2; H, 6.8; N, 5.6. $C_{17}H_{17}ON$ requires C, 81.3; H, 6.8; N, 5.6%). The anilide of the stable $\alpha\beta$ -acid obtained in the same way has m. p. 86° (Found: C, 81.1; H, 6.8; N, 5.7%). The anilides can also be obtained by treating an ice-cold solution of the acid and aniline in dry pyridine with thionyl chloride.

The *acid chloride*, prepared by warming the $\beta\gamma$ -acid with an excess of thionyl chloride for 20 minutes and distilling the product in a good vacuum, boiled at 140°/18 mm. The $\alpha\beta$ -isomeride boiled at 142°/18 mm. On pouring either acid chloride into water it was found that the acid produced was no longer pure, but contained 10—14% of the other isomeride, which could be separated by the copper salt process.

The *ethyl ester* prepared from the $\beta\gamma$ -acid chloride had b. p. 143°/14 mm., $d_4^{13.5}$ 1.0285, $n_D^{13.5}$ 1.52953, $[R_L]_D$ 61.26 (calc., 59.82) (Found: C, 76.2; H, 7.9. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%). The ester gave on ozonisation a good yield of acetaldehyde, which was identified by means of β -naphthol; a trace of propiophenone was also obtained, and some acetophenone doubtless derived by hydrolysis from the benzoylacetic ester produced. The $\alpha\beta$ -ester, prepared for comparison, had b. p. 145°/14 mm., $d_4^{13.5}$ 1.0234, $n_D^{13.5}$ 1.52827, $[R_L]_D$ 61.45, and gave propiophenone and glyoxylic acid on treatment with ozone.

Interconversion of the $\alpha\beta$ - and $\beta\gamma$ -acids. (1) A solution of 5 g. of either acid in 40 c.c. of 50% aqueous potassium hydroxide was boiled for a definite time. The acids were then isolated and the

* The isolation of propiophenone in this case and of butyrophenone from the higher homologue is most likely due to the admixture of a small amount of the *allo*-acid, which would not be removed in the copper salt process.

amount of conversion was estimated by the copper salt process. The results are given on p. 2749.

(2) Each acid (10 g.) was refluxed for an hour with an excess of 50% sulphuric acid. The acids were then estimated as before and the neutral products were separated by distillation in a vacuum. The low fraction consisted of α -ethylstyrene, b. p. 81–82°/20 mm. (Found: C, 90.7; H, 9.2. $C_{10}H_{12}$ requires C, 90.9; H, 9.1%), which on oxidation with alkaline permanganate gave propiophenone; this was identified by its semicarbazone. The high fraction, b. p. 170°/16 mm., appeared to consist of β -phenylvalerolactone (Found: C, 74.6; H, 6.9. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.8%).

β -Propylcinnamic and β -Phenyl- Δ^{β} -hexenoic Acids.—The unsaturated ester was obtained by the phosphorus oxychloride process (see p. 2752) in 55% yield (some butyrophenone was recovered); it had b. p. 158–160°/19 mm., d_4^{25} 1.0079, n_D^{25} 1.52640, $[R_L]_D$ 66.59 (calc., 64.44).

On hydrolysis a mixture of acids was obtained which was separated into its constituents by the copper salt method; the salt of the $\alpha\beta$ -acid is less soluble in ether than that in the ethyl series and it is necessary to extract it twice for complete separation. The $\alpha\beta$ -acid formed needles, m. p. 96.5°, from petroleum (Found: C, 75.2; H, 7.1. Calc.: C, 75.8; H, 7.4%). The $\beta\gamma$ -acid was a liquid (Found: C, 75.4; H, 7.4%). The structure of the acids was proved by oxidation with alkaline permanganate, the solid acid giving butyrophenone (semicarbazone, m. p. 189°) and oxalic acid, and the liquid acid propionic and benzoic acids. Both acids on dry distillation gave α -propylstyrene, b. p. 86°/14 mm., which was oxidised to butyrophenone by alkaline permanganate.

The same *anilide*, m. p. 108° (Found: N, 5.4. $C_{18}H_{19}ON$ requires N, 5.3%), was obtained from both acids by the phosphorus pentachloride method (see p. 2754). With thionyl chloride in pyridine, however, the $\alpha\beta$ -acid gave mainly an *anilide*, m. p. 114° (Found: N, 5.3%), although some of the *anilide*, m. p. 108°, also was produced. The latter was the sole product from the $\beta\gamma$ -acid, so it is presumably the $\beta\gamma$ -compound. Both *anilides* gave a mixture of acids on hydrolysis.

The same *amide*, crystallising from ethyl acetate in needles, m. p. 101°, was obtained from both acids (Found: N, 7.4. $C_{12}H_{15}ON$ requires N, 7.4%) and was probably the $\beta\gamma$ -compound, since it was produced with the aid of phosphorus pentachloride.

The *acid chlorides* were prepared as described on p. 2754; that derived from the $\alpha\beta$ -acid had b. p. 160°/40 mm., and the $\beta\gamma$ -isomeride boiled at 159°/40 mm. The acids regenerated from them were each found to contain 14–20% of the isomeric compound.

Heating either chloride for 3 hours gave a mixture containing 53—55% of the $\beta\gamma$ -compound.

The *ethyl* esters were prepared from the acid chlorides and therefore were not homogeneous; the $\alpha\beta$ -ester boiled at 161°/31 mm., the $\beta\gamma$ -ester at 148°/16 mm. The *methyl* esters could, however, be prepared by an alternative method, namely, by the action of methyl sulphate on the sodium salts; the $\alpha\beta$ -ester had b. p. 135°/12 mm., $d_4^{18.2}$ 1.0017, $n_D^{18.2}$ 1.52146, $[R_L]_D$ 62.10 (calc., 59.82) (Found : C, 76.4; H, 8.0. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%); the $\beta\gamma$ -ester had b. p. 133°/12 mm., $d_4^{19.5}$ 1.0297, $n_D^{19.5}$ 1.53305, $[R_L]_D$ 61.53 (Found : C, 76.4; H, 8.0%). On oxidation with ozone the $\alpha\beta$ -ester gave an oily ozonide, from which butyrophenone and glyoxylic acid were obtained on decomposition. The ozonide of the $\beta\gamma$ -ester was crystalline and on decomposition gave propaldehyde, benzoylactic acid, m. p. 104° (Found : C, 65.8; H, 4.9. Calc. : C, 65.9; H, 4.9%), and butyrophenone, the last being due to the presence of some of the $\alpha\beta$ -isomeride in the ester used (this had been prepared through the acid chloride). The propaldehyde was identified by collecting it in well-cooled petroleum (by means of a stream of nitrogen) and passing in dry ammonia; a precipitate of the aldehyde-ammonia was then formed which deliquesced, giving the compound $C_{15}H_{19}N_3$, m. p. 74° (Waage, *Monatsh.*, 1883, **4**, 708).

The interconversion of the acids was carried out as described for the lower homologues and the results have already been given. In the experiments with sulphuric acid a *lactone*, m. p. 94—97°, b. p. 178°/14 mm., was isolated (Found : C, 75.6; H, 7.4. $C_{12}H_{14}O_2$ requires C, 75.6; H, 7.4%), and also α -propylstyrene, b. p. 86°/14 mm. (Tiffeneau, *Compt. rend.*, 1906, **143**, 650) (Found : C, 90.1; H, 9.7. Calc. : C, 90.4; H, 9.6%), which gave butyrophenone on oxidation.

allo- β -Propylcinnamic acid was prepared in the same way as the lower homologue, although in poorer yield; it melted at 86.5° and gave an amide, m. p. 101° (Stoermer, Grimm, and Laage, *loc. cit.*), which was not identical with the amide, m. p. 108°, described above.

β -isoPropylcinnamic and β -Phenyl- γ -methyl- Δ^{β} -pentenoic Acids.—*iso*Butyrophenone was condensed with ethyl bromoacetate in the usual way, and the benzene solution of the product treated with phosphorus oxychloride. From the mixture, half the ketone employed was recovered and the unsaturated ester, b. p. 154—160°/25 mm., $d_4^{20.8}$ 1.0158, $n_D^{20.8}$ 1.52561, $[R_L]_D$ 65.88 (calc., 64.44), isolated in 38% yield.

On hydrolysis a liquid mixture of acids was obtained in addition to a little *isobutyrophenone*. The acids were separated by the copper salt method, exactly as in the case of the propylcinnamic

acids. The $\alpha\beta$ -acid, isolated in 53% yield, formed needles, m. p. 94°, from petroleum (Found: C, 75.6; H, 7.4. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%) and gave, on oxidation with permanganate, oxalic acid and isobutyrophenone (*semicarbazone*, plates from alcohol, m. p. 182°. Found: N, 20.7. $C_{11}H_{15}ON_3$ requires N, 20.5%). The $\beta\gamma$ -acid appeared to be present in somewhat smaller quantity (47%) and formed rosettes of needles, m. p. 95° (Found: C, 75.7; H, 7.4%). It gave benzoic and acetic acids and acetone on oxidation.

The *anilides* were prepared as described on p. 2754. The $\beta\gamma$ -acid gave the same anilide, m. p. 121°, by both methods (Found: N, 5.4. $C_{18}H_{19}ON$ requires N, 5.3%); the $\alpha\beta$ -acid gave small quantities of another anilide, m. p. 99° (Found: N, 5.3%), by the pyridine method and by the phosphorus pentachloride method; this is, therefore, probably the $\alpha\beta$ -anilide.

Only one *amide*, presumably the $\beta\gamma$ -compound, was obtained; it crystallised from ethyl acetate in needles, m. p. 113° (Found: N, 7.5. $C_{12}H_{15}ON$ requires N, 7.4%).

The *acid chlorides* boil at 153°/26 mm. ($\alpha\beta$) and 153°/30 mm. ($\beta\gamma$) respectively; they each contain 10—20% of the other isomeride. On heating for 3 hours at 140—150° a mixture is obtained containing about 55% of the $\beta\gamma$ -compound.

The *esters* were prepared from the acid chlorides and therefore were not entirely homogeneous, although the products obtained from them on oxidation with ozone were mainly those to be expected. The $\alpha\beta$ -esters boiled at 166°/42 mm. (methyl) and 161°/31 mm. (ethyl), the $\beta\gamma$ - at 166°/42 mm. and 161°/33 mm. respectively.

The isomerisation of the acids was carried out as described above. In the experiments with sulphuric acid α -isopropylstyrene, b. p. 89°/15 mm. (Klages, *Ber.*, 1903, **36**, 3691), was isolated. This hydrocarbon was also obtained by dry distillation of either the $\alpha\beta$ - or the $\beta\gamma$ -acid (Found: C, 90.0; H, 9.8. Calc.: C, 90.4; H, 9.6%); it gave isobutyrophenone on oxidation. A *lactone*, b. p. 178°/16 mm., also was obtained.

δ -Phenyl- $\Delta\gamma$ -penten- β -one.—This ketone was obtained in about 25% yield by the action of zinc methyl iodide on the chloride of β -methylcinnamic acid, the procedure described in Part I (J., 1923, **123**, 1361) being followed; it was isolated in the form of its *semicarbazone*, m. p. 191° (Found: N, 19.5. $C_{12}H_{15}ON_3$ requires N, 19.4%). The *ketone* regenerated from this boiled at 133—136°/12 mm.; it solidified, forming large plates, m. p. 100° (Found: C, 82.4; H, 7.6. $C_{11}H_{12}O$ requires C, 82.5; H, 7.5%).

On oxidation with ozone and subsequent decomposition the ketone gave acetophenone, but no trace of formaldehyde. Acetophenone was also obtained by treating the ketone with permanganate.

Unsuccessful attempts were made to prepare the ketone by the action of acetyl chloride on the magnesium derivative of β -bromo- α -methylstyrene (Schroeter, *Ber.*, 1907, **40**, 1594) and also by the action of α -chlorostyrene (Friedel, *Compt. rend.*, 1867, **67**, 1192) on ethyl sodioacetoacetate; in the latter case, phenylacetylene was produced.

The ketone was not affected by standing with cold sodium ethoxide for 3 days, or by boiling with 25% sulphuric acid for 2 hours; the pure semicarbazone was obtained from it in each case. An attempt was made to alkylate it by means of ethyl iodide in presence of "molecular" sodium in benzene, but although there was a vigorous reaction no ethyl derivative was isolated, the product being an oil of high boiling point. The ketone could not be condensed with ethyl sodiomalonate.

δ -Phenyl- Δ^{γ} -hexen- β -one and δ -Phenyl- Δ^{δ} -hexen- β -one.—These two ketones were obtained in 20—25% yield by the action of zinc methyl iodide on the chlorides of β -ethylcinnamic acid and its $\beta\gamma$ -isomeride respectively.

The $\alpha\beta$ -ketone boiled at 138°/14 mm. and yielded a *semicarbazone* which formed plates, m. p. 158° (Found: N, 18.4. $C_{13}H_{17}ON_3$ requires N, 18.2%). The *ketone* was regenerated from this by means of oxalic acid (Found: C, 82.5; H, 8.2. $C_{12}H_{14}O$ requires C, 82.8; H, 8.1%). On oxidation with ozone, it gave propiophenone.

The $\beta\gamma$ -ketone also boiled at 138°/14 mm.; it gave a *semicarbazone* which crystallised from alcohol in plates, m. p. 185° (Found: N, 18.5%). The *ketone* regenerated from this (Found: C, 82.6; H, 8.1%), on oxidation with ozone, gave acetaldehyde.

Ethylation of the two ketones. The pure ketones, on treatment in benzene solution with ethyl iodide and "molecular" sodium, gave the same ethylation product in poor yield (1 g. from 6 g. of ketone) in addition to a small quantity of initial material and a considerable quantity of high-boiling by-products. The ethylated ketone, b. p. 140—146°/14 mm., was isolated in the form of its *semicarbazone*, m. p. 174°. This, however, was not readily formed (Found: C, 69.3; H, 8.2; N, 16.3. $C_{15}H_{21}ON_3$ requires C, 69.5; H, 8.1; N, 16.2%), and the quantity obtained was not sufficient for the regeneration of the ketone. A very small quantity of the new ketone was treated with cold alkaline permanganate; acetic acid was formed but no propiophenone could be detected, and therefore the ethylated ketone doubtless has the $\beta\gamma$ -structure, CHMe:CPh·CHEt·COMe.

Interconversion of the two ketones. The two ketones, after being kept in cold alcoholic sodium ethoxide for 2 days, were isolated and each was converted into the semicarbazone, which was fraction-

ally crystallised from ethyl acetate-petroleum and then from dilute alcohol. In each case isomerisation had taken place to the extent of 25—35%. It was difficult to estimate this value exactly because the semicarbazones formed a definite mixture, m. p. 126°, which could be separated into its constituents only with great difficulty and inevitable loss (compare Kon and Linstead, *loc. cit.*).

Boiling the ketones for 2 hours with an excess of 50% sulphuric acid, or keeping them for 2 days in cold 1% alcoholic potassium hydroxide, produced 20—30% change in each case. The two isomerides, therefore, have approximately the same stability.

Attempts to condense the ketones with ethyl sodiomalonate were unsuccessful.

Condensation of Propiophenone with Acetone.—Attempts were made to prepare the two ketones described above by the direct condensation of propiophenone with acetone by the agency of sodium ethoxide; a variety of conditions was tried, such as allowing the ketones to stand with sodium ethoxide in ethereal or alcoholic solution or without a solvent; in one instance the alcoholic solution was boiled for 4½ hours. In all cases about half of the propiophenone was recovered unchanged and the required ketone, which was the $\alpha\beta$ -compound, was formed only to the extent of 5%. High-boiling products were formed in considerable quantity in all cases, but the only definite compound isolated, b. p. 194—199°/16 mm., was obtained when the condensation was carried out in alcoholic solution. It readily gave a *semicarbazone*, m. p. 204° (Found: C, 70.4; H, 7.8; N, 15.7. $C_{16}H_{21}ON_3$ requires C, 70.9; H, 7.8; N, 15.5%). The ketone regenerated therefrom gave propiophenone on oxidation with permanganate and propiophenone and acetone on treatment with ozone and therefore may have the formula $CEtPh:CH:CO:CH:CM_e_2$. Such a compound, however, should form a semicarbazido-semicarbazone, and this was not obtained.

Attempts were also made to condense butyrophenone and *iso*-butyrophenone with acetone, but none of the required ketones appeared to be formed. The action of zinc methyl iodide on the chlorides of the propyl- and *isopropyl*-cinnamic acids led to mixtures from which no semicarbazones or other crystalline derivatives could be isolated.

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