129. *Catalytic Influences in Three-Carbon Tautomerism. Part V. Acid Catalysis in Ketones and Esters.*

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It was shown in Part II (Kon, J., 1931, 248) that certain unsaturated ketones capable of tautomerism could be converted into equilibrium mixtures with the aid of mineral acids, and that the proportion of tautomerides formed was the same as that produced by alkaline catalysts; *e.g.*, *cyclo*hexylideneacetone was converted to the extent of some 77% into *cyclo*hexenylacetone.

The experiments now described were undertaken with the object of testing the application of this reaction to other suitable ketones and also to unsaturated esters; the important bearing of this on the esterification of unsaturated acids by the customary methods is obvious.

Ketones.—The examples selected for study were the four isomeric homomesitones $C_8H_{14}O$ (Abbott, Kon, and Satchell, J., 1928, 2514; Kon and Leton, J., 1931, 2496):

(I.) CMeEt:CH·COEt ⇌ CHMe:CMe·CH·COEt (II.)
(III.) CMeEt:CMe·COMe ⇌ CHMe:CMe·CMe·COMe (IV.)

The conditions of equilibration and the method of analysis were those used in Part II (*loc. cit.*); mobilities were calculated as before (Kon and Linstead, J., 1929, 1269).

Ketone.	Catalyst.	Mobility, $k_1 + k_2$.	Half-change. period (mins.).	% Δ^{α}- at equil.
I and II	HCl	0·093	9·4	58
,,	H_2SO_4	0·0337	20·5	57
,,	H_3PO_4	0·0047	147	57
III and IV	HCl	0·0137	51	18
,,	H_2SO_4	0·00474	146	18
,,	H_3PO_4	0·00169	410	18

From these results it will be seen that (i) the order of catalytic activity is $HCl > H_2SO_4 > H_3PO_4$, (ii) the mobility of the ketones (III) and (IV) is much less than that of (I) and (II), as already observed with alkaline catalysts, although the difference is not quite so pronounced. No great importance attaches to the mobility values, for the rates observed fluctuate somewhat widely (see Experimental); but the retarding effect of the α-methyl group in (III) and (IV) is clearly seen, whilst its effect on the equilibrium is also similar to that previously noted. (iii) The point of equilibrium in the ketones (III) and (IV) is the same as that previously determined, but in the pair (I) and (II) it is considerably nearer the Δ^β-side than the value (67% Δ^α-) found with alkaline catalysts; the difference is sufficiently large not to be adventitious. It must therefore be concluded that the equilibria attained with acid catalysts are not necessarily the same as those produced in the presence of sodium ethoxide.

Some experiments have also been carried out on the isomerisation of *iso*pulegone to pulegone in non-aqueous solvents with trichloroacetic acid as a catalyst. The change proceeds at a convenient rate at 25° with 2*N*-solutions of ketone and acid and goes to completion, as previously observed (Kon, *loc. cit.*); it is much more rapid in chloroform than in acetone or acetonitrile, the mean mobilities being 0·10, 0·041, and 0·042 respectively; it cannot, therefore, depend on the dielectric constants of the solvents, for these are 5·1, 21·5, and 38·8 respectively. Further experimental work is required before the full implications of this observation can be profitably discussed.

Esters.—Similar treatment with mineral acids was also applied to esters, except that higher concentrations of reactants were used (2 equivs. of 2*N*-acid in alcoholic solution) and final equilibria were checked with 10 equivs. of 8*N*-acid; this is necessary because equilibrations with 2*N*-hydrogen chloride do not proceed to completion. For this reason no quantitative significance can be attached to the mobilities determined with this acid; and even with sulphuric acid the rates observed, calculated on the assumption of a unimolecular reaction, fluctuate within wide limits and are only approximate. Nevertheless, the same value for the composition of the equilibrium mixture is obtained with hydrogen chloride and with sulphuric acid in every case and analysis shows that little or no addition of alcohol, etc., takes place; the equilibrium values can therefore be regarded as sufficiently reliable.

Ester (Δ^β-form).	Mobility with HCl.	Mobility with H_2SO_4.	% Δ^α- at equil.	
*cyclo*Pentylideneacetic	?	0·198	52	[60] *
α-Methyl*cyclo*pentylideneacetic	?	0·057	75	[88]
*cyclo*Hexylideneacetic	?	0·0183	25·5	[38]
β-Methylpentenoic	?	0·0086	60	[75]
Δ^α-Hexenoic	nil	nil	100	[92]
Δ^β-Hexenoic	nil	nil	0	[92]

* Equilibrium points attained with sodium ethoxide are given in brackets.

The most striking fact observed is that the isomeric hexenoic esters are not changed at all, in sharp contrast with the rapid equilibration with sodium ethoxide (Kon, Linstead, and Maclennan, J., 1932, 2454), which might be connected with the rapid addition of alcohol to the double bond of the Δ^α-form, causing artificial disturbance of the equilibrium; but this does not account for the change from the Δ^α- to the Δ^β-form, which definitely does occur (Kon, Linstead, and Maclennan, *loc. cit.*). A somewhat similar behaviour has, however, been noted in the esters of the citraconic group; these are inert to acids but are rapidly equilibrated on treatment with sodium ethoxide (Kon and Coulson, J., 1932, 2568).

Another significant fact is that the equilibrium points of the other esters differ considerably from those ascertained with sodium ethoxide, being nearer the Δ^β-side, just as in the case of the ketones (I) and (II); the equilibrium evidently depends on the nature of the catalyst.

The effect of the α-methyl group in retarding tautomeric change is again noticeable, but the order in which the esters can be arranged according to their mobilities is not the same as that determined in the presence of sodium ethoxide, the positions of β-methylpentenoic and *cyclo*hexylideneacetic esters being interchanged. This order is also different from that of the mobilities of the corresponding acids in alkali (cf. Kon and Thakur, J., 1930, 2217; Goldberg and Linstead, J., 1928, 2343; Linstead, J., 1927, 2579; Kon, Linstead, and Wright, this vol, p. 599).

The complete lack of mobility of the hexenoic esters is in good agreement with the fact that perfectly homogeneous esters are obtained on esterifying the two acids with alcoholic sulphuric acid or by the Fischer–Speier method. All the other acids now examined give esters containing appreciable amounts of their isomerides, and the extent of isomerisation is invariably greater with hydrogen chloride than with sulphuric acid (Table I). The conversion occurs during or after esterification, because the unesterified acids recovered in these experiments are in all cases the pure initial materials.

TABLE I.

Acid.	Isomerisation, %. With HCl.	Isomerisation, %. With H_2SO_4.	Acid.	Isomerisation, %. With HCl.	Isomerisation, %. With H_2SO_4.
*cyclo*Pentylideneacetic	32	12	*cyclo*Hexenylacetic	8	7
*cyclo*Pentenylacetic	38	22	β-Methyl-Δ^{α}-pentenoic	3	1
α-Methyl*cyclo*pentylideneacetic	11	6	β-Methyl-Δ^{β}-pentenoic	18	14
α-Methyl*cyclo*pentenylacetic	14	8	Δ^{α}-Hexenoic	nil	nil
*cyclo*Hexylideneacetic	5	1·5	Δ^{β}-Hexenoic	nil	nil

In attempting to correlate these observations it is thus necessary to account for three seemingly anomalous facts; the incomplete interconversion of esters with dilute hydrogen chloride, the lack of mobility of the hexenoic esters, and the shifting of the equilibrium towards the Δ^{β}-side in the mobile esters and also in the ketones (I) and (II). The last difficulty appears at first sight to be the least, for some differences may be anticipated as the result of differences in the temperatures at which alkaline and acid equilibrations are carried out (25° and 100° respectively); if the change from Δ^{α}- to Δ^{β}- is accompanied by absorption of heat, the difference expected would be in the sense observed, although it is doubtful whether it would be of sufficient magnitude. The addition of alcohol to the Δ^{α}-form, observed in alkaline equilibrations, would also cause a displacement of the equilibrium in the required direction, but again it is questionable whether the small amount of addition observed could cause such large displacements.

The incomplete equilibration with dilute hydrogen chloride suggests that the mode of action of this catalyst is specific, for although it causes some isomerisation, no equilibrium as such is produced; the gradual diminution of the velocity constants, calculated on the assumption of a unimolecular reaction mechanism (see Experimental), shows this clearly.

It is therefore necessary to admit the possibility that the changes now observed in esters are only formally tautomeric, for although a mixture of isomerides in definite proportions is produced in some cases, there may be no direct interconversion of the two forms. An explanation of this nature has been put forward by Linstead and Noble (Part III, p. **611**) and the facts so far ascertained are consistent with it, particularly the lack of mobility of the hexenoic esters. An alternative would be the formation of a co-ordination complex on the lines suggested by Carothers and Berchet (*J. Amer. Chem. Soc.*, 1932, **55**, 2807) and by Johnson (*ibid.*, p. 3029) to account for some abnormal reactions of three-carbon systems. It is proposed to institute experiments to determine whether the latter mechanism applies to the cases under discussion.

EXPERIMENTAL.

Materials.—The ketones (I), (II), (III), and (IV), prepared as described by Abbott, Kon, and Satchell (*loc. cit.*) and by Kon and Leton (*loc. cit.*), were regenerated from their semicarbazones by Kon's method (J., 1930, 1616) with the exception of (II), which was used without purification. The ketone (IV) was obtained solely from the semicarbazone, m. p. 163°, and was therefore Kon and Leton's form *b*. On one occasion a semicarbazone of m. p. 162° was obtained, which depressed the m. p. of the semicarbazone of m. p. 163°; the ketone regenerated from it, b. p. 53°/11 mm., $d_{4^{\circ}}^{20^{\circ}}$ 0·8542, n_{D} 1·4367, had an iodine addition of over 100%, the solution being completely decolorised in 2 minutes. This ketone could not be equilibrated and was recovered completely unchanged after 240 minutes' heating with alcoholic sulphuric acid; a semicarbazone, m. p. 162° without purification, was formed from the product of this experiment. On ozonolysis, acetaldehyde was produced from it, but no trace of formaldehyde, which would have been formed from the isomeride CH_2:CH·CHMe·CHMe·COMe; the second oxidation product was not identified.

Fresh attempts were made to synthesise the ketone (II) by the action of ethyl-zinc or -magnesium iodide on the chloride of the pure Δ^{β}-β-methylpentenoic acid, which has only lately become available (Kon, Linstead, and Wright, *loc. cit.*), but without success, although its Δ^{α}-isomeride was readily obtained by the same method from the Δ^{α}-acid. *iso*Pulegone was prepared as described by Kon (*loc. cit.*), and the esters as described by Kon, Linstead, and Maclennan (*loc. cit.*) and by us (J., **1932**, 2461); the pure acids were the specimens described there.

Acetone and acetonitrile were dried over calcium chloride for a week and redistilled before use; chloroform was previously washed with water. A. R. Trichloroacetic acid was dried in a vacuum over phosphoric oxide before use.

Procedure.—The equilibration of ketones was carried out as described in Part II (*loc. cit.*). For that of esters, 2*N*-solutions of dry hydrogen chloride and of pure sulphuric and phosphoric acids in absolute alcohol were used, the requisite quantity being added to 2—3 g. of the ester previously weighed into a tube, which was then sealed, and treated as usual.

The analysis of mixtures of ketones and of esters was carried out iodometrically with the aid of reference curves given by Abbott, Kon, and Satchell (*loc. cit.*), Kon (J., **1931**, 248), Kon and Leton (*loc. cit.*), Kon, Linstead, and Maclennan (*loc. cit.*), and by us (*loc. cit.*). The physical properties of the products were determined in every case as a check, but are not quoted.

Results.—These are given below. Ketones (I) and (II) were recovered to the extent of only 30—60% in the longer experiments with hydrogen chloride, and final equilibria were determined by using a mixture of the two ketones. The recovery with sulphuric and phosphoric acids was 70—80%.

Material.	Re-agent.	Time, mins.	*J*, %.	% Δ^{α}-.	$k_1 + k_2$.	Material.	Re-agent.	Time, mins.	*J*, %.	% Δ^{α}-.	$k_1 + k_2$.
(I)	HCl	10	25·3	78·0	0·0729	(II)	H_2SO_4	30	57·5	36·0	0·0328
,,	,,	20	34·0	68·0	0·0698	,,	,,	60	50·9	46·0	0·0268
,,	,,	30	39·5	60·0	0·0828	,,	,,	480	44·0	54·0	—
(II)	,,	10	52·0	44·8	0·151	Mixture	,,	60†	42·0	56·5	—
,,	,,	20	47·0	50·6	0·106	,,	,,	240	40·8	58·0	—
,,	,,	30	45·9	52·0	0·0781	(I)	H_3PO_4	60	16·2	88·2	0·00553
Mixture	,,	—	35·2	67·1	—	,,	,,	120	27·2	76·0	0·00692
,,	,,	60*	39·8	59·5	—	,,	,,	360	34·0	69·8	0·00388
,,	,,	240	40·7	58·0	—	(II)	,,	30	73·4	6·0	0·00367
(I)	H_2SO_4	10	17·0	87·0	0·0365	,,	,,	120	63·0	23·0	0·00425
,,	,,	30	25·3	78·0	0·0243	,,	,,	240	55·4	40·0	0·00495
,,	,,	60	39·2	61·0	0·0415	,,	,,	480	49·0	48·0	0·00375
(II)	,,	10	66·5	19·7	0·0419	Mixture	,,	480	41·8	57·0	—
,,	,,	20	60·0	30·0	0·0370	,,	,,	967‡	39·6	60·0	—

The sample marked * had $d^{20^\circ}_{2^\circ}$ 0·8532, n_D 1·4454, and was analytically pure (Found : C, 75·9; H, 10·8. Calc. : C, 76·2; H, 11·1%); those marked † and ‡ both gave C, 75·7; H, 10·9%.

(III)	HCl	10	16·0	90·0	0·0130	(IV)	H_2SO_4	120	86·8	18·0	—
,,	,,	15	21·9	85·0	0·0134	,,	,,	300	81·0	26·0	—
,,	,,	30	36·2	74·0	0·0127	Mixture	,,	45	86·8	18·2	—
,,	,,	60	60·3	52·0	0·0156	(III)	H_3PO_4	30	8·3	95·8	0·00173
(IV)	,,	10	86·8	18·0	—	,,	,,	120	20·8	86·0	0·00156
Mixture	,,	—	82·9	22·7	—	,,	,,	270	40·4	50·4	0·00165
,,	,,	30	87·2	18·0	—	,,	,,	540	66·0	46·0	0·00198
(III)	H_2SO_4	35	20·0	86·8	0·00493	,,	,,	1080†	76·0	34·0	0·00151
,,	,,	160	48·1	64·0	0·00481	(IV)	,,	30	88·0	16·0	0·00837
,,	,,	210	64·0	48·0	0·00478	,,	,,	60	92·5	4·0	0·0366?
,,	,,	240	66·0	46·0	0·00447	,,	,,	120‡	85·3	21·0	—
,,	,,	570*	83·3	24·0	—	,,	,,	300	83·2	24·0	—
(IV)	,,	30	91·1	6·0	—	,,	,,	1080	78·1	31·0	—
,,	,,	60	88·0	16·0	—	Mixture	,,	180	87·4	18·3	—

Both the sample marked * and that marked † were analysed and gave low figures for carbon (74·5 and 73·5% respectively) and had therefore undergone somewhat extensive decomposition; the mixtures obtained by prolonged heating must therefore be ignored, and for this reason the final equilibrium point was determined by treating a suitable mixture of ketones (containing 22·7% of Δ^{α}-ketone) for a shorter time. The sample marked ‡ gave correct figures on analysis (Found: C, 75·8; H, 10·9%). The iodometric method of analysis, however, measures the amount of unsaturation and therefore of the Δ^{β}-form present; for this reason, even if some addition of alcohol, hydrogen halide, etc., occurs after long periods of heating, as denoted by a low carbon content, the amount of unsaturated material determined iodometrically still gives a correct estimate of the Δ^{β}-ketone present.

An experiment was made to see whether Kon and Leton's form *a* of the ketone (IV) is produced on equilibration of the form *b*. A quantity of the latter (*J*, 96·4%) was heated with alcoholic sulphuric acid for 5 hours, and the recovered ketone treated with aluminium amalgam to remove any Δ^{α}-ketone. The ketone then had b. p. 55°/14 mm., $d_{4^{\circ}}^{20^{\circ}}$ 0·8549, n_D 1·4386, *J* 93·5%; the amount of conversion was therefore small.

Experiments with iso*Pulegone.*—Equal volumes of 2*N*-solutions of pure *iso*pulegone and of trichloroacetic acid were mixed after having been kept in a thermostat at 25° for 0·5 hour; 20 c.c. samples were removed at intervals, poured into dilute sodium carbonate in slight excess, and the ketone recovered as usual and its composition determined iodometrically.

Solvent.	Time, hrs.	*J*, %.	Pulegone, %.	$k_1 + k_2$.	Solvent.	Time, hrs.	*J*, %.	Pulegone, %.	$k_1 + k_2$.
$CHCl_3$	2	54·7	36·0	0·223	$COMe_2$	10	54·6	36·0	0·0446
,,	5·5	48·0	50·0	0·126	,,	24	40·0	63·0	0·0414
,,	15	36·2	68·0	0·078	,,	48	35·8	69·0	0·0244
,,	31	21·1	91·0	0·078	,,	96†	18·6	94·0	—
,,	96	17·7	96·0	—	MeCN	2	62·9	10·0	0·0527
,,	148*	10·2	100·0	—	,,	9	55·0	34·0	0·0581
$COMe_2$	5·5	59·1	24·0	0·0498	,,	18	45·2	55·0	0·044
					,,	48	40·0	63·0	0·020

The samples marked * and † gave on analysis C, 78·4, 78·6; H, 10·4, 10·3 (Calc.: C, 78·9; H, 10·5%).

Equilibrations of Esters.—Ethyl cyclo*pentenylacetates.*

Ester.	Re-agent.	Time. hrs.	*J*, %.	% Δ^{α}-.	$k_1 + k_2$.	Ester.	Re-agent.	Time, hrs.	*J*, %.	% Δ^{α}-.	$k_1 + k_2$.
Δ^{α}-	2*N*-HCl	0·5	12·0	90·0	0·466	Δ^{β}-	2*N*-HCl	4	64·9	35·0	0·279
,,	,,	1	17·9	84·0	0·405	,,	,,	14	63·5	37·0	0·0887
,,	,,	4	22·0	79·0	0·144	,,	,,	47	57·8	42·0	0·0345
,,	,,	16	30·3	71·0	0·0578	,,	,,	110	58·1	42·0	—
,,	,,	47	33·4	68·0	0·0234	,,	,,	240	58·2	42·0	—
,,	,,	110	39·1	61·0	0·0121	Δ^{α}-	8*N*-HCl	24*	49·0	51·0	—
Δ^{β}-	,,	0·5	81·0	15·6	0·680	Δ^{β}-	,,	16·5†	46·6	53·0	—
,,	,,	1	76·2	23·0	0·583						

The equilibrium thus appears to lie between 51 and 53% of Δ^{α}-ester, but the interconversion with 2*N*-acid comes to a standstill after some 100 hours' heating. A mixture containing 60% of Δ^{α}-ester was not altered in composition after 114 hours' heating with 2*N*-acid. The samples marked * and † were analysed (Found: C, 69·6, 69·5; H, 9·1, 9·0. Calc.: C, 70·1; H, 9·1%). Owing to the steady diminution of mobility with the progress of the reaction, a true estimate of this value was not possible.

In contrast to their behaviour with hydrogen chloride, the two esters readily attain equilibrium with sulphuric acid.

Δ^{α}-	2*N*-H_2SO_4	0·5	6·7	96·5	0·151	Δ^{β}	2*N*-H_2SO_4	1	73·8	25·0	0·654
,,	,,	1	8·9	94·0	0·133	,,	,,	4	66·1	34·0	0·265
,,	,,	4	24·4	77·0	0·162	,,	,,	14	53·7	46·0	0·154
,,	,,	14	33·9	67·0	0·083	,,	,,	47†	48·0	52·0	—
,,	,,	47*	48·0	52·0	—	Δ^{α}-	8*N*-H_2SO_4	24	46·6	53·0	—
Δ^{β}-	,,	0·5	82·0	14·0	0·626	Δ^{β}-	,,	24	44·0	56·0	—

The values obtained with 8*N*-acid are higher in Δ^{α}-content, probably owing to addition. The samples marked * and † were analysed (Found: C, 69·4, 69·7; H, 9·1, 9·0. Calc.: C, 70·1; H, 9·1%).

*Ethyl α-methyl*cyclo*pentenylacetates.* Here again the mobility of the esters diminishes considerably on treatment with dilute hydrogen chloride, but remains fairly constant with sulphuric acid.

Δ^{α}-	$2N$-HCl	1	9·2	92·8	0·339	Δ^{α}-	$2N$-H_2SO_4	1	7·3	95·0	0·223
,,	,,	4	12·0	90·0	0·127	,,	,,	4	9·6	92·0	0·0963
,,	,,	48	13·8	88·0	0·136	,,	,,	14	15·2	83·5	0·077
,,	,,	110	17·0	85·0	0·0083	,,	,,	48	22·5	79·2	0·0371
Δ^{β}-	,,	1	80·6	8·0	0·112	Δ^{β}-	,,	1	81·6	4·0	0·0537
,,	,,	4	75·8	14·0	0·0516	,,	,,	4	78·1	10·5	0·0376
,,	,,	14	65·1	32·0	0·0397	,,	,,	14	63·6	34·0	0·0431
,,	,,	37	63·6	34·0	0·0163	,,	,,	37	44·5	56·0	0·0346
Δ^{α}-	$8N$-HCl	24*	28·0	74·0	—	Δ^{α}-	$8N$-H_2SO_4	24	26·5	75·5	—
Δ^{β}-	,,	24†	26·0	76·0	—	Δ^{β}-	,,	24	28·1	74·0	—

The samples * and † were analysed (Found : C, 71·0, 70·9; H, 9·4, 9·6. Calc. : C, 71·4; H, 9·5%). The equilibrium mixtures obtained with $8N$-sulphuric acid were mixed and analysed (Found : C, 70·5; H, 9·5%); they had evidently undergone a somewhat more extensive change.

Ethyl cyclo*hexenylacetates.* The Δ^{β}-ester employed in these experiments was prepared by the partial esterification of the pure acid, under the conditions of Kon and Thakur (*loc. cit.*), and was evidently purer than the specimen used by Kon and Linstead (*loc. cit.*) as it had a somewhat higher iodine addition. One specimen had $d_{4^\circ}^{20^\circ}$ 0·9751, n_D 1·4612, J 79·2%; the other $d_{4^\circ}^{20^\circ}$ 0·9777, n_D 1·4617, J 79·2%. The Δ^{α}-ester was very similar to Kon and Linstead's specimen. A new reference curve for the analysis of mixtures was constructed from the following values :

Mixture (% Δ^{α}-)	100	90	75	50	25	10	0
J, %	7·4	16·0	30·1	50·0	66·3	77·0	79·2

Ester.	Re-agent.	Time, hrs.	J, %.	% Δ^{α}-.	$k_1 + k_2$.	Ester.	Re-agent.	Time, hrs.	J, %.	% Δ^{α}-.	$k_1 + k_2$.
Δ^{α}-	$2N$-HCl	15	13·6	93·0	0·00661	Δ^{β}-	$7{\cdot}5N$-HCl	24†	67·3	24·0	—
,,	,,	24	16·1	90·6	0·00566	Δ^{α}-	$2N$-H_2SO_4	4	7·2	98·5	0·00513
,,	,,	48	17·7	88·8	0·00341	,,	,,	24	31·3	74·0	0·0179
,,	,,	110	22·0	84·0	0·00221	,,	,,	48	44·5	57·0	0·0181
Δ^{β}-	,,	4	75·5	10·0	—	Δ^{β}-	,,	4	76·0	11·0	—
,,	,,	24	75·4	10·0	—	,,	,,	24	68·0	23·0	—
,,	,,	120	75·4	10·0	—	Δ^{α}-	$8N$-H_2SO_4	24‡	66·0	25·0	—
Δ^{α}-	$7{\cdot}5N$-HCl	24*	65·6	26·0	—	Δ^{β}-	,,	24‡	65·6	26·0	—

The samples marked * and † were analysed (Found : C, 71·1, 69·8; H, 9·4, 9·2. Calc. : C, 71·4; H, 9·5%). The two samples marked ‡ were mixed and analysed (Found : C, 71·1; H, 9·4%); the esters evidently had not undergone appreciable decomposition. It will be noted that interconversion with dilute hydrogen chloride does not proceed to completion.

Ethyl β-*methylpentenoates.*

Δ^{α}-	$2N$-HCl	4	7·4	96·0	0·0263	Δ^{β}-	$8N$-HCl	24†	39·5	59·5	—
,,	,,	18	10·6	91·8	0·0145	Δ^{α}-	$2N$-H_2SO_4	4	5·9	97·0	0·0195
,,	,,	36	13·0	88·0	0·0099	,,	,,	18	7·1	94·2	0·00711
,,	,,	72	16·0	85·0	0·0065	,,	,,	54	18·5	83·9	0·0095
Δ^{β}-	,,	1	74·4	9·0	0·162	,,	,,	110	23·0	77·0	0·0077
,,	,,	4	69·3	20·0	0·101	Δ^{β}-	,,	4	73·6	14·0	0·00663
,,	,,	24	69·9	20·0	—	,,	,,	24	67·5	23·0	0·0201
Δ^{α}-	$8N$-HCl	24*	43·0	57·0	—	Δ^{α}-	$8N$-H_2SO_4	24‡	39·0	60·0	—
,,	,,	24	39·0	60·0	—	Δ^{β}-	,,	24‡	39·5	59·5	—

The samples marked * and † were analysed (Found : C, 67·1, 66·9; H, 9·9, 9·5. Calc. : C, 67·6; H, 9·9%); they had therefore undergone some change. The specimens marked ‡ were mixed and analysed (Found : C, 67·3; H, 9·8%); they were evidently essentially unchanged. The values for the mobility obtained with hydrogen chloride are too erratic for the calculation even of an approximate constant.

Ethyl hexenoates. These esters remained unchanged on treatment with dilute or concentrated hydrogen chloride or sulphuric acid and did not suffer addition. An experiment with ethyl β-ethoxyhexoate, formed by the addition of alcohol to the Δ^{α}-ester (Kon, Linstead, and Maclennan, *loc. cit.*), showed that this ester also remains completely unchanged on treatment with concentrated or dilute acids.

Esterification Experiments.—In order to make the experiments comparable amongst themselves, the following procedure was adopted : 5·0 g. of the pure acid was heated in a sealed tube with 10 c.c. of $2N$-alcoholic acid for 4 hours to 100°. The contents of the tube were then poured into about 150 c.c. of water, and the mixture twice extracted with ether. The extract was washed with water, 10% aqueous sodium hydroxide, again with water, dried, evaporated, and the residue distilled (yield 4·5—5·3 g.). The physical properties of the ester were determined in every case but are not quoted; its composition was ascertained iodometrically, the results being given in Table I. The alkaline washings allowed small amounts of Δ^{α}-acids to be recovered on acidification and extraction; the esterification of the Δ^{β}-acids was complete. The isomeric α-methyl*cyclo*pentenylacetic acids were an exception, as 1·1—1·6 g. of unesterified acid were recovered in every experiment; these acids were found to be unchanged.

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