CXC.—*The Chemistry of the Three-carbon System. Part XXVI. Some Substituted Acrylic Acids.*

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Certain regularities in the influence of alkyl substituents on the mobility and position of equilibrium of tautomeric unsaturated acid systems have recently been observed and correlated (Goldberg and Linstead, J., 1928, 2343; Linstead, J., 1929, 2498) and have been further exemplified by subsequent work (Linstead and Mann, J., 1930, 2064; Kon and Thakur, *ibid.*, p. 2217). The influence of α-alkyl groups on the mobility has, however, presented some difficulty. Goldberg and Linstead showed that the α-methyl-*n*-pentenoic acids and the *n*-pentenoic acids themselves underwent conversion with approximately the same ease, whereas Kon and Thakur observed a large diminution of mobility in *cyclo*pentylidene- and *cyclo*hexylidene-acetic acids on the introduction of an α-methyl group. Similar observations were made with substituted itaconic acids by Linstead and Mann (this vol., p. 733), as a result of which it was suggested that an α-alkyl group only depressed the mobility when introduced into a molecule already substituted on adjacent carbon atoms.

Well-defined examples of the considerable retarding effect of the α-alkyl group on the mobility of heavily substituted acrylic acids are provided in the present work, which deals with the following systems :

(I.) $CH_2Me\cdot CEt{:}CH\cdot CO_2H$ $CHMe{:}CEt\cdot CH_2\cdot CO_2H$ (II.)
(III.) $CH_2Me\cdot CEt{:}CMe\cdot CO_2H$ $CHMe{:}CEt\cdot CHMe\cdot CO_2H$ (IV.)
(V.) $CH_2Et\cdot CMe{:}CH\cdot CO_2H$ $CHEt{:}CMe\cdot CH_2\cdot CO_2H$ (VI.)
(VII.) $CH_2Et\cdot CMe{:}CEt\cdot CO_2H$ $CHEt{:}CMe\cdot CHEt\cdot CO_2H$ (VIII.)

The equilibria and mobilities of these were determined by the standard methods (Linstead, J., 1927, 2579); but for the more inert acids it was often convenient to obtain the final equilibrium in boiling alkali, a suitable mixture of isomeric acids being used as initial material. The results are summarised below :

System.	Equilibrium, % $\alpha\beta$-.	Mobility (t in hours).
I $\rightleftharpoons$ II	21	0·64
III $\rightleftharpoons$ IV	50	0·0058
V $\rightleftharpoons$ VI	33	0·39
VII $\rightleftharpoons$ VIII	57	0·0030

The large retardation of mobility by the α-group revealed by these figures has already been commented upon. In practice, the effect is so considerable that, for example, the acids (VII) and (VIII) are almost unchanged by 24 hours' treatment with a large excess of aqueous potash at 100°. In other respects the new figures agree with the general rules, the stabilisation of the αβ-phase by the α-substituent and of the βγ-phase by the β-substituent (in comparison with the corresponding acids with only one β-substituent) being clearly shown. As usual, the lengthening of the chain beyond the δ-carbon has but little effect on the position of equilibrium.

It was essential for the purpose of the present quantitative work that the acids studied should be quite free from isomeric impurity and this was made possible by the use of the partial esterification method, controlled by iodometric analysis (Eccott and Linstead, J., 1929, 2153). In this way, for example, ββ-diethylacrylic acid and its βγ-isomeride (I and II) were obtained in a state of purity which had not been possible in the previous work (Kon and Linstead, J., 1925, **127**, 616). The earlier determination of the equilibrium between these acids was carried out with a βγ-acid obviously containing some of the αβ-isomeride and this accounts for the difference between the old figure (5% αβ-; Linstead, J., 1927, 355) and that now given.

β-Methyl-β-*n*-propylacrylic acid (V) has been described by Gardner and Haworth (J., 1909, **95**, 1963) as a liquid which, from the method of preparation employed, may have contained some of the isomeric acid (VI). We find that this acid, quite free from its βγ-isomeride, slowly deposits a *solid form* of m. p. 40° when cooled to −20°. The liquid filtrate from this has the chemical and physical properties required for the pure αβ-acid and undoubtedly contains a *second form* of the acid probably contaminated with some of the solid acid in solution. We have been unable to effect the conversion of the liquid into the solid acid by the action of mineral acid, alkali or acetic anhydride. The acid chloride prepared from the liquid acid is a mixture which yields no homogeneous solid derivatives but gives a small amount of the solid acid on treatment with formic acid. This acid evidently provides another example of the occurrence of two geometrical isomerides of a monobasic acid with an αβ-double bond, the existence of which in unsymmetrical ββ-dialkylacrylic acids has been previously suspected (Kandiah and Linstead, J., 1929, 2151; Kon and Thakur, *loc. cit.*, p. 2223). It is more usual for stereoisomeric acids of this type to give homogeneous acid chlorides derived from the stable form (compare Newbery, J., 1925, **127**, 295) and the behaviour of methylpropylacrylic acid is therefore abnormal in this respect.

EXPERIMENTAL.

General Methods.—These methods were used throughout except where special mention is made.

Preparation. The appropriate ketones and α-bromo-esters were condensed with zinc in benzene by the Reformatsky reaction. To obtain the αβ-acids, the resulting β-hydroxy-esters were hydrolysed by alkali to the acids and dehydrated with boiling acetic anhydride (Kon and Linstead, *loc. cit.*). The crude acids were purified by partial esterification, the quantities of reagents recommended by Kon and Thakur (*loc. cit.*) being used. The βγ-acids were prepared by dehydrating the β-hydroxy-esters by the method of Darzens (*Compt. rend.*, 1911, **152**, 1601) and hydrolysing the crude βγ-esters so obtained with cold 5% alcoholic alkali. The crude acids were then purified by partial esterification.

Iodine additions. These values (J) were determined by Linstead and May's methods (J., 1927, 2565), reaction periods of 10 minutes being used for the acids in sodium bicarbonate solution and of 1 hour for the esters in chloroform solution. Mixtures of acids were analysed with the aid of reference curves in the usual manner.

β-*Ethylpentenoic Acids.*—Crude ββ-diethylacrylic acid (I) with J 8·3% was submitted to partial esterification for 6 hours. The unesterified acid (50% yield) then had J 1·2% and was taken to be the pure αβ-acid. It had b. p. 122°/17 mm., $d_{4^\circ}^{18\cdot0^\circ}$ 0·97159, $n_{\mathrm{D}}^{18\cdot0^\circ}$ 1·46867, $[R_L]_{\mathrm{D}}$ 36·69 (calc., 35·71). The crude βγ-ester (90% yield by the Darzens method) had J 49·4% and on hydrolysis gave a good yield of an acid with J 48·8%. The crude acid was subjected to partial esterification for 6 hours, giving a 30% yield of the βγ-ester, b. p. 78—80°/17 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·90241, $n_{\mathrm{D}}^{20\cdot0^\circ}$ 1·43237, $[R_L]_{\mathrm{D}}$ 44·84 (calc., 44·95); J 78·7%. The βγ-acid (II) obtained from it had b. p. 122°/17·5 mm., $d_{4^\circ}^{21\cdot2^\circ}$ 0·96398, $n_{\mathrm{D}}^{21\cdot2^\circ}$ 1·44803, $[R_L]_{\mathrm{D}}$ 35·49 (calc., 35·71), J 64·8%. The purity of the acid and of the ester from which it was derived was shown by the fact that the acid, when subjected to a second partial esterification for 4 hours, yielded an ester with *J* 78·3% and properties identical with those given above.

Equilibrations. Reference curve :

Mixture (% αβ)......	100	90	85	75	50	25	15	10	0
J (%)	1·2	11·3	14·6	21·8	38·3	52·1	56·8	59·6	64·8

The equilibrations were carried out under standard conditions, but the final equilibrium value was checked by an experiment on the αβ-acid at the b. p. The physical properties of the equilibrated acids were determined as a check but are not recorded. The mean figures for the mobility and points of equilibrium have already been given (p. 1412).

Acid.	Time (hours).	*J* %.	αβ-Acid %.	Acid.	Time (hours).	*J* %.	αβ-Acid %.
αβ	2	9·1	93·0	αβ	24	43·3	41·0
,,	4	18·4	80·0	,,	48	50·9	26·5
,,	6	22·5	74·0	,,	96 at b.p.	53·8	21·0
,,	10	31·0	61·5	βγ	72	54·5	19·0
				,,	90	53·8	21·0

β-*Methylhexenoic Acids.*—*Ethyl* β-*hydroxy*-β-*methylhexoate* was obtained in 50—55% yield from ethyl bromoacetate and methyl *n*-propyl ketone; b. p. 98°/13 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·9479, $n_{D}^{20\cdot0^\circ}$ 1·43087 (Found : C, 62·3; H, 10·4. $C_9H_{18}O_3$ requires C, 62·1; H, 10·3%). The acid was an uncrystallisable liquid (Found : Ag in *silver* salt, 42·9. $C_7H_{13}O_3Ag$ requires Ag, 42·6%).

β-*Methyl*-Δ^{α}-*hexenoic acid* (β-methyl-β-propylacrylic acid) (V) was obtained in 45% yield. The crude acid, b. p. 112—116°/9 mm., *J* 6·2%, was subjected to partial esterification for 7 hours. The recovered acid had b. p. 120°/14 mm., $d_{4^\circ}^{19\cdot2^\circ}$ 0·96836, $n_{D}^{19\cdot2^\circ}$ 1·46659, $[R_L]_D$ 36·68 (calc., 35·71), *J* 1·4%. Another sample after two partial esterifications had b. p. 117—118°/10 mm., *J* 1·7%. On being kept for some time in a freezing mixture, it deposited hard prismatic crystals, m. p. 40°, unchanged by crystallisation from benzene (Found : C, 65·9; H, 9·6. $C_7H_{12}O_2$ requires C, 65·6; H, 9·5%); the mother-liquor on further cooling deposited other crops of crystals, but these melted just below room temperature, although they could be kept on a porous tile cooled below 10°; we regard these as a mixture of the two forms of the αβ-acid. The liquid acid could not be converted into the solid form by boiling for 1 hour with concentrated hydrochloric acid or for 3 hours with acetic anhydride; cold aqueous sodium hydroxide was also without effect. A solid dibromide could not be obtained.

A specimen of the liquid αβ-acid (5 g.) was dissolved in chloroform and treated with ozonised oxygen for 24 hours, the solvent being then removed under reduced pressure. The residue was treated with water and gently distilled in steam; methyl propyl ketone passed over and was identified in the form of its semicarbazone (m. p. and mixed m. p. 109°), and oxalic acid was identified in the residue.

β-*Methyl*-Δ^{β}-*hexenoic Acid* (VI).—The crude ester (85% yield) yielded an acid, b. p. 114—122°/12 mm., *J* 36%. This was subjected to partial esterification for 13 hours, giving the pure βγ-ester, b. p. 84—85°/26 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·89609, $n_{D}^{20\cdot0^\circ}$ 1·43087, $[R_L]_D$ 45·00 (calc., 44·95), *J* 80·2%. The *acid* obtained from it had b. p. 113°/10 mm., $d_{4^\circ}^{20\cdot7^\circ}$ 0·95487, $n_{D}^{20\cdot7^\circ}$ 1·44692, $[R_L]_D$ 35·72 (calc., 35·71), *J* 56·0% (Found: C, 65·6; H, 9·3; *M*, by titration, 127·8. $C_7H_{12}O_2$ requires C, 65·6; H, 9·5%; *M*, 128·1). A second specimen of the crude βγ-acid was partially esterified for only 7 hours, but the ester had properties identical with the above (*J* 80·0%). In another preparation, the hydroxy-ester was dehydrated with phosphorus oxychloride in benzene, yielding 65% of crude βγ-ester. This gave an acid of *J* 31·6% which after partial esterification and hydrolysis gave the pure acid, *J* 55·2%.

The pure βγ-acid (4 g.) was dissolved in 200 c.c. of saturated sodium hydrogen carbonate solution and 650 c.c. of 3% potassium permanganate were added in small quantities, the mixture being cooled in ice. After 3 days, the excess of permanganate was destroyed with sodium hydrogen sulphite, and the liquid filtered and evaporated to dryness. The organic acids were liberated from the residue with hydrochloric acid and taken up in ether, and the ether removed. The residue slowly deposited crystals of oxalic acid; the liquid portion consisted of acetic and propionic acids, which were converted into their *p*-toluidides (m. p. 148° and 123° respectively) for identification.

Equilibrations. Reference curve:

Mixture (% αβ)............	100	90	75	70	50	30	25	10	0
J (%)	1·4	10·4	18·6	21·0	32·0	42·0	44·7	51·5	56·0

Equilibrations under standard conditions gave the following values: the physical properties of the equilibration products were determined but are not recorded; their equivalents were in every case checked by titration with standard barium hydroxide.

Acid.	Time (hours).	*J* %.	αβ-Acid %.	Acid.	Time (hours).	*J* %.	αβ-Acid %.
αβ	6	13·6	84·0	βγ	6	51·3	10·0
,,	24	26·5	60·5	,,	24	45·4	23·0
,,	48	34·0	46·0	,,	48	39·5	35·0
,,	72	37·5	39·5	,,	75	40·8	33·0
,,	96	39·5	35·5	,,	120	40·7	33·0
,,	115	40·8	33·0	50% mixture	50	36·4	41·0
					70	40·0	34·0

α-Methyl-β-ethylpentenoic Acids.—Ethyl β-hydroxy-α-methyl-β-ethylvalerate, from diethyl ketone and ethyl α-bromopropionate (70—80% yield), had b. p. 105—108°/17 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·96220, $n_D^{20\cdot0^\circ}$ 1·43597 (Found: C, 64·0; H, 10·5. $C_{10}H_{20}O_3$ requires C, 63·7; H, 10·7%). The acid obtained from it on hydrolysis was a colourless liquid smelling strongly of propionic acid.

α-Methyl-β-ethyl-Δ^α-pentenoic acid (III). The crude acid (50% yield) had b. p. 119—121°/14 mm. and *J* 16·9%. It was freed from the βγ-isomeride by partial esterification (see p. 1413), but owing to the low esterification constant of the α-substituted acids a much longer time had to be allowed for this; after several preliminary experiments it was found that 48 hours were sufficient. The pure αβ-*acid* (*α-methyl-ββ-diethylacrylic acid*) had b. p. 122°/12 mm., $d_{4^\circ}^{20\cdot5^\circ}$ 0·96018, $n_D^{20\cdot5^\circ}$ 1·47183, $[R_L]_D$ 41·06 (calc., 40·33), *J* 1·6% (Found: C, 67·7; H, 9·6; Ag in *silver* salt, 43·5. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%. $C_8H_{13}O_2Ag$ requires Ag, 43·4%). The pure αβ-acid was oxidised with potassium permanganate as described on p. 1415, except that the reaction mixture was distilled in steam after removal of the manganese dioxide; diethyl ketone was readily isolated from the distillate by means of ether and identified by its semicarbazone (m. p. 135—136°; mixed m. p. 137°).

α-Methyl-β-ethyl-Δ^β-pentenoic acid (IV). The crude ester was obtained by the dehydration of the hydroxy-ester by means of phosphorus oxychloride or, better, by the Darzens method (*loc. cit.*), the latter giving a 90% yield. The ester, b. p. 84—90°/19—20 mm., was hydrolysed, and the acid (*J* 59·4%) subjected to partial esterification for 4½ hours, giving the pure βγ-ester (20% yield; a much longer period can safely be allowed), b. p. 76—78°/13 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·89862, $n_D^{20\cdot0^\circ}$ 1·43417, $[R_L]_D$ 49·32 (calc., 49·57), *J* 65·8%. This on hydrolysis gave the βγ-*acid*, b. p. 116—117°/14 mm., $d_{4^\circ}^{20\cdot3^\circ}$ 0·95548, $n_D^{20\cdot3^\circ}$ 1·45003, $[R_L]_D$ 40·08 (calc., 40·33), *J* 78·3% (Found: C, 67·8; H, 9·8; *M*, by titration, 142·2. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%; *M*, 142·1). As a check on the purity of the acid, a portion of it was again partially esterified for 4 hours; the ester obtained had properties similar to the above, *J* 66·4%.

Neither this acid nor its αβ-isomeride could be characterised by the formation of solid derivatives, as none of these had any tendency to crystallise.

Equilibrations. Reference curve:

Mixture (% αβ)	100	90	75	62·5	50	25	10	0
J (%)	1·6	11·9	26·5	37·4	47·8	64·3	72·3	78·3

Equilibration was extremely slow under standard conditions and for this reason most of the experiments were carried out at the

b. p. in a copper flask; the point of equilibrium was checked by equilibrating mixtures of known composition with stronger alkali; the molecular weight of the equilibrated acids was checked by titration in every case and the physical properties were also determined but are not recorded.

Acid.	% KOH.	Time (hours).	J %.	$\alpha\beta$-Acid %.	Acid.	% KOH.	Time (hours).	J %.	$\alpha\beta$-Acid %.
$\alpha\beta$	25	24	4·8	96·5	$\beta\gamma$	25	120	71·9	11·0
,,	25	120	6·2	95·5	50·2 $\alpha\beta$	25	240	47·1	50·5
,,	25	330	8·0	94·0	50·1 $\alpha\beta$	40	72 at b.p.	47·7	50·0
,,	25	336 at b.p.	11·9	90·0	59·3 $\alpha\beta$	40	69 at b.p.	43·1	56·0
					38·9 $\alpha\beta$	40	114½ at b.p.	50·1	46·0

β-Methyl-α-ethylhexenoic Acids.—Methyl *n*-propyl ketone and ethyl α-bromobutyrate gave a 50—55% yield of ethyl β-hydroxy-β-methyl-α-ethylhexoate, the main fraction passing over at 120°/15 mm.; $d_{4^\circ}^{22\cdot0^\circ}$ 0·94514, $n_{\mathrm{D}}^{22\cdot0^\circ}$ 1·43618. The acid obtained on hydrolysis was a thick liquid smelling of butyric acid.

β-Methyl-α-ethyl-Δ^α-hexenoic acid (VII). After partial esterification for 48 hours the pure *acid* was obtained, b. p. 127°/12 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·95258, $n_{\mathrm{D}}^{20\cdot0^\circ}$ 1·46916, $[R_L]_{\mathrm{D}}$ 45·66 (calc., 44·95), J 1·5% (Found: C, 69·6; H, 10·1; Ag in *silver* salt, 41·2. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3; Ag in silver salt, 41·0%). The pure acid on oxidation with permanganate gave methyl propyl ketone, which was isolated in the form of the semicarbazone.

β-Methyl-α-ethyl-Δ^β-hexenoic acid (VIII). The crude ester (80% yield) yielded an acid which was subjected to partial esterification for 19 hours, giving the pure βγ-ester, b. p. 90°/14 mm., $d_{4^\circ}^{19\cdot5^\circ}$ 0·88788, $n_{\mathrm{D}}^{19\cdot5^\circ}$ 1·43568, $[R_L]_{\mathrm{D}}$ 54·18 (calc., 54·19), J 48·3%. The *acid* this gave on hydrolysis had b. p. 130°/13 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·93536, $n_{\mathrm{D}}^{20\cdot0^\circ}$ 1·45073, $[R_L]_{\mathrm{D}}$ 44·81 (calc., 44·95), J 71·9% (Found: C, 68·8; H, 10·2; M, 156·2. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%; M, 156·1). Its purity was proved by repeating the partial esterification, an ester with an iodine addition of 47·7% being obtained.

As with the previous pair of acids, no crystalline derivatives could be obtained.

Equilibrations. Reference curve:

Mixture (% $\alpha\beta$)	100	90	75	62·5	50	25	10	0
J (%)	1·5	12·7	27·7	37·8	47·3	63·3	68·9	71·9

In mixtures containing a high proportion of βγ-acid, a distinct "back reaction" is observed, that is, the colour of the starch indicator returns owing to the liberation of more iodine. This difficulty was overcome by the method used by Kon and Thakur (*loc. cit.*, p. 2224).

For the determination of the point of equilibrium, 40% potassium hydroxide solution at the boiling point was again employed.

Acid.	% KOH.	Time (hours).	*J* %.	$\alpha\beta$-Acid %.	Acid.	% KOH.	Time (hours).	*J* %.	$\alpha\beta$ Acid %.
$\alpha\beta$	25	186	3·4	98·0	$\beta\gamma$	25	288	65·9	19·5
,,	25	288	6·0	96·0	51·4 $\alpha\beta$	40	43 at b.p.	43·5	56·5
$\beta\gamma$	25	186	66·3	17·0	60·4 $\alpha\beta$	40	92 at b.p.	42·7	57·0

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