361. *The Chemistry of the Three-carbon System.*
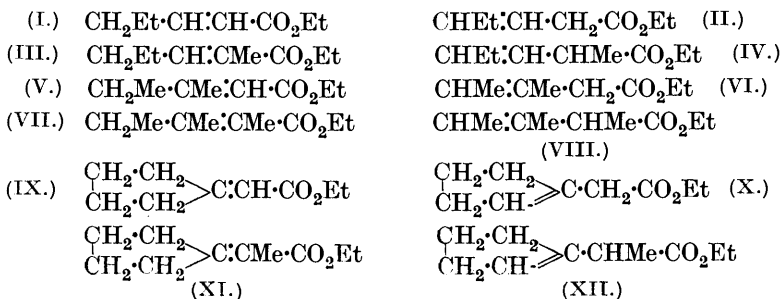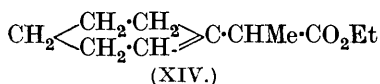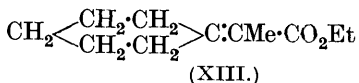*Part XXIX.   Tautomerism of Unsaturated Esters.*

By G. A. R. KON, R. P. LINSTEAD, and G. W. G. MACLENNAN.

THE object of the present investigation was to collect quantitative data on the mobilities and positions of equilibrium in pairs of αβ- and βγ-unsaturated esters and to endeavour to connect these with the structure of the esters.

Up to the present, comparatively few esters have been examined: ethyl *cyclo*hexylideneacetate and its βγ-isomeride (Kon and Linstead, J., 1929, 1269) and the *iso*hexenoic esters (Linstead, *ibid.*, p. 2498) have, however, been fully investigated; a few dicyclic esters have also been studied by Thakur (this vol., pp. 2120, 2139, 2147, 2157).

The following pairs of αβ- and βγ-esters have now been examined : hexenoic (I and II), α-methylhexenoic (III and IV), β-methyl-pentenoic (V and VI), αβ-dimethylpentenoic (VII and VIII), *cyclo*-pentenylacetic (IX and X), α-methyl*cyclo*pentenylacetic (XI and XII), and α-methyl*cyclo*hexenylacetic (XIII and XIV) :

(I.) $CH_2Et \cdot CH\dot{:}CH \cdot CO_2Et$ $CHEt\dot{:}CH \cdot CH_2 \cdot CO_2Et$ (II.)

(III.) $CH_2Et \cdot CH\dot{:}CMe \cdot CO_2Et$ $CHEt\dot{:}CH \cdot CHMe \cdot CO_2Et$ (IV.)

(V.) $CH_2Me \cdot CMe\dot{:}CH \cdot CO_2Et$ $CHMe\dot{:}CMe \cdot CH_2 \cdot CO_2Et$ (VI.)

(VII.) $CH_2Me \cdot CMe\dot{:}CMe \cdot CO_2Et$ $CHMe\dot{:}CMe \cdot CHMe \cdot CO_2Et$

(VIII.)

(IX.) $\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} {>} C\dot{:}CH \cdot CO_2Et$ $\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH\underline{} \end{matrix} {>} C \cdot CH_2 \cdot CO_2Et$ (X.)

$\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} {>} C\dot{:}CMe \cdot CO_2Et$ $\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH\underline{} \end{matrix} {>} C \cdot CHMe \cdot CO_2Et$

(XI.)   (XII.)

$$CH_2\!\!<\!\!^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}\!\!>\!\!C\!:\!CMe \cdot CO_2Et \qquad CH_2\!\!<\!\!^{CH_2 \cdot CH_2}_{CH_2 \cdot CH\!:}\!\!>\!\!C \cdot CHMe \cdot CO_2Et$$

(XIII.)   (XIV.)

The pure esters, treated with sodium ethoxide, underwent conversion into equilibrium mixtures of $\alpha\beta$- and $\beta\gamma$-unsaturated isomerides; the results obtained under Kon and Linstead's standard conditions are in Table I.

TABLE I.

Esters.	% $\alpha\beta$-Ester at equilm.	Mobility.
Hexenoic	92 (?)	153
isoHexenoic*	10 (?)	High
α-Methylhexenoic	95	151
β-Methylpentenoic	75	26
αβ-Dimethylpentenoic	94·5	2
cycloPentenylacetic	60	835
α-Methylcyclopentenylacetic	88	84
cycloHexenylacetic †	38	8·1
α-Methylcyclohexenylacetic	5	0·15

      * Linstead, *loc. cit.*   † Kon and Linstead, *loc. cit.*

The value given for the hexenoic esters is regarded as only approximate because, just as in the *iso*hexenoic esters (Linstead, *loc. cit.*), there is a rapid addition of alcohol with the formation of a β-ethoxy-ester. It is the αβ-ester which undergoes this addition; this is seen from the fact that, in the experiments with the βγ-ester, the iodine addition of the product (which is a direct measure of the βγ-content, both αβ- and ethoxy-ester being practically inert) falls rapidly, but the formation of the ethoxy-ester is not appreciable at first, that is, until a sufficient amount of αβ-ester has been produced. The formation of βγ-ester from the αβ- reaches a maximum value of 8% and this is taken as the equilibrium value.

In the other esters, which have a substituent in the β-position, the formation of alcohol-addition products is insignificant and the equilibrium values obtained can properly be regarded as structural constants.

The figures given in Table I disclose remarkable differences both in mobilities and in the proportions of the isomerides in the equilibrium mixtures; *e.g.*, the mobility of the *cyclo*pentenylacetic esters is 100 times greater than that of the otherwise exactly similar esters of the *cyclo*hexane series and is of the same order as the mobility of *cyclo*hexenylacetone (Kon and Linstead, *loc. cit.*).

This extremely high mobility suggested that these esters might have another common feature with the unsaturated ketones, namely, the capability to undergo alkylation, a view which is superficially even more probable when it is remembered that both these changes are supposed to proceed through the intermediate formation of an enolide ion. Under conditions under which ketones of equal

mobility readily fix an alkyl group, however, no definite evidence of alkylation of these esters could be obtained. There is, therefore, no simple connexion, such as was at one time assumed, between the tautomeric mobility and the capacity for alkylation of unsaturated substances.

The retarding effect of an α-substituent on mobility is again clearly apparent in all but the α-methylhexenoic esters, which have no substituent on the β-carbon atom; this bears out the suggestion that this effect is only seen in systems with an α- and a β-substituent (Linstead and Mann, J., 1931, 733). The esters are, in this respect, similar to the acids from which they are derived, but this resemblance ceases when the effect of the α-substituent on the position of equilibrium is considered. In the straight-chain esters and in those with a *cyclo*pentane ring an α-methyl group displaces the equilibrium towards the αβ-side, just as it does in acids (compare Kon, Leton, Linstead, and Parsons, J., 1931, 1411). In the *cyclo*hexane derivatives it has a pronounced effect in the opposite direction, analogous to that observed in ketones (Kon and Leton, J., 1931, 2496; Kon and Thakur, J., 1930, 2217). The other effects of structure on equilibrium are those to be expected on general grounds and do not call for special comment.

The application of electronic conceptions to tautomerism (Ingold, Shoppee, and Thorpe, J., 1926, 1477) has been extended to cover acid equilibria in particular (compare Linstead, *loc. cit.*), although it was suggested that a number of additional factors must be taken into consideration. However, the lack of generality in the effects observed and the differences between otherwise exactly similar systems now brought to light, together with those accumulated during recent years, cannot be reconciled with any simple theory. It appeared at first that the various phenomena might be explained by assuming two different mechanisms by which equilibration may proceed, one covering acids and the other neutral systems—ketones, nitriles; and esters. There are, however, inconsistencies in the behaviour of the latter which make it preferable to defer theoretical discussion for the present.

Experimental.

Methods.—The methods of equilibration used by Kon and Linstead (*loc. cit.*) were employed throughout. The % iodine additions (J) of the equilibrated esters were determined in $CHCl_3$ solution according to Linstead and May's method (J., 1927, 2565); a reaction time of 60 mins. was employed unless otherwise stated, and the results compared with reference curves in the usual way. The physical properties of the equilibrated esters were determined, but are not recorded.

Ethyl Hexenoates (I and II).—Δ^{α}-Hexenoic acid, m. p. 33—34° (Boxer and

Linstead, J., 1931, 742), was esterified through the Ag salt; the ester had b. p. 80°/22 mm., $d_4^{20°}$ 0·8986, $n_D^{20°}$ 1·4348, $[R_L]_D$ 41·22 (calc., 40·33). The Δ^β-ester was similarly obtained, and had b. p. 64°/12 mm., $d_4^{20°}$ 0·8957, $n_D^{20°}$ 1·4255, $[R_L]_D$ 40·61: another specimen prepared by the partial esterification of the crude Δ^β-acid (Boxer and Linstead, *loc. cit.*) had very similar properties.

Equilibrations.   Reference curve :

Mixture, % $\alpha\beta$	100	90	75	50	25	10	0
J, %	2·3	11·9	25·5	49·3	69·1	78·2	83·0

Owing to the considerable addition of EtOH in these equilibrations, the procedure was somewhat modified. Preliminary expts. showed that the ethoxy-ester (*ethyl β-ethoxyhexoate*) could be obtained pure by repeated fractionation, and had b. p. 94°/14 mm., $d_4^{20°}$ 0·9108, $n_D^{20°}$ 1·4160, $[R_L]_D$ 51·77 (calc., 51·44) (Found : C, 63·6; H, 10·5. $C_{10}H_{20}O_3$ requires C, 63·8; H. 10·6%). It does not react appreciably with ICl (J 1·5).

In the actual equilibrations, the mixture of esters recovered (80—88%) was distilled, the total distillable material being collected; this therefore contained the whole of the ethoxy-ester formed. From the iodine addition, the $\beta\gamma$-content of the mixture was determined, whilst its density and refractive index enabled a rough estimate of the amount of ethoxy-ester to be made. The following results were obtained :

Initial material.	Time, hrs.	J, %.	% $\beta\gamma$-Ester.	Initial material.	Time, hrs.	J, %.	% $\beta\gamma$-Ester.
$\alpha\beta$	0·16	6·3	4·5	$\beta\gamma$	0·16	78·9	92·0
$\alpha\beta$	0·33	7·3	5·5	$\beta\gamma$	0·33	70·6	77·0
$\alpha\beta$	0·66	8·0	6·5	$\beta\gamma$	0·66	59·1	61·0
$\alpha\beta$	1·00	7·6	6·0	$\beta\gamma$	1·00	47·6	48·1
$\alpha\beta$	1·50	7·5	6·0	$\beta\gamma$	1·50	34·7	34·5
$\alpha\beta$	2·00	6·5	4·5	$\beta\gamma$	2·00	24·8	23·5
$\alpha\beta$	3·00	5·4	4·0	$\beta\gamma$	3·00	14·7	13·5
$\alpha\beta$	24·00	3·5	2·0	$\beta\gamma$	24·00	3·5	2·0
				Ethoxy-ester	24·00	3·5	2·0

Reducing the conc. of the NaOEt had but little effect, and carrying out the reaction at the b. p. for 2 and 4 hrs. gave a slight increase in $\beta\gamma$-content, a mixture with J 9·6 being obtained from the $\alpha\beta$- and also from ethoxy-ester.

The amounts of ethoxy-ester formed in these expts., calc. from the $d_4^{20°}$ and $n_D^{20°}$ of the mixture, are given below; the values calc. from $n_D^{20°}$ are reproducible, and are considered to be the more reliable.

Initial material.	Time, hrs.	% $\beta\gamma$-Ester.	% Ethoxy-ester.	
			From $n_D^{20°}$.	From $d_4^{20°}$.
$\alpha\beta$....................................	0·66	6·5	31·0	25·0
$\alpha\beta$....................................	1·00	6·0	44·0	43·0
$\alpha\beta$....................................	2·00	4·5	64·0	66·0
$\alpha\beta$....................................	3·00	4·0	76·0	75·0
$\alpha\beta$....................................	24·00	2·0	82·0	92·0
$\alpha\beta$ in N-NaOEt at b. p.	4·00	8·0	56·0	42·0
$\alpha\beta$ in N/10-NaOEt at 25°	8·00	4·5	28·0	20·0
$\beta\gamma$....................................	0·66	58·5	13·0	6·0
$\beta\gamma$....................................	1·00	47·5	15·0	16·0
$\beta\gamma$....................................	2·00	25·5	40·0	30·0
$\beta\gamma$....................................	3·00	13·5	61·0	70·0
$\beta\gamma$....................................	24·00	2·0	82·0	91·0
$\beta\gamma$ in N/10-NaOEt at 25°	24·00	30·5	24·0	21·0
Ethoxy	24·00	2·0	82·0	84·0
Ethoxy at b. p. with N-NaOEt	2·00	8·0	56·0	48·0
Ethoxy ,, ,, ,.	4·00	8·0	59·0	52·0

From these results it can be concluded that the ethoxy-ester is formed from the $\alpha\beta$-ester.

Ethyl α-Methylhexenoates (III and IV).—Butaldehyde (72 g.) was condensed with ethyl α-bromopropionate (181 g.) and Zn (65 g.) in 600 c.c. of dry C_6H_6, a vigorous reaction giving a 70—80% yield of *ethyl β-hydroxy-α-methyl-n-hexoate*. The ester purified by hydrolysis and re-esterification had b. p. 110°/19 mm., $d_4^{20°}$ 0·9639, $n_D^{20°}$ 1·4306, $[R_L]_D$ 46·69 (calc., 46·94) (Found : C, 62·2; H, 10·4. $C_9H_{18}O_3$ requires C, 62·1; H, 10·4%).

The *acid* after crystallisation from hexane had m. p. 50° (Found : C, 57·8; H, 9·7; *M*, monobasic, 147·7. $C_7H_{14}O_3$ requires C, 57·5; H, 9·7%; *M*, 146·1).

It was found impossible to dehydrate this acid with Ac_2O, an acetylated product being formed.

The ester could not be satisfactorily dehydrated by Darzens's method (*Compt. rend.*, 1911, **152**, 1601), but P_2O_5 gave good results. The hydroxy-ester (50 g.), dissolved in 200 c.c. of dry C_6H_6, was boiled under reflux with P_2O_5 (50 g.) for 3 hrs., the C_6H_6 solution filtered off, and the solid extracted with C_6H_6. The combined C_6H_6 solutions gave, on evaporation, a crude unsaturated ester (26 g.), b. p. 60—69°/12 mm., *J* 60·0, and 12 g., b. p. 70—80°/12 mm., *J* 50·0. The lower fraction was hydrolysed and partially esterified for 5 hrs. The proportions of reagents used for this and other partial esterifications were 230 c.c. EtOH and 100 c.c. *N*-alc. HCl per g.-mol. of acid; these are more economical than those formerly used (Eccott and Linstead, J., 1929, 2153; Kon and Thakur, *loc. cit.*). The ester, *J* 77·5, was hydrolysed with cold 5% aq.-alc. alkali, and again esterified for 3 hrs.; the product then had *J* 79·3; after one more hydrolysis and esterification for 1 hr., it was taken as pure $\beta\gamma$-ester; it had b. p. 68—69°/16 mm., $d_4^{20°}$ 0·8847, $n_D^{20°}$ 1·4251, $[R_L]_D$ 45·12 (Found : C, 69·3; H, 10·2. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%).

Subsequently, doubts arose regarding the purity of the material obtained in this way, which appeared to contain some closely related compound (not the $\alpha\beta$-ester). The $\beta\gamma$-ester was therefore synthesised by an alternative method which is described on p. 2453; this had b. p. 78°/25 mm., $d_4^{20°}$ 0·8778, $n_D^{20°}$ 1·4237, $[R_L]_D$ 45·36, *J* 82·0. This value is sufficiently close to that found above, and the reference curve given below therefore requires but little correction. The pure ester was employed to check the value for the final equilibrium (6 hrs.) given on p. 2455.

For the prep. of the pure $\alpha\beta$-ester, the crude $\beta\gamma$-acid was boiled for 2 days with 10 equivs. of 25% KOH aq. The recovered acid (*J* 25 in 10 mins.) was partially esterified for 24 hrs. (*J* 6·6) and finally treated with cold 70% H_2SO_4 (Linstead, this vol., p. 115), and the lactone formed removed; the pure $\alpha\beta$-acid had b. p. 118°/11 mm., $d_4^{20°}$ 0·9627, $n_D^{20°}$ 1·4601, $[R_L]_D$ 36·45 (calc., 35·71), *J* 0. The ethyl ester, prepared through the Ag salt, had b. p. 72°/10 mm., $d_4^{20°}$ 0·9031, $n_D^{20°}$ 1·4407, $[R_L]_D$ 45·61 (calc., 44·95); another specimen was prepared by boiling the pure acid with *N*-alc. HCl and was very similar in properties.

Equilibrations. Reference curve.

Mixture, % $\alpha\beta$	100	90	75	50	25	10	0
J, %	1·0	10·1	25·2	49·2	68·5	76·3	80·2

The equilibration results (8 expts.) are given on p. 2455.

The properties of the equilibration products show that little or no formatio

of ethoxy-ester takes place. This was confirmed by analysis (Found, in the $\beta\gamma$-ester equilibrated for 3·1 hrs. : C, 68·9; H, 9·9. Found, in the $\alpha\beta$-ester equilibrated for 5 hrs. : C, 69·5; H, 10·2. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%). The recoveries of unsaturated esters in the above expts. averaged 80—82%.

Ethyl β-Methylpentenoates.—The esters described by Kon and Nargund (following paper) were used in conjunction with their reference curve.

Equilibrations. The $\alpha\beta$-ester after 43 hrs.' treatment appeared from its physical properties to contain ethoxy-ester, although the amount was not sufficient to be detected by analysis (Found : C, 67·8; H, 9·8. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%). The final equilibrium was therefore determined by equilibrating artificial mixtures of the two esters : the result (4 expts.) is given on p. 2455. The recovery of esters was about 82%.

Ethyl $\alpha\beta$-Dimethylpentenoates.—The $\alpha\beta$-acid (Abbott, Kon, and Satchell, J., 1928, 2514) was purified by partial esterification; owing to the low rate of esterification, it was warmed for an hr., then left over-night. The recovered acid had b. p. 114°/11 mm., $d_4^{20°}$ 0·9854, $n_D^{20°}$ 1·4720, $[R_L]_D$ 36·40, and did not change after a further partial esterification. The pure ester, obtained through the Ag salt, had b. p. 68°/10 mm., $d_4^{20°}$ 0·9156, $n_D^{20°}$ 1·4453, $[R_L]_D$ 45·40 (calc., 44·95), J 1·5. The $\beta\gamma$-acid was obtained as described by Abbott, Kon, and Satchell (*loc. cit.*), except that Darzens' method was used for the dehydration of the hydroxy-ester. The crude ester was subjected to partial esterification for 1 hr., and the recovered acid again treated for 4 hrs. The products were practically identical, that first obtained, b. p. 63°/12 mm., $d_4^{20°}$ 0·9011; $n_D^{20°}$ 1·4298, $[R_L]_D$ 44·73, being taken as pure and used for the reference curve.

Equilibration. Reference curve.

Mixture, % $\alpha\beta$	100	90	75	50	25	10	0
J, %	1·5	11·0	25·0	43·5	57·5	62·0	66·4

As the mobility of the system was low, the final equilibrium was determined by equilibrating mixtures for 24 hrs. : the result (3 expts.) is given on p. 2455.

The recovery of equilibrated material varied from 75 to 86%; no addition of EtOH was observed. The final equilibrium mixture was analysed (Found C, 69·4; H, 10·1. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%).

Ethyl cycloPentenylacetates.—The $\alpha\beta$-ester, prepared from the pure acid through the Ag salt, had b. p. 96°/15 mm., $d_4^{20°}$ 0·9829, $n_D^{20°}$ 1·4728, $[R_L]_D$ 43·80 (calc., 42·75). The $\beta\gamma$-ester was prepared by partial esterification of the $\beta\gamma$-acid for 12 hrs. The ester was hydrolysed, and again esterified for 4 hrs., the resulting ester having b. p. 85°/15 mm., $d_4^{20°}$ 0·9699, $n_D^{20°}$ 1·4545, $[R_L]_D$ 42·78.

Equilibrations. Reference curve. Owing to the high addition of the $\beta\gamma$-ester a reaction time of 10 mins. was adopted, and the curve was constructed from the following values :

Mixture, % $\alpha\beta$	100	90	75	50	25	10	0
J, %	3·1	11·7	26·3	49·9	71·0	83·7	89·2

The result of the equilibration (12 expts.) is given on p. 2455. The recovery of unsaturated material was about 78%.

The fully equilibrated $\alpha\beta$-ester had $d_4^{20°}$ 0·9814, $n_D^{20°}$ 1·4656 (Found : C, 70·1; H, 9·0. $C_9H_{14}O_2$ requires C, 70·1; H, 9·0%), and the fully equilibrated $\beta\gamma$-ester had $d_4^{20°}$ 0·9822, $n_D^{20°}$ 1·4655 (Found : C, 70·0; H, 9·2%). The properties calc. for a mixture containing 60% $\alpha\beta$-ester are $d_4^{20°}$ 0·9809, $n_D^{20°}$ 1·4655.

Attempted Alkylation of Ethyl cyclo*Pentenylacetate.*—(I) The ester (15·4 g.) was treated with a solution of Na (2·3 g.) in dry EtOH (28 c.c.), an excess of MeI added, the mixture boiled for 2—3 hrs., and the ester recovered. Nearly the whole of it boiled at 100—103°/17 mm. and had the properties of the equilibrium mixture of the unmethylated esters ($d_4^{20°}$ 0·9818, $n_D^{20°}$ 1·4655).

(II) The expt. was repeated, K being used instead of Na, and the excess of EtOH removed under reduced press. before the ester (9 g.), dissolved in dry Et$_2$O, was added. The recovered ester (5 g.) had b. p. 102—109°/26—28 mm., $d_4^{20·5°}$ 0·9774, $n_D^{20·5°}$ 1·4626, J 44·0.

(III) The ester (15 g.) was treated with " molecular " Na in C$_6$H$_6$. There was much darkening, but only a part of the metal dissolved. MeI was added after 2 hrs., and the mixture heated until neutral. A fraction (6 g.), b. p. 94—103°/24 mm., $d_4^{20°}$ 0·9698, $n_D^{20°}$ 1·4608, was recovered.

The ester thus appeared to be unmethylated, but as analysis would not enable a decision to be made, the crude ester was treated with NaOEt for 12 hrs. The equilibrated parent ester has J 40·3 in 10 mins., and the equilibrated α-methyl ester has J 15·0 in 30 mins. The addition of the product *after* equilibration should therefore give a better indication as to whether methylation has taken place.

The ester obtained in this way in expt. III had $n_D^{20°}$ 1·4652, J 36·0 in 10 mins.: the ester from expt. II was equilibrated for 1 hr., and had $n_D^{20·5°}$ 1·4637, J 35·5 in 10 mins., and these values did not change on re-equilibrating for 9 hrs.

The experiments show that no appreciable methylation has occurred.

Ethyl α-*Methyl*cyclopentenylacetates.—The pure solid αβ-acid (Wallach and Martins, *Annalen*, 1909, **365**, 273; Kon and Thakur, *loc. cit.*) was esterified through the Ag salt; the ester had b. p. 96°/12 mm., $d_4^{20°}$ 0·9826, $n_D^{20°}$ 1·4754, $[R_L]_D$ 48·21 (calc., 47·37). The βγ-ester was prepared as described by Kon and Thakur (*loc. cit.*), and had b. p. 79°/6 mm., $d_4^{20°}$ 0·9611, $n_D^{20°}$ 1·4534, $[R_L]_D$ 47·32, in good agreement with their figures.

Equilibrations. Reference curve.

Mixture, % αβ	100	90	75	50	25	10	0
J, %	2·4	11·9	26·5	51·2	70·0	78·3	82·7

The result (14 expts.) is given on p. 2455. The recovery of unsaturated esters was about 77% in the equilibrations of short duration ($\frac{1}{2}$—4 hrs.), but much less in the long ones (90 hrs.) owing to the hydrolysis which occurred. There was, however, no addition of EtOH (Found : C, 71·1; H, 9·7. Calc. for C$_{10}$H$_{16}$O$_2$: C, 71·4; H, 9·6%).

Ethyl α-*Methyl*cyclohexenylacetates (XIII and XIV).—The pure αβ-acid, m. p. 78—79° (Auwers and Ellinger, *Annalen*, 1911, **387**, 230; Kon and Thakur, *loc. cit.*), was converted through the Ag salt into the ester, b. p. 109°/10 mm., $d_4^{20°}$ 0·9720, $n_D^{20°}$ 1·4773, $[R_L]_D$ 53·07 (calc., 51·99). The βγ-ester was prepared by Kon and Thakur and had b. p. 104°/13 mm., $d_4^{20°}$ 0·9618, $n_D^{20°}$ 1·4613, $[R_L]_D$ 52·00.

Equilibrations. Reference curve.

Mixture, % αβ	100	90	75	50	25	10	0
J, %	3·2	12·6	26·4	44·5	57·7	63·0	65·7

The equilibrium was determined by equilibrating suitable mixtures for 21 days. The result (4 expts.) is given on p. 2455. The recovery of the equilibrated esters was good, considering the long duration of the expts. : out of

9·5 g. of $\beta\gamma$-ester, 4·5 g. were recovered after 131 days' treatment, together with 1 g. of higher-boiling material possibly containing an addition product. The low fraction was free from ethoxy-ester (Found : C, 72·5; H, 9·8. Calc. for $C_{11}H_{18}O_2$: C, 72·4; H, 9·8%).