# CCLXVI.—*Investigations of the Olefinic Acids. Part III. Homologues of Teraconic, Terebic, and Pyroterebic Acids. Further Evidence of the Effect of Two γ-Alkyl Groups on Three-carbon Tautomerism.*

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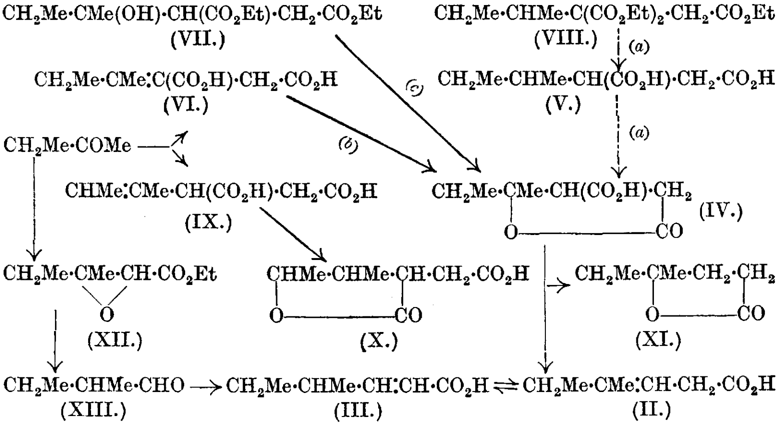
THE striking stability towards alkaline reagents of pyroterebic acid, its ethyl ester, and the related methyl ketone [$CMe_2{:}CH{\cdot}CH_2{\cdot}COR$ (I); R = OH, OEt, Me respectively] recently observed (J., 1928, 2350; 1929, 2503; this vol., p. 909) has provided the only evidence of the large effect of two γ-alkyl groups in favouring the βγ-phase of a three-carbon system. Confirmatory evidence of this general principle has now been obtained from a study of the homologous acid (II), and a further illustration of its working can be found in Reichstein's recent observation (*Ber.*, 1930, **63**, 751) that γγ-dimethylallyl bromide yields pyroterebic acid by conversion into the nitrile and subsequent hydrolysis, under conditions such that crotyl bromide yields largely $\Delta^{\alpha}$-pentenoic acid.

The acid now under discussion (II) is reported by von Auwers and Heyna (*Annalen*, 1923, **434**, 162) to be the product of the reduction of γ-methylsorbic acid with sodium amalgam in acid solution. Recent work on the reduction of sorbic acid and its homologues (Goldberg and Linstead, J., 1928, 2345; Evans and Farmer, J., 1928, 1644; Burton and Ingold, J., 1929, 2027) strongly indicates, however, that such a reduction product would contain a considerable proportion of the γδ-isomeride—on theoretical grounds Burton and Ingold suggest about as much as is formed from sorbic acid itself (some 50%). Apart from this, neither the βγ-acid (II) nor its αβ-isomeride has been prepared, and the bulk of the experimental work now described is concerned with their synthesis.

Pyrolysis of the corresponding paraconic acid (IV) was an obvious line of attack, and three methods for the preparation of this acid were examined: (*a*) oxidation of *sec.*-butylsuccinic acid (V), (*b*) lactonisation of γ-methyl-γ-ethylitaconic acid (VI), and (*c*), following Grignard (*Ann. Chim. Phys.*, 1902, **27**, 550) and Simonsen (J., 1907, **91**, 184), hydrolysis of the γ-hydroxy-ester (VII). In practice, only methods (*b*) and (*c*) proved suitable, and with the former, the preparation of the acid (VI) from methyl ethyl ketone and ethyl succinate was complicated by the presence in the reaction product of a preponderating amount of the corresponding "aticonic" acid (IX), as observed by Stobbe (*Annalen*, 1894, **282**, 280; 1902, **321**, 105). From this aticonic acid Stobbe prepared a lactonic acid (m. p. 125—126°), to which he assigned (*loc. cit.*) first the paraconic



(IV) and then the *iso*paraconic (X) formula. A modification of his process enabled us to separate the dibasic acids (VI and IX). Treatment of the aticonic acid (IX) with mineral acids yielded Stobbe's lactonic acid (m. p. 128°), together with a small amount of an isomeric acid of m. p. 146°. Lactonisation of the itaconic acid gave mainly the new (146°) acid and a smaller amount of the 128°-acid. From this it appeared that the 146°-acid was the desired *γ-methyl-γ-ethylparaconic acid* and that the acid of lower m. p. had the *iso*paraconic acid formula proposed by Stobbe. This view was fully confirmed by the preparation of the 146°-acid free from its isomeride by alkaline hydrolysis of ethyl γ-hydroxy-β-carbethoxy-γ-methyl-*n*-hexoate (VII) (method *c*). The formation of the two lactonic acids side by side from the dibasic acids indicates that these undergo tautomeric change in the acid solution during lactonisation (compare Fichter and Gisiger, *Ber.*, 1908, **42**, 4707; Kon and Linstead, J., 1925, **127**, 616), but not with sufficient rapidity to prevent each unsaturated acid from forming mainly its own lactone. Separation of the lactonic acids is a matter of some difficulty and it is probable that Sircar's "γ-methyl-γ-ethylparaconic acid" (J., 1927, 1257) of m. p. 131—132°, produced by acid hydrolysis of the γ-lactone of β-hydroxy-β-ethylbutane-γδδ-tricarboxylic acid, is a mixture of the two isomerides.

The paraconic acid (IV) can be distilled in part unchanged at atmospheric pressure, but the major portion passes into *γ-methyl-$\Delta^{\beta}$-hexenoic acid* (II) and the corresponding lactone (XI). Slow distillation favours lactone formation, doubtless owing to spontaneous ring closure similar to that observed by Fittig and

Geisler (*Annalen*, 1881, **208**, 37), but as much as 40% of pure unsaturated acid could be obtained under the optimum conditions.

The comparatively rare valeraldehyde (XIII) required for the preparation of the isomeric *γ-methyl-*$\Delta^{\alpha}$*-hexenoic acid* (III) was prepared from *sec.*-butyl bromide and ethyl orthoformate, the alternative method, from methyl ethyl ketone through the glycidic ester (XII) (Darzens, *Compt. rend.*, 1904, **139**, 1214), being unsatisfactory owing to the stability of the oxide ring (compare Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 657).

The αβ- and the βγ-acid so prepared showed the expected differences in properties (see below), and the tautomeric change between them in hot alkali was studied by the standard methods (Linstead, J., 1927, 2579). The equilibrium mixture contained 77% of βγ-acid, and the mobility $10(k_1 + k_2)$ was 3·1 ($t$ in hours). There was thus a general resemblance to the pyroterebic series, the γ-methyl-γ-ethyl group being rather less efficient than the γ-*gem*-dimethyl in stabilising the βγ-phase. The equilibrated αβ-acid treated by the process of partial esterification (Sudborough and Thomas, J., 1914, **99**, 2307; Eccott and Linstead, J., 1929, 2153) readily yielded βγ-acid almost identical in properties with that prepared from the paraconic acid.

| | B. p./ 13 mm. | *M* (titration) (Calc., 128). | $[R_L]_D$ (Calc., 35·60). | %-Iodine addition (10 mins.). |
|---|---|---|---|---|
| *αβ*-Acid ............................ | 125° | 127 | 36·65 | 0·5 |
| Equilibrated *αβ*-acid ........... | 116—122 | 128 | 35·93 | 75·2 |
| Equilibrated *βγ*-acid ........... | — | 128 | 35·98 | 77·3 |
| *βγ*-Acid from equilibrium ...... | 118 | 128 | 35·81 | 93·9 |
| *βγ*-Acid from paraconic acid ... | 118 | 128 | 35·78 | 95·8 |

The general resemblance between the new βγ-acid and pyroterebic acid extended to the reaction with thionyl chloride (compare Linstead, J., 1929, 2504), in that both acids tend to form addition products with hydrogen chloride; even with phosphorus trichloride the new acid yielded slightly chlorinated products, and only on one occasion could a pure derivative of the acid be obtained.

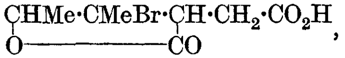
## EXPERIMENTAL.

*Preparation of γ-Methyl-γ-ethyl-itaconic and -aticonic Acids* (VI and IX).—Methyl ethyl ketone and ethyl succinate were condensed by Stobbe's method (*loc. cit.*). To a suspension of dry sodium ethoxide (2 g.-mols.) in anhydrous ether was added slowly, with vigorous shaking, a mixture of the ketone (72 g.) and the ester (174 g.). The mixture was left for several hours in a freezing mixture and then at room temperature for 7—10 days. The semi-solid product was poured into ice-water (400 c.c.), the aqueous layer extracted twice with ether to remove neutral products, and acidified with 50% sulphuric acid. The resulting dark brown oil (A) was separated and allowed to stand; it deposited very little solid, and was taken up in ether and dried with calcium chloride. The residue, after complete removal of the solvent and standing for a week, yielded a considerable quantity of a solid (B) which was then separated from the adhering oil (C). Extraction with ether of the aqueous liquor from which the original oil (A) had separated yielded a mixture (10—15 g.) of the aticonic acid and succinic acid, from which the former was obtained pure by extraction with chloroform and recrystallisation first from chloroform and then from water (4 g.).

The solid (B) was the almost pure aticonic acid. It was freed from a trace of dark-coloured impurity by trituration with light petroleum, and then had m. p. 135° (60 g.). When extracted with successive small quantities of ether, the last portion to dissolve was the pure aticonic acid (m. p. 141°), which indicated that no appreciable amount of the itaconic acid, which is much less soluble in ether, could be present. On crystallisation from boiling water containing a little animal charcoal, $\gamma$-methyl-$\gamma$-ethylaticonic acid (IX) was obtained pure (45 g.); it forms hard aggregates of nodules, m. p. 141° (Stobbe, *loc. cit.*, gives 141—142°) (Found: C, 56·1; H, 7·1; *M* by titration, 172. Calc.: C, 55·8; H, 7·0%; *M*, dibasic, 172).

The oil (C), mainly a mixture of acid esters, was boiled with an equal weight of 25% aqueous sodium hydroxide for ½ hour, cooled, and acidified. (Under these conditions no appreciable tautomeric change occurs in the acids.) After standing for 2 hours, the separated solid was filtered off and dried. Extraction of this solid with ether removed a mixture of acids which could not be readily separated, and left a less soluble residue of m. p. 172—178°, which after crystallisation from water yielded the pure itaconic acid (10 g.). $\gamma$-Methyl-$\gamma$-ethylitaconic acid (VI) crystallises from hot water in needles, which melt at 186° (decomp.) with slow heating. The m. p. is several degrees higher with rapid heating (compare Stobbe, *loc. cit.*, who gives m. p. 181° with slow heating) (Found: C, 55·9; H, 6·7%; *M*, 172).

*Lactonisation of the acids.* (i) Through the bromo-lactonic acid. $\beta$-Bromo-$\beta\gamma$-dimethylbutyrolactone-$\alpha$-acetic acid,



$$\begin{array}{l}\mathrm{CHMe{\cdot}CMeBr{\cdot}CH{\cdot}CH_2{\cdot}CO_2H}\\ \mathrm{O\text{————————}CO}\end{array},$$

was prepared from the aticonic acid by Stobbe's method (*Annalen*, 1894, **282**, 314), 33% of the pure acid being obtained as bold prismatic needles from water, m. p. 160—161° (Found: Br, 31·9.

Calc.; Br, 31·8%). Reduction of this with either zinc and acetic acid or sodium amalgam yielded mixed products, and was not proceeded with.

(ii) With hot mineral acids. Uniform results were obtained with 50% sulphuric acid, constant-boiling hydrobromic acid, and concentrated hydrochloric acid, and two typical experiments are described below.

(*a*) The aticonic acid (2 g.) was heated on the water-bath for 3 hours with 48% hydrobromic acid (50 c.c.), and the product neutralised with sodium carbonate and re-acidified. Extraction with ether yielded 1·9 g. of a crystalline solid, which was recrystallised from water. The first crop on further crystallisation from a mixture of ether and light petroleum yielded hard prismatic needles of the *iso*paraconic acid, m. p. 128°. The fraction more soluble in water was allowed to crystallise slowly from ether and light petroleum, and yielded two well-defined types of crystal: prismatic needles, similar to the above, and soft shining overlapping plates. There was no tendency for mixed crystal formation, but several aggregates were found in which the prisms had been " cemented " together by the plates. These crystals were separated by hand-picking and recrystallisation from the above mixed solvents. The plates (the paraconic acid) were then obtained in a state of purity; m. p. 146°. The product remaining in solution after this series of crystallisations was a mixture of these two acids having m. p. 112—124° and the correct equivalent.

(*b*) The itaconic acid (2 g.) was heated on the water-bath with 50% sulphuric acid (50 c.c.) until completely dissolved (some 5 hours). The product (1·9 g.) was worked up as above, and on crystallisation from water yielded the crude 146°-acid, which was purified as before and identified (mixed m. p.) with that already prepared. The portion more soluble in water was separated as above, prismatic needles being obtained, m. p. 128° alone or when admixed with the sample already prepared.

$\gamma$-Methyl-$\gamma$-ethyl*iso*paraconic acid (X) (probably identical with Stobbe's acid, m. p. 125—126°) crystallises from concentrated hydrochloric acid in hard prismatic needles, m. p. 128°, the m. p. being unchanged on cooling and redetermination, but being depressed to 115° by admixture with the 146°-acid (Found: C, 55·5; H, 7·1; *M*, monobasic, 172. Calc.: C, 55·8; H, 7·0%; *M*, 172). After the initial titration a further equal amount of baryta was neutralised when the solution was heated with excess of the reagent, corresponding to the opening of the lactone ring.

$\gamma$-*Methyl*-$\gamma$-*ethylparaconic acid* (IV) forms soft plates from water, m. p. 146°, unchanged on solidification and redetermination (Found :

C, 55·8; H, 7·0; *M*, monobasic, 171. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%; *M*, 172). A further equal amount of baryta was neutralised when the neutral solution was heated with excess of the reagent.

*Synthesis of the Paraconic Acid from Ethyl Acetosuccinate.*—Grignard (*loc. cit.*) has shown that ethyl acetosuccinate reacts mainly in the enolic phase with magnesium methyl iodide, leading to decomposition of the latter without condensation. The same difficulty was met with in the present case, the best yield of condensation product being obtained by slowly adding 144 g. ($\frac{2}{3}$ g.-mol.) of the ester in 3 vols. of ether to 1 g.-mol. of well-cooled magnesium ethyl iodide. After 3 hours' further standing in a freezing mixture, the product was isolated in the usual manner and separated by fractionation into unchanged ethyl acetosuccinate (90 g.; b. p. 150°/15 mm.) and a high fraction (33 g.; b. p. 150—170°/15 mm.) mainly composed of ethyl γ-hydroxy-β-carbethoxy-γ-methyl-*n*-hexoate (VII). Magnesium ethyl bromide gave a lower yield of this high fraction.

50 G. of the crude high-boiling fraction, 850 g. of 10% aqueous caustic potash (50% alkali caused extensive hydrolysis to succinic acid), and sufficient alcohol to effect solution were left at room temperature over-night. The acid fraction of the product, isolated by extraction in the usual manner, was left in an evacuated desiccator for several days. The separated solid was freed from adhering liquid (mainly lævulic acid) by suction, washed on porous earthenware with light petroleum, and crystallised from water. γ-Methyl-γ-ethylparaconic acid then separated in the pure condition in soft plates, m. p. 146—147°, alone or when admixed with the acid prepared from methylethylitaconic acid (Found: C, 55·6; H, 6·9%).

Preparation of this paraconic acid from *sec.*-butylsuccinic acid (V)—method (*a*)—had to be abandoned, as no appreciable quantity of the intermediate ester (VIII) could be prepared by any of the methods successfully used for the *iso*propyl homologue.

*Preparation of Methylethylacetaldehyde* (XIII).—*sec.*-Butyl alcohol was slowly distilled with 3 equivs. of 48% hydrobromic acid, distillation being stopped when the temperature rose above 80°. The bromide layer was washed with concentrated hydrochloric acid (which recovered some 5—10% of unchanged alcohol), dried with calcium chloride, and redistilled; yield, 76% of b. p. 90—93°. This bromide was converted into the aldehyde by the following method, all other conditions giving poor yields.

Magnesium *sec.*-butyl bromide, from 16 g. of metal and 88 g. of the bromide in 400 c.c. of ether, was decanted from a little unchanged metal into a dry flask, and ethyl orthoformate (55 g.—rather more than ½ equiv.) was slowly added. No reaction was apparent at first, but towards the end of the addition a white crystalline solid separated. The mixture was heated under reflux for an hour, the solvent removed, and the residue heated on the steam-bath for an hour with constant shaking, much heat being developed as the last traces of ether came off. The resulting hard solid mass was cooled, and decomposed with water and a scant excess of dilute acid. The oily layer (of the acetal) was separated, and more was liberated from the water by salting out but not by extraction. The combined acetal layer was heated on the water-bath under reflux for 15 minutes with 3 vols. of 20% sulphuric acid, the air in the flask being displaced by carbon dioxide. The aldehyde layer was separated by salting out, and at once converted into its bisulphite compound, which was filtered off, washed well with ether, and dried on porous earthenware. A further small quantity of aldehyde could be isolated as bisulphite compound by similar treatment of the ethereal extracts of the aqueous layer after the hydrolysis of the acetal; yield, 30 g. of dry bisulphite compound (25% on the bromide).

Methylethylacetaldehyde was liberated from the bisulphite compound with sodium carbonate, dried over calcium chloride, and distilled, the entire product boiling at 92—93° (Fourneau and Ribas, *Bull. Soc. chim.*, 1927, **41**, 1054, give 90° for the *r*-aldehyde; Ehrlich, *Ber.*, 1907, **40**, 2556, gives 90—92° for the *d*-aldehyde). All work with this substance was carried out in an atmosphere of carbon dioxide. The *semicarbazone* crystallised from aqueous alcohol in very small needles, m. p. 103° (Found: N, 29·2. $C_6H_{13}ON_3$ requires N, 29·4%).

The aldehyde was also prepared, but in very poor yield, by the Darzens–Claisen method.

$\gamma$-Methyl-$\gamma$-ethylglycidic ester (XII) was prepared in 32% yield by Claisen's method (*Ber.*, 1905, **38**, 707), but better by the following process: Dry sodium ethoxide (2 g.-mols.), cooled in a freezing mixture, was treated slowly and with constant shaking with a mixture of methyl ethyl ketone (130 g.) and ethyl chloroacetate (220 g.). The product was kept over-night, heated for 5 hours at 100°, and decomposed in the cold with very dilute sulphuric acid. The glycidic ester, extracted by means of ether, was dried and redistilled, 160 g. (56%) being obtained, b. p. 91—95°/17 mm. It was hydrolysed by being poured into the calculated amount of saturated sodium ethoxide, and an equivalent amount of water added. On cooling the hot solution in a freezing mixture, an almost quantitative yield of the sodium salt of the glycidic acid was obtained. This was washed with alcohol and ether and used without further purification. Some 15% of crude aldehyde (b. p. 88—98°) was obtained by isolating the acid from this salt and distilling it very slowly in the vacuum of an oil pump, the distillate being collected in a receiver cooled in a freezing mixture and in traps immersed in liquid air, but other methods gave only traps of aldehyde and much high-boiling product.

*γ-Methylhexenoic Acids.*—(1) βγ-*Acid from the paraconic acid.* γ-Methyl-γ-ethylparaconic acid (23 g.) was heated as rapidly as possible in the apparatus described by Goldberg and Linstead (*loc. cit.*). At 260° (thermometer in the liquid), distillation occurred without charring. The colourless liquid so obtained was distilled in a current of steam, which left a residue of 4 g. of the crude paraconic acid. The steam-distillate was treated with sodium bicarbonate (25 g.) and saturated with salt, and the lactonic material was extracted with ether (3·9 g.; product A). The bicarbonate solution after acidification and extraction yielded 6·7 g. of βγ-acid. Slower heating appeared to favour production of the lactone.

*γ-Methyl-$\Delta^{\beta}$-hexenoic acid,* so prepared, is a colourless liquid with the unpleasant smell characteristic of such substances. It has b. p. 118°/12 mm., $d_{4^\circ}^{16\cdot7^\circ}$ 0·9644, $n_{\mathrm{D}}^{16\cdot7^\circ}$ 1·4512, $[R_L]_{\mathrm{D}}$ 35·78 (Calc., 35·60) (Found: for a sample prepared as described on p. 2072, C, 65·4; H, 9·4; *M*, 128. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%; *M*, 128). Auwers and Heyna (*loc. cit.*) give for the reduction product of γ-methylsorbic acid, $d_{4^\circ}^{20^\circ}$ 0·966, $n_{\mathrm{D}}^{20^\circ}$ 1·4503, $[R_L]_{\mathrm{D}}$ 35·67. (They describe this substance as a liquid, and presumably "Schmelzp. 111°" is a misprint.) The acid readily changes on exposure to air, and a specimen kept in a corked flask for 6 weeks yielded 25% of high-boiling material on redistillation. This change was accompanied by a large decrease in iodine addition, a rise in the equivalent, and a fall in the carbon and hydrogen percentages, indicating some form of oxidation. This makes it essential that experiments with this acid should be performed on freshly prepared material.

The lactonic product (A, above) distilled entirely at 103—104°/10 mm., and was undoubtedly identical with Grignard's γ-methyl-γ-ethylbutyrolactone (*loc. cit.*, p. 559). It had $d_{4^\circ}^{16\cdot5^\circ}$ 0·9983, $n_{\mathrm{D}}^{16\cdot5^\circ}$ 1·4460, $[R_L]_{\mathrm{D}}$ 34·22, and did not solidify in a freezing mixture (Found: C, 65·4; H, 9·7; equiv., by warming with excess of baryta and back titration, 129. Calc.: C, 65·6; H, 9·4%; equiv., 128).

(2) αβ-*Acid from methylethylacetaldehyde.* 63 G. of malonic acid were dissolved in dry pyridine (83 g.) and 35 g. of the aldehyde added, the air in the flask being displaced by carbon dioxide. The mixture was kept for 4 days at room temperature, and then warmed

for some hours on the water-bath. The acid (41 g., 80%) was isolated from the product in the usual manner, and a little aldehyde was recovered as bisulphite compound from the low-boiling fraction.

*γ-Methyl-$\Delta^{\alpha}$-hexenoic acid* is a colourless liquid which does not solidify at – 15°. It has b. p. 125°/13 mm., $d_{4^\circ}^{20\cdot3^\circ}$ 0·9441, $n_D^{20\cdot3^\circ}$ 1·4526, $[R_L]_D$ 36·65 (Calc., 35·60) (Found : C, 65·6; H, 9·6; *M*, by titration, 127. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%; *M*, 128).

The acid chloride, b. p. 65—66°/11 mm., prepared by using thionyl chloride, readily yielded the *anilide*, prismatic needles from benzene and light petroleum, m. p. 110° (Found : C, 76·7; H, 8·5. $C_{13}H_{17}ON$ requires C, 76·8; H, 8·4%). The p-*toluidide*, prepared similarly, crystallised from aqueous alcohol in long needles, m. p. 92° (Found : C, 77·2; H, 8·8. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·8%).

*Equilibration of the Acids.*—The pure acids and mixtures in known proportion had the following iodine additions in 10 minutes (Linstead and May, J., 1927, 2565) :

| αβ-Acid, % ........ | 100 | 80 | 60 | 40 | 20 | 0 (βγ-acid) |
|---|---|---|---|---|---|---|
| Iodine addition ... | 0·5 | 20·5 | 39·6 | 59·4 | 79·0 | 95·8 |

The acids were equilibrated in the usual way, except that a temperature of 104° was used in error and the mobility is therefore slightly high. The unsaturated acid was freed from hydroxy-acid and lactone by the standard technique, and its composition found iodometrically, the absence of extraneous impurity being checked in several cases by determination of the equivalent.

| Starting material ........... | αβ- | αβ- | αβ- | αβ- | αβ- | αβ- | βγ- |
|---|---|---|---|---|---|---|---|
| Time (hrs.) ..................... | 2 | 4 | 6 | 10 | 16 | 20 | 16 |
| Iodine addition of product | 34·5 | 52·3 | 65·1 | 73·0 | 74·7 | 75·2 | 77·3 |
| βγ-Acid, % ..................... | 34·5 | 52·9 | 66·0 | 73·9 | 75·7 | 76·2 | 78·3 |

From the intermediate values from the αβ-side the mobility given on p. 2066 was calculated.

*βγ-Acid from equilibrium mixture.* The αβ-acid (24 g.) was equilibrated for 20 hrs. and yielded 18·3 g. of equilibrium mixture (properties on p. 2066), together with 1·6 g. of non-steam-volatile and 1·4 g. of neutral material. 17·5 G. of the equilibrium mixture (which could not be separated into its constituents by fractionation) were added to *N*-alcoholic hydrochloric acid (41 c.c.) and absolute alcohol (123 c.c.). After 4 hours the product was separated by the usual method (Eccott and Linstead, *loc. cit.*) into 14 g. of ester, b. p. 78°/11 mm., and 4·5 g. of acid boiling mainly at 124—126°/14 mm., with an iodine addition of only 25%. On careful hydrolysis with cold 10% aqueous-alcoholic potash, the ester yielded the almost pure βγ-acid (9·0 g.) with $d_{4^\circ}^{17\cdot4^\circ}$ 0·9633, $n_D^{17\cdot4^\circ}$ 1·4510, and the other properties given on p. 2066. This showed the same tendency towards the spontaneous formation of high-boiling products as the material already described.

*Derivatives of the* $\beta\gamma$-*acid.* $\gamma$-Methyl-$\Delta^{\beta}$-hexenoic acid (from the paraconic acid) was dissolved in an equal amount of benzene and warmed on the water-bath for 15 minutes with 1 equiv. of phosphorus trichloride (compare Eccott and Linstead, this vol., p. 909). The product, which contained no unchanged acid, boiled over the range 60—80°/15 mm. On refractionation, above 50% was obtained of b. p. 64—68°/16 mm., which yielded an anilide crystallising in long needles. These melted rather indefinitely at 77—78° and contained a trace of chlorine. Repeated recrystallisation from aqueous alcohol and from mixtures of benzene, ether, or acetone with light petroleum did not alter the m. p. (Found: C, 76·5; H, 8·7%).

Treated similarly, the $\beta\gamma$-acid obtained from the equilibrated $\alpha\beta$-acid yielded an acid chloride of b. p. 65—68°/15 mm., and an anilide melting indefinitely at 83° and containing traces of chlorine, which again could not be removed by simple crystallisation. This did not depress the m. p. of the anilide already prepared. One sample which had been kept for some time first in an evacuated desiccator and later in the air ultimately yielded a chlorine-free product. From this, after repeated recrystallisation from aqueous alcohol, the pure *anilide* was obtained as bold needles, m. p. 91°, unchanged by further crystallisation (Found: C, 76·9; H, 8·6. $C_{13}H_{17}ON$ requires C, 76·8; H, 8·4%). A mixture of this with the $\alpha\beta$-anilide (m. p. 110°) melted at about 83°, and one with the impure $\beta\gamma$-anilide (m. p. 77—78°) at 78°.

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