360. *α-Methylhexenoic and αβ-Dimethylpentenoic Acids.*

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IN view of the contradictory evidence regarding the effect of an α-methyl group on the interconversion of unsaturated acids, it was decided to investigate the interconversion of the α-methylhexenoic acids (I) and (II) and the αβ-dimethylpentenoic acids (III) and (IV).

(I.) $CH_2Et{\cdot}CH{:}CMe{\cdot}CO_2H$ $CHEt{:}CH{\cdot}CHMe{\cdot}CO_2H$ (II.)

(III.) $CH_2Me{\cdot}CMe{:}CMe{\cdot}CO_2H$ $CHMe{:}CMe{\cdot}CHMe{\cdot}CO_2H$ (IV.)

Both pairs of acids yielded equilibrium mixtures on treatment with alkali, and the following results were obtained under Linstead's standard conditions (J., 1927, 2579):

System.	Equilibrium (% αβ-acid).	Mobility.
I $\rightleftharpoons$ II	88—90	18·8
III $\rightleftharpoons$ IV	72—73	0·12

The figures for the first pair of acids are in good agreement with those previously given for the α-methylpentenoic acids (Goldberg and Linstead, J., 1928, 2343). The values for the second pair of acids similarly agree with those for the related acids studied by Kon, Leton, Linstead, and Parsons (J., 1931, 1411), especially as regards mobility. The results clearly bring out the difference in the effect of the α-substituent, which greatly depresses the mobility of the system if there is already a substituent in the β-position, but has very little effect on the mobility of the straight-chain acids (pentenoic and hexenoic) (compare Linstead and Mann, J., 1931, 733; Kon, Leton, Linstead, and Parsons, *loc. cit.*). The effects on the positions of equilibrium are in each case those to be expected.

The βγ-acid (II) prepared as described on p. 2458 evidently contained an isomeric impurity, because the equilibrium mixture obtained from it differed from that produced from the αβ-acid. It was therefore prepared by methylating ethyl butylidenemalonate to the ester $CHEt{:}CH{\cdot}CMe(CO_2Et)_2$ and removing one carboxyl group from the corresponding acid by heating. The resulting acid consisted largely of the desired acid (II) with only a small amount of the isomeride (I), which was easily removed by subsequent treatment. The acid so obtained gave values for the equilibrium coincident with those obtained from the αβ-acid and was therefore pure.

EXPERIMENTAL.

Methods.—The determination of mobilities and positions of equilibrium was carried out by the methods previously used (compare Goldberg and Linstead, *loc. cit.*).

a-Methylhexenoic Acids.—The *αβ*-acid employed was the specimen described in our following paper. The *βγ*-acid was prepared by the hydrolysis of the purest *βγ*-ester described at the same time; it had b. p. 107°/11 mm., $d_{4^\circ}^{20^\circ}$ 0·9396, $n_{\mathrm{D}}^{20^\circ}$ 1·4390, $[R_L]_{\mathrm{D}}$ 35·86 (calc., 35·71), M(monobasic) 127·7 (calc., 128·1), and J 72·5 in 10 mins. It could not be further purified by repeating the partial esterification and hydrolysis. This specimen was used for the mobility determinations marked*. The pure *βγ*-acid was prepared as follows: ethyl butylidenemalonate (70 g.) was treated with NaOEt in EtOH, and the mixture boiled with an excess of MeI until neutral; the methylated ester (60 g.) had b. p. 130—140°/18 mm., $d_{4^\circ}^{20^\circ}$ 0·9862, $n_{\mathrm{D}}^{20^\circ}$ 1·4378, $[R_L]_{\mathrm{D}}$ 60·66. It was hydrolysed by cold KOH to *a-carboxy-a-methyl-*Δ^β*-hexenoic acid*, m. p. 130° (decomp.) after crystn. from hexane (Found: C, 56·1; H, 6·9; M, dibasic, 173·6. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%; M, 172·1).

The dibasic acid (25 g.) was heated at 125—130° for 2 hrs.; the cold residue was dissolved in $NaHCO_3$ aq., some 6 g. of neutral material removed by extraction with Et_2O, and the acid recovered and distilled, 11 g., b. p. 116—120°/18 mm., being obtained, in addition to 1 g. still containing some dibasic acid. From the main fraction, 9 g., b. p. 86—87°/1—2 mm., were obtained on redistillation. This was subjected to partial esterification, and the pure ester (see following paper) hydrolysed with cold 5% aq.-alc. KOH to the acid, b. p. 122°/24 mm., $d_{4^\circ}^{20^\circ}$ 0·9353, $n_{\mathrm{D}}^{20^\circ}$ 1·4379, $[R_L]_{\mathrm{D}}$ 35·93 (calc., 35·71). This was used for the reference curve and the determination of the final equilibrium.

Equilibrations. Reference curve.

Mixture, % *αβ* ……	0	10	25	50	75	90	100
J, % ………………	83·5	77·6	66·4	45·4	23·3	8·8	0

Acid.	Time, hrs.	J, %.	% *αβ*-Acid.	Acid.	Time, hrs.	J, %.	% *αβ*-Acid.
*βγ**	3	40·1	55·7	*αβ*	3	5·1	93·5
*βγ**	6	28·7	69·0	*αβ*	6	6·0	92·5
*βγ**	96	23·0	75·0	*αβ*	96 at b. p.	8·4	90·0
βγ	24	9·8	88·5	*αβ*	160 at b. p. with 40% KOH aq.	8·8	90·0

The equivs. of the equilibrated samples were checked in every case but are not recorded.

αβ-Dimethylpentenoic Acids.—The *αβ*-acid employed was the specimen described in our following paper. The *βγ*-acid was obtained by the hydrolysis of the pure *βγ*-ester described there and had b. p. 104°/11 mm., $d_{4^\circ}^{20^\circ}$ 0·9618, $n_{\mathrm{D}}^{20^\circ}$ 1·4461, $[R_L]_{\mathrm{D}}$ 35·53 (calc., 35·71), M(monobasic) 128·1 (calc., 128·1).

Equilibrations. Reference curve.

Mixture, % *αβ* ……	0	10	25	50	75	90	100
J, % ………………	77·0	72·4	63·2	44·7	24·7	11·1	2·9

Mixtures rich in *βγ*-acid gave an appreciable back reaction, but since equilibrium is on the side of the $\alpha\beta$-acid it was not deemed necessary to use any special precautions on this account.

Acid	Time, hrs.	*J*, %.	% $\alpha\beta$-Acid.
$\beta\gamma$	17 with 25% KOH aq.	70·4	13·0
$\beta\gamma$	41 ,, ,, ,,	68·1	17·0
$\beta\gamma$	119 with 40% KOH aq. at b. p.	50·7	41·5
$\alpha\beta$	130 ,, ,, ,, ,,	12·4	89·0
84% $\alpha\beta$	140 ,, ,, ,, ,,	22·2	77·0
75% $\alpha\beta$	168 ,, ,, ,, ,,	26·0	72·5
78% $\alpha\beta$	119 ,, ,, ,, ,,	26·0	72·5

The equivs. of the equilibrated samples were checked in every case but are not recorded.

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