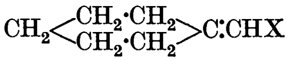
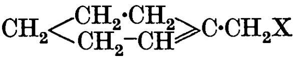
CCLXXXIII.—*The Chemistry of the Three-Carbon System. Part XXV. The Effect of the Methyl Group on the Tautomerism of Acids and Ketones of the* cyclo*Pentane and* cyclo*Hexane Series.*

By George Armand Robert Kon and Ram Simha Thakur.

The present investigation was undertaken with the object of determining the effect of a substituent methyl group on the mobility and the equilibrium in the system

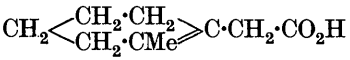
(I.)

$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C{:}CHX$


$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}\gg C\cdot CH_2X$
(II.)

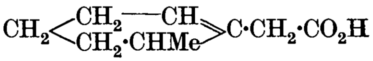
(X = CO_2H or COMe.)

the substituent being introduced in all the four possible positions; the α-substituted *cyclo*pentane compounds were subsequently examined for the sake of comparison. The results with acids and with ketones are considered separately.

Acids.—All the acids used had been previously obtained, although some had not been completely purified. The position of the double bond in the *o*-methyl-βγ-acid, which was undecided by previous investigators, has been definitely proved to be Δ^1 (III), not Δ^6 (IV); the constitution of the meta-compound was not finally settled (see Experimental) but it appears to be the 3-methyl-Δ^6-acid. The mobilities and equilibria of the acids in potassium hydroxide solutions were determined by the standard procedure used by Linstead (J., 1927, 2579) and by Goldberg and Linstead (J., 1928, 2343), except for minor modifications in analytical technique (see Experimental), and the results are summarised in Table I, the parent acids being included for comparison.


$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CMe\end{matrix}\gg C\cdot CH_2\cdot CO_2H$

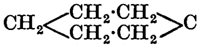
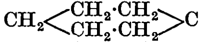
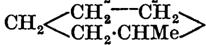
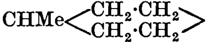
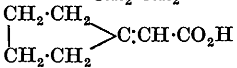
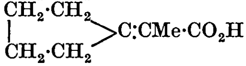
(III.)


$CH_2<\begin{matrix}CH_2-CH\\ CH_2\cdot CHMe\end{matrix}\gg C\cdot CH_2\cdot CO_2H$

(IV.)

The most striking feature of these results is the very marked effect of the α-methyl group. It causes appreciable shifting of the equilibrium towards the αβ-side in both the *cyclo*pentane and the *cyclo*hexane series, in agreement with the observation of Goldberg and Linstead (*loc. cit.*) on straight-chain acids; in addition, it retards the mobility of the system so greatly that only approximate measurements of mobility were possible with α-methyl*cyclo*hexylideneacetic acid. This effect on mobility was not observed by Goldberg and Linstead although it occurs in some neutral systems (Abbott, Kon, and Satchell, J., 1928, 2514; Kandiah and Linstead, J., 1929, 2139),

TABLE I.

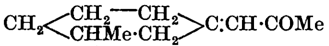
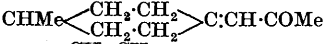
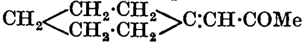
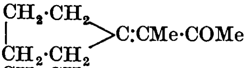
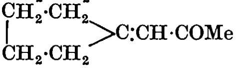
Acid ($\alpha\beta$-form shown).	% $\alpha\beta$ at equilibrium.	Mobility, $10(k_1+k_2)$.	Half-change period.
 $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C{:}CH\cdot CO_2H$ (Linstead)	12	1	8 hrs.
 $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C{:}CMe\cdot CO_2H$	32	0·0075	?
 $CH_2<\begin{matrix}CH_2\text{—}CH_2\\CH_2\cdot CHMe\end{matrix}>C{:}CH\cdot CO_2H$	11·5	0·15	50 hrs.
 $CH_2<\begin{matrix}CH_2\text{—}CH_2\\CHMe\cdot CH_2\end{matrix}>C{:}CH\cdot CO_2H$	9	0·27	26 hrs.
 $CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C{:}CH\cdot CO_2H$	7	0·42	17 hrs.
 $\begin{matrix}CH_2\cdot CH_2\\ \vert \\ CH_2\cdot CH_2\end{matrix}>C{:}CH\cdot CO_2H$ (Goldberg & Linstead)	14	22·0	25 mins.
 $\begin{matrix}CH_2\cdot CH_2\\ \vert \\ CH_2\cdot CH_2\end{matrix}>C{:}CMe\cdot CO_2H$	38	0·58	14 hrs.

Again, the introduction of a methyl group in the *cyclo*hexane ring has a general slight retarding effect on the mobility, as would be expected, but it has practically no effect on the position of equilibrium which is displaced towards the βγ-side to a slight extent; this displacement should be greatest in the ortho-compound where the methyl group occupies the γ-position with respect to the three-carbon system itself (compare Linstead, J., 1929, 2498), whilst the meta- and para-substituents merely serve to lengthen the substituent chain, but the facts point to the reverse order, $p>m>o$.

Ketones.—All the βγ-unsaturated ketones studied had been previously obtained, but with the exception of α-methyl*cyclo*pentylideneacetone (Bardhan, J., 1928, 2591) their αβ-isomerides were unknown. Unfortunately, all attempts to prepare the α- and *o*-methyl*cyclo*hexane compounds failed, the βγ-forms being invariably obtained, although the 3- and 4-*methyl*cyclo*hexylideneacetones* were readily prepared by standard methods. For this reason, it was impossible to determine their mobility and point of equilibrium, but it must be assumed that the latter is practically coincident with that of the pure βγ-ketone in both cases because the pure ketones show no change in physical properties or iodine addition after prolonged treatment with sodium ethoxide. The mobility of the ortho-methyl ketone must be fairly high because it undergoes the Michael reaction with ethyl sodiomalonate, a behaviour which is usually taken as proof of the existence of an αβ-phase. The α-methyl compound failed to condense with ethyl sodiomalonate but considerable difficulty was also experienced with α-methyl*cyclo*pentylideneacetone, which is stable in its αβ-phase—the mobility of this ketone has been definitely demonstrated. It must also be remembered that the entirely analogous α-ethyl*cyclo*hexenylacetone does actually condense with ethyl sodiomalonate (Kon and Narayanan, J., 1927, 1536), so the present failure to effect condensation of the α-methyl ketone must be attributed to conditions rather than to complete lack of mobility on the part of the ketones.

The equilibration of the remaining pairs of ketones has been carried out under the standard conditions of Kon and Linstead (J., 1929, 1269) with the results shown in Table II. The mobility of the meta-methyl ketones has not been determined owing to lack of material, but it appears to be of the same order as that of the para-compound and the parent substance. The point of equilibrium of the para-compound is somewhat uncertain. Values corresponding with about 13% of αβ were obtained from the αβ-side with sodium *iso*propoxide, and also with sodium ethoxide from the βγ, the latter being regarded as the more trustworthy by Kon and Linstead (*loc. cit.*), but more prolonged treatment of both ketones with sodium ethoxide leads to mixtures of apparently high αβ-content (nearly 20%); this is probably due to somewhat rapid addition of the elements of ethyl alcohol to the αβ-ketone.

TABLE II.

Ketone (αβ-form shown).	% αβ at equilibrium.	Mobility.
 $CH_2<\substack{CH_2-CH_2\\ CHMe\cdot CH_2}>C{:}CH\cdot COMe$	25	—
 $CHMe<\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}>C{:}CH\cdot COMe$	13·5	600—700
 $CH_2<\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}>C{:}CH\cdot COMe$	30 (Kon and Linstead)	700
 $\substack{CH_2\cdot CH_2\\ \vert\\ CH_2\cdot CH_2}>C{:}CMe\cdot COMe$	64	3000
 $\substack{CH_2\cdot CH_2\\ \vert\\ CH_2\cdot CH_2}>C{:}CH\cdot COMe$	About 75 (estimated, cf. Kon, this vol., p. 1616).	3000

It will be seen that the introduction of an α-methyl group displaces the equilibrium towards the βγ-side in both *cyclo*hexane and *cyclo*pentane ketones (as it does in the homomesitones; Abbott, Kon, and Satchell, *loc. cit.*), that is, its effect is the reverse of that observed in the acids. It does not appear to affect mobility to a great extent, at any rate in the *cyclo*pentane series, a fact for which we cannot at present offer any explanation. The effect of the methyl group in the meta- and the para-position of the *cyclo*hexane ring is, as would be expected, not very pronounced; but in the ortho-position it appears to exercise considerable influence in the stabilisation of the βγ-phase to the almost complete exclusion of the αβ (compare above), such an effect being in agreement with the prediction based on the electronic hypothesis (compare Linstead, *loc. cit.*).

When these observations are compared with those made on the acids, striking differences are revealed, especially with regard to the effect of the α- and the ortho-methyl group. The former greatly depresses the mobility of the acid and favours the αβ-phase; it favours the βγ-phase in ketones, whilst its effect on mobility is uncertain. The ortho-methyl group has little effect in the acids and favours the βγ-phase in the ketones.

It is necessary to emphasise the fact that the same positive substituent can produce two totally opposed effects according to whether it is introduced into an acid or a ketone of otherwise analogous structure. It remains to be discovered whether acids, owing to the presence of a permanent free pole, constitute a group apart, and whether general rules connecting structure with tautomerism can be laid down, for example, to cover all other tautomeric compounds (esters, nitriles, ketones, etc.).

EXPERIMENTAL.

A. *Acids.*

α-Methyl Acids.—(1) α-*cyclo*Hexylidenepropionic acid was obtained as described by Auwers and Ellinger (*Annalen*, 1911, **387**, 230). The solid acid was accompanied by a liquid which was a mixture of the above acid with its βγ-isomeride. The αβ-acid could be separated from this in the pure state by the method of Bougault (*Ann. Chim. Phys.*, 1908, **14**, 145), but the best results were achieved by partially esterifying the acid mixture. The original conditions used by Eccott and Linstead (J., 1929, 2153) were somewhat modified; for 1 g.-mol. of mixed acids only 460 c.c. of alcohol and 200 c.c. of *N*-alcoholic hydrogen chloride were used and found to give satisfactory results in all cases; the method of working up the product was the same. The time required varied in different experiments; in the present instance 24 hours were needed to produce the pure βγ-ester, whilst 72 hours were required when preparing pure αβ-acid, to ensure that all the βγ-acid present had been esterified. In this way 40 g. of liquid mixed acids (see above) gave 15 g. of βγ-ester, b. p. 103—104°/10 mm., 5 g. of a higher-boiling fraction probably containing the αβ-ester, and 15 g. of pure solid αβ-acid (Found in silver salt : Ag, 41·3. Calc. : Ag, 41·4%). The *anilide*, prepared through the acid chloride, formed needles from dilute methyl alcohol, m. p. 126° (Found : C, 78·5; H, 8·3. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·3%). The p-*toluidide*, similarly obtained, formed stout needles from methyl alcohol or benzene,

m. p. 161° (Found : C, 78·7; H, 8·6. $C_{16}H_{21}ON$ requires C, 79·0; H, 8·6%).

(2) α-Δ^1-*cyclo*Hexenylpropionic acid, previously obtained as a liquid by Auwers and Ellinger, solidified when pure on being cooled in a freezing mixture; m. p. 38° after crystallisation from pentane. The physical properties of the supercooled liquid differed somewhat from those recorded by Auwers and Ellinger : b. p. 120—124°/1 mm., $d_{4^\circ}^{20\cdot6^\circ}$ 1·0332, $n_D^{20\cdot6^\circ}$ 1·48405, $[R_L]_D$ 42·59 (Calc. : 42·75). The ethyl ester, prepared through the silver salt, was similar to theirs : b. p. 111°/19 mm., $d_{4^\circ}^{19\cdot7^\circ}$ 0·9660, $n_D^{19\cdot7^\circ}$ 1·4627, $[R_L]_D$ 51·90 (Calc. : 51·99).

The *anilide* formed needles, m. p. 123—124°, from methyl alcohol (Kandiah and Linstead's m. p. 56° is due to a misprint) (Found : C, 78·4; H, 8·1. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·3%). The p-*toluidide*, long, silky needles from ethyl acetate–petroleum, had m. p. 108° (Found : C, 79·0; H, 8·7. $C_{16}H_{21}ON$ requires C, 79·0; H, 8·6%).

For the analysis of mixtures of the two acids, Linstead and May's method (J., 1927, 2565) was used, and a reference curve constructed from the following values for additions of iodine in 10 mins. :

Mixture (% αβ)	100	90	75	50	25	15	10	0
Addition (%)	0	10·9	26·1	48·6	66·4	71·5	74·4	78·8

The accuracy of the curve was checked by two examples; mixtures containing 40% and 60% of αβ-acid had additions of 55·5 and 39·8 respectively (Calc. from curve, 56·1 and 39·7).

Equilibrations. A few experiments were carried out under Linstead's standard conditions but the change was extremely slow and the tubes employed underwent considerable corrosion after some 320 hours. Later experiments were carried out in copper flasks, stronger alkali and a higher temperature being used. Experiments were also made starting with mixtures of the two acids, the results being given in Table III.

TABLE III.

Acid.	% KOH.	Temp.	Time (hours).	Iodine addition, %.	αβ-Acid, %.
αβ	25	100°	80	5·1	94·3
,,		,,	320	11·1	90·0
,,	36·6	B. p.	43·5	22·5	79·0
,,	,,	,,	97	46·9	51·5
,,	35·6	,,	139	62·6	30·5
βγ	36·6	,,	102	72·7	12·5
,,	,,	,,	168	60·4	34·0
50·1 βγ 49·9 αβ	,,	,,	72	60·9	33·0
69·7 βγ 30·3 αβ	,,	,,	146	62·6	30·5

The mean value for the point of equilibrium is thus 32% αβ. Only the first two experiments serve for the calculation of the mobility, which is approximately 0·0075.

2-*Methyl Acids*.—(1) 2-Methyl*cyclo*hexylideneacetic acid was obtained in needles, m. p. 68·5° after crystallisation from pentane. A liquid by-product was subjected to partial esterification (see above) and yielded more of the solid acid as well as some βγ-ester. The *amide*, prepared through the acid chloride, formed prisms from benzene–petroleum, m. p. 112° (Found : C, 70·3; H, 9·7. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%). The *anilide* formed small prisms from dilute methyl alcohol, m. p. 99° (Found : C, 78·1; H, 8·2. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·3%).

(2) 2-*Methyl*-Δ^1-cyclo*hexenylacetic acid*. The crude ester obtained by dehydrating the hydroxy-ester (from 2-methyl*cyclo*hexanone and ethyl bromoacetate) with phosphorus oxychloride had a somewhat low iodine addition of 60·5 in 30 minutes. It was hydrolysed in the cold with 5% alcoholic alkali, and the acid subjected to partial esterification for 4 hours. The resulting ester had b. p. 111—112°/18 mm., $d_{4^\circ}^{22\cdot8^\circ}$ 0·9655, $n_{\mathrm{D}}^{22\cdot8}$ 1·46529, $[R_L]_{\mathrm{D}}$ 52·18 (Calc. : 51·99), iodine addition 66·6% in 30 mins. The acid obtained from it had b. p. 106—108°/2 mm., $d_{4^\circ}^{21\cdot1^\circ}$ 1·0373, $n_{\mathrm{D}}^{21\cdot1^\circ}$ 1·48704, $[R_L]_{\mathrm{D}}$ 42·74 (Calc. : 42·75), iodine addition 80·8 (in 10 mins.); on repeating the esterification and hydrolysis an acid with an iodine addition of 84·7 was obtained, and solidified in a freezing mixture; m. p. 10—14° (Found in silver salt : Ag, 41·2. Calc. : Ag, 41·4%). A specimen of the pure βγ-acid was dissolved in cold sodium hydrogen carbonate solution, and the requisite amount of 3% potassium permanganate added. The filtered solution was evaporated to a small bulk, extracted with ether, acidified, and again repeatedly extracted with ether. The acid obtained on evaporation did not solidify; it was freed from a small amount of volatile acid (unchanged βγ) and esterified, fractions of b. p. 112—120°, 122—127°, 127—140°, and >140°, all at 13 mm., being obtained and separately hydrolysed. The highest fraction yielded an acid which did not solidify, gave a red colour with ferric chloride and was not identified; from all the other fractions some solid was obtained and this, on crystallisation from ethyl acetate, melted at 148—149° and proved to be adipic acid; the position of the double bond in the βγ-acid must therefore be Δ^1, otherwise an acid with a branched chain would have been formed.

The *amide* crystallised from dilute alcohol or benzene–petroleum in lustrous plates, m. p. 138° (Found : C, 70·4; H, 9·7. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%). The *anilide* crystallised from dilute alcohol or ethyl acetate–petroleum in long silky needles, m. p. 143° (Found : C, 78·5; H, 8·4. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·3%).

For the iodometric analysis of mixtures of the two acids a reference curve was constructed from the following values :

Mixture (% $\alpha\beta$)	100	90	75	50	25	10	0
Addition (% in 10 mins.)	0·5	10·5	25·3	47·8	65·8	79·6	84·7

Test mixtures : 5% $\alpha\beta$: Found 82·1. Calc. 82·2.
15% $\alpha\beta$: Found 76·3. Calc. 76·3.

Equilibrations. The following experiments were carried out under Linstead's standard conditions :

Acid.	Time (hours).	Iodine addition, %.	$\alpha\beta$-Acid, %.	Acid.	Time (hours).	Iodine addition, %.	$\alpha\beta$-Acid, %.
$\beta\gamma$	45	83·4	2·5	$\alpha\beta$	72	54·7	42·3
,,	69·5	80·7	7·5	,,	120	72·7	20·2
,,	168	78·9	11·0	,,	216	78·6	12·0
$\alpha\beta$	36	34·7	64·5	,,	312	78·7	11·6
,,	63	51·4	46·0				

The equilibrium value is therefore about 11·3%αβ. The mobility calculated from the above results is 0·15, and the half-change period 59 hours; the agreement between the observed and the calculated values is very close.

3-*Methyl Acids.*—(1) 3-*Methyl*cyclo*hexylideneacetic acid.* The acid as obtained by the dehydration of the corresponding hydroxy-acid was generally a liquid mixture of αβ- and βγ-acids and these could be separated by partial esterification as described on p. 2220. The purified αβ-acid solidified on standing in the cold for a few days and melted at 45—46°; its iodine addition was below 1%. After several crystallisations from hexane it formed silky needles, m. p. 90°, *i.e.*, much higher than that of Auwers and Ellinger's acid (*loc. cit.*). It would appear that the low-melting acid is a mixture of stereoisomerides.

The *amide* crystallised from ethyl acetate in silky needles, m. p. 143—144° (Found : C, 70·4; H, 9·8. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%). The p-*toluidide* crystallised from methyl alcohol in stellate clusters of needles, m. p. 136° (Found : C, 78·6; H, 8·4. $C_{16}H_{21}ON$ requires C, 79·0; H, 8·6%).

(2) 3-*Methyl*-Δ^1-cyclo*hexenylacetic acid* (?). The crude ester obtained by the dehydration of the corresponding hydroxy-ester with phosphorus oxychloride was hydrolysed and the acid subjected to partial esterification for 3—4 hours. The ester so obtained had b. p. 112°/17 mm., $d_{4^\circ}^{20\cdot5^\circ}$ 0·9530, $n_D^{20\cdot5^\circ}$ 1·4594, $[R_L]_D$ 52·28 (Calc. : 51·99), and its iodine addition in chloroform was 57·8% in 10 mins. On hydrolysis it gave an acid, b. p. 126°/2 mm., which immediately solidified on cooling and crystallised from hexane in large laminæ, m. p. 38°. A specimen of the acid was oxidised exactly as described on p. 2222. A very small quantity (insufficient for identification) of a solid melting at 94—98° was isolated, probably consisting of

β-methyladipic acid. The accompanying gum was esterified and the ester re-hydrolysed, but a solid could not be obtained. The formation of β-methyladipic acid would point to the presence of the Δ^6-acid. It is hoped to determine the structure of the solid βγ-acid in the near future.

For the analysis of the mixtures of the two acids a reference curve was made from the following values :

Mixture (% αβ)	100	90	80	75	50	25	0
Addition (% in 10 mins.) ...	1·2	10·2	18·6	21·8	37·8	48·2	53·8

It was found that the iodine addition of the βγ-acid varied considerably, erratic values being obtained with the same sample of the acid at different times. Titrations were carried out without previously acidifying the solutions, and different times (5—30 mins.) were tried without success. Bougault's method also failed because the formation of iodo-lactone from the βγ-acid was incomplete, and there was some reaction with the αβ-acid at the same time. The difficulty was finally overcome by utilising the fact that, as is generally found in such cases, the additions of mixtures containing a large proportion of the αβ-acid were reproducible and only mixtures of high βγ-content were erratic. The mixture (of high βγ-content) was mixed with a known quantity of pure αβ-acid, and the composition of the new mixture determined in the usual way; a simple calculation then gave the composition of the original mixture. It was found advisable to carry out several such experiments on one mixture as a check. The determination of composition of the equilibrium mixture will illustrate the procedure :

Equilibrated acid, %.	αβ-Acid added, %.	Iodine addition, %.	Total αβ content, from reference curve.	% αβ in equilibrated acid.
100	0	51·7	13·0	13·0
20	80	17·2	81·7	8·5
25	75	20·5	76·6	6·4
50	50	35·6	54·0	8·0

The equilibrium mixture thus appears to contain about 8% of αβ-acid.

Equilibrations. The following experiments were carried out under Linstead's standard conditions :

Acid.	Time (hours).	Iodine addition, %.	αβ-Acid, %.	Acid.	Time (hours).	Iodine addition, %.	αβ-Acid, %.
αβ	12	23·0	73·5	αβ	82·5 (at b. p.)	52·7	8·5
,,	24	33·8	57·0				
,,	40	42·7	39·0	βγ	80 (at b. p.)	51·7	10·2
,,	60	46·9	29·0				
,,	80	48·9	23·0				

The mobility calculated from these figures is 0·27, and the half-change period about 26 hours.

4-*Methyl Acids.*—(1) 4-Methyl*cyclo*hexylideneacetic acid had m. p. 66° after purification as in the previous case (Perkin, Pope, and Wallach, J., 1909, **95**, 1791). The p-*toluidide* crystallised from benzene–petroleum in clusters of needles, m. p. 119° (Found: C, 78·9; H, 8·6. $C_{16}H_{21}ON$ requires C, 79·0; H, 8·6%).

(2) 4-Methyl-Δ^1-*cyclo*hexenylacetic acid had m. p. 42—43° (Perkin, Pope, and Wallach, *loc. cit.*). The p-*toluidide* separated from benzene–petroleum in small needles, m. p. 111° (Found: C, 79·0; H, 8·7. $C_{16}H_{21}ON$ requires C, 79·0; H, 8·6%).

For the analysis of mixtures of the two acids a reference curve was constructed from the following values:

Mixture (% $\alpha\beta$)	100	90	75	50	25	10	0
Addition (% in 10 mins.) ...	0	8·9	19·2	31·6	41·1	45·3	48·6

Test mixture: 60% $\alpha\beta$: Found 27%. Calc. 26·7%.

The same difficulty in the titration of mixtures rich in $\beta\gamma$-acid was experienced as in the preceding case and was overcome by the same process. The values marked * in the table below were obtained in this way.

Equilibrations. The following experiments were carried out under Linstead's standard conditions, the last two on the $\beta\gamma$-acid and the others on the $\alpha\beta$-acid:

Time (hrs.).	Temp.	Iodine addition, %.	$\alpha\beta$-Acid, %.	Time (hrs.).	Temp.	Iodine addition, %.	$\alpha\beta$-Acid, %.
12	100°	26·2	61	48	B. p.	45·5	9, 8*
24	,,	34·8	42	86	,,	47·2	4·5, 6·3*
36	,,	39·5	29·5	168	100°		7·5*
48	,,	42·5	21·0	86	B. p.	46·1	7·5, 6·3*
24	B. p.	42·7	20·0, 19*	168	100		6·3*

The equilibrium values vary somewhat; the mean is about 7% $\alpha\beta$. The mobility calculated from these figures is 0·42; the calculated values agree very well with those actually found. The half-change period is 17 hours.

Five-membered-ring Acids.—(1) α-*Methyl*cyclo*pentylideneacetic acid* (Wallach and Martins, *Annalen*, 1909, **365**, 272). The crude acid obtained in the usual way was accompanied by a liquid from which more of the solid $\alpha\beta$-acid, together with some $\beta\gamma$-ester, was obtained by partial esterification.

(2) α-*Methyl*-Δ^1-cyclo*pentenylacetic acid.* The crude acid, obtained as described by Bardhan (*loc. cit.*), was subjected to partial esterification for 38 hours at room temperature; the mixture was then gently warmed for 2 or 3 hours; 112 g. of acid gave 100 g. of pure ester, and 16 g. of $\alpha\beta$-acid were recovered. The ester had b. p. 82—83°/10 mm., $d_{4°}^{18·4°}$ 0·9616, $n_D^{18·4°}$ 1·45393, $[R_L]_D$ 47·35 (Calc.: 47·37), and an iodine addition of 84·9% in 30 mins. The

ester was hydrolysed in the usual way; the pure acid had b. p. 113—115°/1 mm., $d_{4°}^{19·4°}$ 1·0366, $n_{D}^{19·4°}$ 1·47497, $[R_L]_D$ 38·05 (Calc. 38·13); it had a remarkably high iodine addition (96·1%).

A reference curve for the analysis of mixtures of the two acids was constructed from the following values :

Mixture (% αβ)	100	90	75	50	25	10	0
Addition (% in 10 mins.) ...	1·5	12·6	29·3	56·4	77·9	89·3	96·1

Test Mixtures : 40% αβ : Found 65·4. Calc. from curve, 65·2.
60% αβ : Found 46·7. Calc. from curve, 45·8.

Equilibrations. The following experiments were carried out under Linstead's standard conditions :

Acid.	Time (hours).	Temp.	Iodine addition, %.	αβ-Acid, %.
αβ	12	100°	32·3	72·2
,,	20	,,	54·3	52·0
,,	60	,,	62·7	43·0
,,	80	,,	64·0	41·5
,,	213	,,	65·0	40·5
,,	90	B. p.	64·8	40·0
βγ	12	100°	81·7	20·0
,,	24	,,	73·6	30·5
,,	40	,,	70·2	35·0
,,	60	,,	68·2	36·5
,,	213	,,	68·0	37·0
,,	90	B. p.	69·1	36·0

It will be seen that the values for the equilibrium reached from the two sides diverge somewhat; the mean value is 38% of αβ. The mobility calculated from these figures is 0·58, and the half-change period 14 hours.

B. *Ketones.*

α-Methyl-Δ^1-cyclo*hexenylacetone.*—All attempts to obtain the αβ-isomeride of this ketone by the Blaise–Maire or Grignard reaction were fruitless, although it was found that the αβ-acid chloride was readily obtained and gave the original solid acid on treatment with dilute sodium carbonate. In all cases the *same* ketone, identical with that obtained by Kon (J., 1926, 1792), was produced in fair yield. The properties of the ketone regenerated from the pure semicarbazone by means of oxalic acid agreed with those already published; the iodine addition (in chloroform solution) was 97·4% in 10 mins. and 85·3% in 5 mins.

The pure ketone was warmed on the steam-bath for 3½ hours with an excess of 1·4*N*-sodium ethoxide; it was then recovered and found to have the same physical properties and iodine addition (97·0% in 10 mins.; 85·6% in 5 mins.); another specimen was kept at room temperature with excess of *N*-sodium ethoxide but was also recovered unchanged.

The ketone (10 g.) was heated for a week with 10 g. of ethyl malonate and 1·5 g. of sodium in 45 c.c. of alcohol. On being worked up in the usual way, about 3 g. of a brown, viscous mass, giving a red colour with ferric chloride, were obtained, but this could not be induced to crystallise; a crystalline dihydroresorcinol could not be obtained from it on hydrolysis with potassium hydroxide.

2-*Methyl*-Δ^1-cyclo*hexenylacetone*.—This ketone was prepared by condensing 2-methyl*cyclo*hexanone with acetone as described by Wallach (*Annalen*, 1912, **394**, 383), and was also synthesised by the Blaise–Maire reaction from 2-methyl-Δ^1-*cyclo*hexenylacetyl chloride (b. p. 105—107°/18 mm.) and zinc methyl iodide by using the modified process described by Dickins, Hugh, and Kon (J., 1928, 1630). The ketone was exactly the same in both cases; the semicarbazone on recrystallisation melted at 168° (Wallach gives m. p. 173—174°) in each case and so did a mixture of the two. This establishes the position of the double bond in Wallach's ketone as Δ^1. The ketone regenerated from the semicarbazone had properties agreeing with Wallach's (b. p. 102°/15 mm., $d_{4°}^{20\cdot9°}$ 0·9333, $n_D^{20\cdot9°}$ 1·4774, $[R_L]_D$ 46·09) and an iodine addition of 91·4%.

All attempts to prepare the αβ-isomeride from 2-methyl*cyclo*hexylideneacetyl chloride failed, the same βγ-ketone being obtained, although the pure αβ-acid could be regenerated from the chloride on treatment with dilute sodium carbonate.

Both the synthetic βγ-ketone and that prepared by Wallach's method were recovered unchanged after 14 hours' treatment with excess of 1·5*N*-sodium ethoxide, no diminution in the iodine addition being observed. It must be assumed that the equilibrium mixture is indistinguishable from the pure βγ-ketone by the methods at our disposal.

The ketone was heated with ethyl sodiomalonate as described on p. 2226 for three days, and 1·2 g. of a solid condensation product were finally obtained; this crystallised from ethyl acetate–petroleum in silky needles, m. p. 134°, and consisted of *ethyl* 2-*methyl*cyclo*hexane*spirocyclo*hexane*-3 : 5-*dione*-6-*carboxylate* (Found : C, 67·3; H, 8·3. $C_{15}H_{22}O_4$ requires C, 67·7; H, 8·3%). Some unchanged ketone was also recovered from the neutral portion of the reaction product in the form of its semicarbazone, m. p. 168° (3 g.).

3-*Methyl Ketones*.—(1) 3-*Methyl*cyclo*hexylideneacetone*. A 40—60% yield of ketonic fraction, b. p. 95—96°/11 mm., was obtained from zinc methyl iodide and 3-methyl*cyclo*hexylideneacetyl chloride (b. p. 112°/12 mm.). This was converted into the sparingly soluble *semicarbazone*, which crystallised from methyl alcohol in plates, m. p. 191° (Found : C, 62·8; H, 9·0. $C_{11}H_{19}ON_3$ requires C, 63·2; H, 9·1%). The pure *ketone* was regenerated from it by Kon's method (this vol., p. 1616) and had b. p. 91—93°/6—7 mm., $d_{4^\circ}^{18\cdot3^\circ}$ 0·9235, $n_D^{18\cdot3^\circ}$ 1·48571, $[R_L]_D$ 47·27 (Calc. : 45·82). The αβ-structure of the ketone was confirmed by suspending it in ice-cold dilute sodium hydrogen carbonate and adding a slight excess of ice-cold 3% potassium permanganate solution with constant shaking. After separation of the manganese dioxide, the liquid was thoroughly extracted with ether and the extract on evaporation gave a ketonic residue which was treated with semicarbazide, the semicarbazone of 3-methyl*cyclo*hexanone being obtained and identified as usual.

(2) 3-*Methyl*-Δ^1-cyclo*hexenylacetone.* The βγ-acid (p. 2223) was converted into the acid chloride, b. p. 95°/11 mm., and this gave a 55% yield of ketonic fraction with zinc methyl iodide. The semicarbazone on crystallisation melted at 153—154° (Wallach, *loc. cit.*, gives m. p. 150°). The pure ketone regenerated by Kon's method had b. p. 86—88°/7—8 mm., $d_{4^\circ}^{16\cdot8^\circ}$ 0·9200, $n_D^{16\cdot8^\circ}$ 1·46986, $[R_L]_D$ 46·12 (Calc. : 45·82). The ketone was also prepared by Wallach's method (*loc. cit.*) and gave a semicarbazone identical with the above (m. p. and mixed m. p. 153—154°).

For the analysis of mixtures of the two ketones a reference curve was constructed from the following values :

Mixture (% αβ)	100	90	75	50	25	10	0
Addition (% in 10 mins.) ...	15·0	24·5	37·9	55·6	68·7	74·3	77·9

Equilibrations. Owing to the scarcity of the αβ-ketone, no measurements of mobility were made. The two ketones were kept with an excess of *N*-sodium ethoxide for 18 hours at 25° ; the product from the αβ-ketone had $d_{4^\circ}^{17\cdot7^\circ}$ 0·9216, $n_D^{17\cdot7^\circ}$ 1·47193, iodine addition 67·0 (= 28% αβ), that from the βγ had $d_{4^\circ}^{17\cdot7^\circ}$ 0·9213, $n_D^{17\cdot7^\circ}$ 1·47212, iodine addition 68·9 (= 24·5% αβ). The treatment was repeated but practically identical values were obtained. The value reached from the βγ-side (about 25% αβ) is regarded as the more trustworthy (compare Kon and Linstead, *loc. cit.*).

Condensation with ethyl sodiomalonate. The βγ-ketone was condensed with ethyl sodiomalonate as described above, but the product did not solidify. It was therefore hydrolysed to 3-*methyl*-cyclo*hexane*spirocyclo*hexan*-3 : 5-*dione*, which solidified on being kept in a vacuum and crystallised from ethyl acetate–petroleum, m. p. 135—136° (Found : C, 73·9 ; H, 9·2. $C_{12}H_{18}O_2$ requires C, 74·2 ; H, 9·4%).

4-*Methyl Ketones.*—(1) 4-Methyl*cyclo*hexylideneacetone was prepared exactly as the 3-methyl compound. The *semicarbazone* crystallised from methyl alcohol in plates, m. p. 176—177° (Found : C, 63·1 ; H, 9·1. $C_{11}H_{19}ON_3$ requires C, 63·2 ; H, 9·1%). The ketone regenerated from it by Kon's method had b. p. 94°/9 mm.,

$d_{4°}^{16·8°}$ 0·92694, $n_D^{16·8°}$ 1·48594, $[R_L]_D$ 47·11 (Calc.: 45·82). In some preparations a semicarbazone was obtained, melting after repeated crystallisation at 145°; the ketone regenerated from it had properties very similar to the above, and its iodine addition (12·9%) also agreed with an αβ-structure; the semicarbazone is thus analogous to the low-melting form of *cyclo*hexylidenemethyl ethyl ketone semicarbazone (Dickins, Hugh, and Kon, *loc. cit.*; compare Abbott, Kon, and Satchell, *loc. cit.*).

The structure of the new ketone was confirmed by oxidation to 4-methyl*cyclo*hexanone exactly as described on p. 2228.

(2) 4-Methyl*cyclo*hexenylacetone was prepared from the corresponding acid (yield 50—55%) and converted into the semicarbazone, m. p. 125—126° (Wallach gives m. p. 122—123°). The ketone regenerated by Kon's method had b. p. 85°/8 mm., $d_{4°}^{16·3°}$ 0·9178, $n_D^{16·3°}$ 1·46836, $[R_L]_D$ 46·10 (Calc.: 45·82).

For the analysis of mixtures of the two ketones a reference curve was constructed from the following values:

Mixture (% αβ)	100	90	75	50	25	10	0
Addition (% in 10 mins.) ...	8·35	20·3	35·3	57·6	71·9	77·8	80·6

Test Mixtures: 40% αβ: Found 64·4. Calc. from curve 64·0.
60% αβ: Found 49·7. Calc. from curve 49·4.

Equilibrations. The following experiments were carried out under Kon and Linstead's standard conditions. The physical properties of the equilibrated ketones were also determined as a check but are not quoted.

Ketone.	Time (mins.).	Iodine addition, %.	αβ-Ketone, %.	Ketone.	Time (mins.).	Iodine addition, %.	αβ-Ketone, %.
αβ	10	51·9	57·0	βγ	10	78·2	9·0
,,	20	65·1	37·5	,,	20	76·8	13·5
,,	30	70·2	29·0	,,	30	76·8	13·5

The combined material from the first three experiments and also that from the second three experiments were treated for 4 hours with excess of sodium ethoxide; the products had additions of 73·5 (= 21·5% αβ) and 74·6 (= 19% αβ) respectively. Similar experiments with sodium *iso*propoxide (3 hours) gave additions of 76·9 (= 13% αβ) and 74·3 (= 19·8% αβ) (see p. 2219). The mobility can only be calculated approximately and varies from 600 to 700.

Condensation with ethyl sodiomalonate. The βγ-ketone was condensed with ethyl sodiomalonate as in previous cases, the mixture being heated over-night. The ester formed in good yield did not solidify and was therefore hydrolysed to 4-*methyl*cyclo*hexane*spirocyclo*hexane*-3 : 5-*dione*, which crystallised from ethyl acetate in clusters of small needles, m. p. 168° (Found: C, 74·1; H, 9·2. $C_{12}H_{18}O_3$ requires C, 74·2; H, 9·4%).

Five-membered-ring Ketones.—(1) *α-Methyl*cyclo*pentylideneacetone.* The semicarbazone of this ketone was prepared as described by Bardhan (*loc. cit.*). The lower-melting form when repeatedly crystallised from a *large* quantity of methyl alcohol gave crystals of the higher-melting form; mixtures of the two melted at intermediate temperatures. The lower-melting form was converted by Kon's method into the ketone, which had properties practically identical with those of the ketone described below; a portion of it was reconverted into the semicarbazone and this on crystallisation from much methyl alcohol gave the higher-melting form. The pure αβ-ketone was obtained from the latter by Kon's method and had b. p. 95·5—96°/11 mm., $d_{4^\circ}^{19\cdot0^\circ}$ 0·9601, $n_D^{19\cdot0^\circ}$ 1·49737, $[R_L]_D$ 42·12 (Calc.: 41·22); the exaltation of the molecular refraction is somewhat higher than that found by Bardhan, whose specimen had been regenerated by means of hot aqueous oxalic acid. The smell of the ketone is remarkably like that of the homomesitone, CMeEt:CMe·COMe (Abbott, Kon, and Satchell, *loc. cit.*).

(2) *α-Methyl-Δ¹-*cyclo*pentenylacetone.* The semicarbazone of this ketone, m. p. 144° (Bardhan, *loc. cit.*), gave the pure ketone by Kon's method; b. p. 74°/10 mm., $d_{4^\circ}^{19\cdot0^\circ}$ 0·9216, $n_D^{19\cdot0^\circ}$ 1·4635, $[R_L]_D$ 41·32 (Calc.: 41·22). The smell of this ketone is camphoraceous and reminiscent of the homomesitone, CHMe:CMe·CHMe·COMe.

For the analysis of mixtures of the two ketones a reference curve was constructed from the following values:

Mixture (% αβ)	100	90	75	50	25	10	0
Addition (% in 10 mins.) ...	5·4	14·9	29·2	53·3	77·3	88·5	93·6

Test Mixtures: 40% αβ: Found 62·7. Calc. from curve 62·8.
60% αβ: Found 44·0. Calc. from curve 43·6.

Equilibrations. The following experiments were carried out under Kon and Linstead's standard conditions. The physical properties of the equilibrated ketone were also determined as a check but are not quoted.

Ketone.	Time.	Iodine addition, %.	αβ-Ketone, %.	Ketone.	Time.	Iodine addition, %.	αβ-Ketone, %.
αβ	5 mins.	31·8	72·0	βγ	30 mins.	40·0	63·8
,,	3 hrs.	37·5	66·5	,,	45 ,,	39·4	64·5
,,	24 ,,	39·5	64·3	,,	75 ,,	39·7	64·0
βγ	5 mins.	53·7	49·5	,,	24 hrs.	39·7	64·0
,,	15 ,,	40·9	62·5				

The equilibrated ketone was analysed (Found: C, 78·2; H, 10·2. Calc.: C, 78·2; H, 10·2%).

The point of equilibrium is thus 64% αβ; the mobility calculated from these figures is about 3000.

Condensation with ethyl sodiomalonate. Bardhan was unable to effect this condensation; after 4 days' heating (starting with equilibrated ketone), we isolated a small amount of oily ester which gave on hydrolysis cyclo*pentane*spiro-2-*methyl*cyclo*hexane*-3 : 5-*dione*, m. p. 118—119° after crystallisation from ethyl acetate–petroleum (Found : C, 73·2 ; H, 8·9. $C_{11}H_{16}O_2$ requires C, 73·3 ; H, 8·9%).

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