CCCXLI.—*The Quantitative Estimation of Mixtures of Isomeric Unsaturated Compounds. Part II. Iodometric Methods.*

By REGINALD PATRICK LINSTEAD and CECIL JOHN MAY.

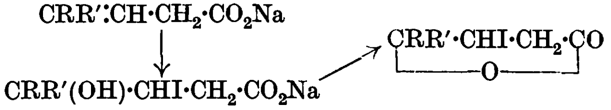
RAPID and quantitative addition of halogens to unsaturated substances is known to be prevented if the double bond is in the αβ-position with respect to a negative group. In the case of iodine this prevention has been observed with a variety of compounds and is responsible for the low " iodine numbers " sometimes obtained.

For mixtures of isomerides of the type $CHRR_1{\cdot}CH{:}CHX$ (αβ) + $CRR_1{:}CH{\cdot}CH_2X$ (βγ), where X is CO_2H, CO_2R, COR, or other negative group, the velocity of addition of halogen depends on the proportion of the isomerides present, and a bromine addition method for the analysis of such mixtures, based on this principle, has been described (this vol., p. 355). The present communication deals with the application of iodometric methods for the same purpose.

I. *Acids.*

Iodine may be added to unsaturated acids in the form of the chloride (Hübl, Wijs), the bromide (Hanus), or as hypoiodous acid (Margosches, Bougault). In the present work these methods were tested by means of mixtures of two representative unsaturated acids, Δ^1-*cyclo*hexenylacetic acid (βγ) and *cyclo*hexylideneacetic acid (αβ). The αβ-acid showed a much lower reactivity in every case, but the methods did not yield uniformly satisfactory results. Under the conditions of Hübl and of Wijs the end-point in the back titrations was not clearly marked. The use of nascent hypoiodous acid from iodine, moist ether, and mercuric oxide (Bougault) was unsatisfactory for quantitative measurements. The method of Margosches and his collaborators (*Ber.*, 1924, **57**, 996) was of value when a high velocity of reaction was required (see p. 2569). In general, the sodium salt method of Bougault was most satisfactory (*Compt. rend.*, 1904, **139**, 864; *Ann. Chim. Phys.*, 1908, **14**, 145).

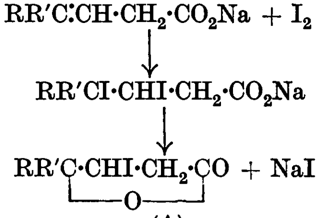
Bougault observed that when iodine in aqueous potassium iodide was added to unsaturated acids in sodium bicarbonate solution, αβ-acids were apparently unchanged whilst βγ-acids reacted to give as final products β-iodo-γ-lactones (I). Ponzio and Gastaldi (*Gazzetta*, 1912, **42**, ii, 92) suggested that αβ-acids react extremely slowly under these conditions, and their view has now been confirmed. The difference between the reactivities of the isomerides, however, is large and hence the reaction, as suggested by Bougault, is of value for analytical purposes. According to Bougault the reaction of the βγ-acids takes place by the addition of nascent hypoiodous acid; which must involve the formation of the intermediate (II).



(II.) (I.)

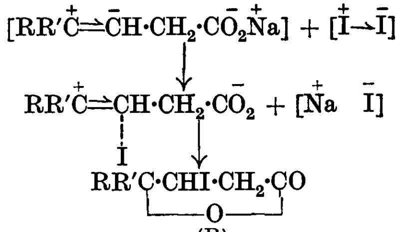
$$\begin{array}{c} CRR'{:}CH{\cdot}CH_2{\cdot}CO_2Na \\ \downarrow \\ CRR'(OH){\cdot}CHI{\cdot}CH_2{\cdot}CO_2Na \end{array} \nearrow \underbrace{CRR'{\cdot}CHI{\cdot}CH_2{\cdot}CO}_{O}$$

Whilst the present work is not claimed to represent a full study of this reaction, the mechanism suggested above cannot be passed without comment. In the first place addition of this type would involve an exceptionally high velocity coefficient for the reaction, account being taken of the facts that the formation of lactone is often extremely fast and the concentration of hypoiodous acid in the presence of the excess of sodium bicarbonate is very small (compare Francis, *J. Amer. Chem. Soc.*, 1925, **47**, 2340). Again, the sodium salt of a γ-hydroxy-acid such as (II) should show no tendency to lactonise in alkaline solution. We suggest that the mechanism of the reaction is represented either by (A) or by (B), which is a modification of (A) based on the views of Francis (*loc. cit.*) on bromine addition, the first stage being the addition of positive iodine to the negative β-carbon of the ionised salt.*



$$\begin{array}{c} RR'C{:}CH\cdot CH_2\cdot CO_2Na + I_2 \\ \downarrow \\ RR'CI\cdot CHI\cdot CH_2\cdot CO_2Na \\ \downarrow \\ RR'\underbrace{C\cdot CHI\cdot CH_2\cdot CO}_{O} + NaI \end{array}$$

(A)



$$\begin{array}{c} [RR'\overset{+}{C}\rightleftharpoons\overset{-}{C}H\cdot CH_2\cdot C\overset{-}{O_2}\overset{+}{Na}] + [\overset{+}{I}\rightarrow\overset{-}{I}] \\ \downarrow \\ RR'\overset{+}{C}\rightleftharpoons\underset{I}{C}H\cdot CH_2\cdot\overset{-}{CO_2} + [\overset{+}{Na}\quad\overset{-}{I}] \\ \downarrow \\ RR'\underbrace{C\cdot CHI\cdot CH_2\cdot CO}_{O} \end{array}$$

(B)

The velocity of addition *inter alia* would be inversely proportional to the concentration of the salt of the di-iodo-acid (or its ionic equivalent) and would therefore be greatest when this was most rapidly removed as the insoluble lactone. The lack of reactivity of the $\alpha\beta$-acids can thus be attributed in part to the instability of the α-iodo-β-lactones which would be formed as final products. Recent investigations have shown that the presence of two β-substituents has a stabilising influence on the β-lactone ring and facilitates its formation, as anticipated by the Thorpe–Ingold modification of the Baeyer theory (private communication from Mr. S. F. Biggs). It is therefore to be expected that addition of iodine to $\alpha\beta$-acids may be appreciable in the case of $\beta\beta$-disubstituted acids. We find that with a large excess of iodine under the conditions of Bougault, *cyclo*hexylideneacetic acid gives 32% addition in 24 hours, while with equivalent amounts of reagents the reaction occurs to the extent of some 1% per hour.

The method described by Bougault (*loc. cit.*), which depends on the actual isolation and weighing of unchanged acid ($\alpha\beta$) and of iodo-lactone, gives only approximately correct figures, as it is not possible to obtain complete reaction of the $\beta\gamma$-acid without some conversion of the $\alpha\beta$. In addition, β-iodo-lactones are unsatisfactory substances for quantitative estimation owing to the ease with

---

* We are indebted to Professor R. Robinson, F.R.S., for this suggestion.

which the iodine atom is displaced by hydroxyl. The following methods of analysis give satisfactory results.

(1) *When the pure isomeric acids are available.* The reaction of iodine with the mixed sodium salts is carried out as described in the experimental portion of this paper. The use of the concentrations suggested by Bougault leads to irregular results and in general the presence of an excess of iodine is detrimental. The most satisfactory results are obtained by using equivalent quantities of *N*/20-iodine and *N*/15-acid (against alkali). A curve connecting composition and percentage addition of iodine is constructed as described in Part I and the compositions of unknown mixtures are found by reference to it. This method is more convenient than that involving bromine addition and the absence of substitution reactions renders it more accurate. The experimental error does not exceed 1%.

(2) *When the isomeric acids cannot be isolated in the pure state.* With certain acids (see *e.g.*, Kon and May, this vol., p. 1549) it is either impossible to obtain definite evidence of homogeneity or else no methods are available for the complete separation of the isomerides, and the interpolation method can no longer be used. In these circumstances the separation method of Bougault has been applied to obtain the value for the position of equilibrium in the *cyclo*heptylideneacetic acids (Kon and May, *loc. cit.*), and the figure so obtained remains to be checked by the more accurate method now available. Attempts were also made to isolate pure di*iso*butylacrylic acid from mixtures by this method, but very little was obtained owing to the velocity of reaction of the αβ-acid with iodine. It has now been found possible to apply a correction for this source of error, which prevents the direct determination of the iodine taken up by the βγ-acid. The extrapolation method described below takes advantage of the *relatively* small reaction of an αβ-acid in mixtures containing its isomeride.

If iodine absorption is plotted against time for a pure βγ-acid, the curve will be that of an ordinary bimolecular reaction, ultimately becoming asymptotic to the line of 100% addition. The curve for the αβ-isomeride will follow the same general course, but over the period during which βγ-addition goes to completion it will approximate to a straight line. For a mixture of the two acids, the curve will resemble that for the pure βγ-acid, but instead of becoming asymptotic to a line parallel to the time axis it will continue along a line representing the αβ-addition after all the βγ-acid has reacted. If, therefore, this rectilinear portion of the curve is continued back to meet the axis, the point of intersection will represent the addition due to the βγ-acid alone. Or, if a_1 and a_2 are the addition values after times t_1 and t_2, then βγ-addition $= a_1 - t_1 (a_2 - a_1)/(t_2 - t_1)$.

It is, of course, only a first approximation to assume that the rate of $\alpha\beta$-addition remains constant during the progress of the $\beta\gamma$-reaction : actually it progressively decreases. The error involved, however, is not large if the conditions of experiment are carefully controlled. To test the accuracy of results so obtained, a series of titrations was carried out with mixtures of Δ^1-*cyclo*hexenyl- and *cyclo*hexylidene-acetic acids of known composition; the curves are shown in Fig. 2.

The strengths of the solutions and the details of the titrations are similar to those described in the experimental portion of this paper for the interpolation method (p. 2573). For a given mixture, four or five determinations of iodine addition must be made at accurately known intervals of time. The following additional features require attention.

(i) In general, the time for complete reaction lies between 2 and 3 hours, provided that the amount of $\beta\gamma$-acid is not above 50% and that the theoretical amount of iodine for 100% addition has been added. Sometimes, however, strict adherence to these conditions makes it necessary to extend the titrations for an inconveniently long time. The period may be shortened by employing an excess of iodine, but this device leads to the occurrence of side reactions. The necessary increase in reaction velocity may be brought about by applying the method of Margosches (*loc. cit.*), which eliminates potassium iodide by using alcoholic solutions of iodine. The retarding influence of potassium iodide on the reaction velocity is clearly shown by the following figures for the reaction with hydrosorbic acid ($CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$) : Solutions of 0·0696 g. ($0{\cdot}61 \times 10^{-3}$ g.-mol.) of the unsaturated acid in 10 c.c. of saturated bicarbonate solution and of 0·1580 g. ($0{\cdot}613 \times 10^{-3}$ g.-mol.) of iodine in 25 c.c. of 50% ethyl alcohol were added in the order named to 10 c.c. of water containing a definite quantity of potassium iodide. The % reactions were :

KI (g.-mol. × 10^{-3}) ...	0	0·157	0·314	0·470	0·784	0·941	1·157
% Addition in 10 mins.	54·4	48·2	43·2	40·6	36·2	34·0	32·8

The occurrence of side reactions is not eliminated by this modification, for the curve for the pure $\beta\gamma$-acid shows a noticeable rise above 100% absorption. This does not appear to affect the results appreciably and it would seem that the effects of the side reaction are eliminated by the process of extrapolation employed.

(ii) While it is necessary to use sufficient iodine to ensure the virtual completion *of the $\beta\gamma$-reaction* within a reasonable time, any considerable excess over this amount is to be avoided; the amount of iodine used may therefore be reduced below the theoretical quantity for complete reaction of both acids, provided that an excess of 10—20% above that required for complete βγ-addition is used. The requisite amount can be determined by carrying out a rough preliminary examination of the mixture.

(iii) The most satisfactory method of conducting the experiments is to mix the acid and iodine solutions in bulk and to remove aliquot portions for titration at definite times. This can, however, only be done when the lactone formed is soluble in the particular solution employed. Otherwise there is a tendency for the precipitated lactone to carry down iodine, and it becomes necessary to prepare a number of separate solutions, similar in all respects, each one being titrated as a whole. Iodine occluded in this way does not harm the accuracy of each individual titration, as the lactone is dissolved by the chloroform which is first added.

The application of this method to the determination of the tautomeric equilibria in the dipropyl- and di*iso*butyl-acrylic acids is described on p. 2575.

II. *Neutral Substances.*

The substances examined were ketones and esters, but the methods employed should be applicable to nitriles, substituted esters such as cyano-esters, and probably to olefines containing a phenyl substituent. These compounds were known to add on halogens much more readily than the corresponding acids and it was therefore necessary to find considerably milder reaction conditions. In the first place, the use of bromine in an inert solvent was tried at lower concentrations than those used for the acids (Part I, *loc. cit.*). This work was carried out on the isomeric ketones (III) and (IV) and it was only under extremely mild conditions that the addition to the βγ-ketone (III) was sufficiently slow to be measured. The reference figures for the pure ketones being known, the equilibrium between them was studied :

$$\text{(III.) CHMe:CEt·CH}_2\text{·COMe} \rightleftharpoons \text{CH}_2\text{Me·CEt:CH·COMe (IV.)}$$

It has been shown (Kon and Linstead, J., 1925, **127**, 815) that this interconversion occurs in cold sodium ethoxide solution, the extent of the change in 28 hours being 15% βγ ⟶ αβ and 35% αβ ⟶ βγ. It is now found, by the bromine method of analysis, that equilibrium is attained in about 30 hours and is approximately 14% αβ-ketone ⇌ 86% βγ-ketone. The experimental error, however, is high, at least 2%, and a redetermination by the more accurate iodine chloride method given below has not yet been possible owing to lack of material.

Use of Iodine Chloride.—The well-known Hübl method for the determination of iodine numbers may be modified to give satisfactory results. It has been applied in a number of cases, but only three, namely, ethyl styrylacetate ($CHPh{:}CH{\cdot}CH_2{\cdot}CO_2Et$), ethyl *cyclo*hexylideneacetate, and ethyl Δ^1-*cyclo*hexenylacetate, will be described. As in the Hübl method, the unsaturated substance or mixture of substances is allowed to react with iodine chloride prepared from mercuric chloride and iodine in alcoholic solution. The concentrations of the reagents are, however, lower than those under Hübl's conditions and the substances are brought together in equivalent amounts. When the pure isomerides are available, an addition curve is constructed in the usual way and the composition of an unknown mixture is determined by reference to it. The experimental procedure for this method is given on p. 2578. In cases where the pure isomerides are not available the extrapolation method already described should be of value; we have, however, not yet tested it.

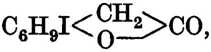
No evidence of the movement of the double bond in ethyl styrylacetate could be obtained by comparing its iodine figures before and after treatment with sodium ethoxide (compare Linstead and Williams, J., 1926, 2735), for the action of this agent led to partial hydrolysis and partial polymerisation.

Unlike ethyl styrylacetate, ethyl Δ^1-*cyclo*hexenylacetate shows no tendency to condense in the $\alpha\beta$-phase under the conditions of the Michael reaction and therefore it was not expected that sodium ethoxide would cause any tautomeric change in this ester. At 60°, however, the isomeric esters were readily interconvertible and analyses by the iodine chloride method indicated that an equilibrium was reached in the neighbourhood of 10% $\alpha\beta$-ester $\rightleftharpoons$ 90% $\beta\gamma$-ester; the equilibrium mixture derived from the $\alpha\beta$-ester was carefully hydrolysed and substantially pure $\beta\gamma$-acid obtained. The equilibrium figure is close to that (12% $\alpha\beta \rightleftharpoons$ 88% $\beta\gamma$) found for the corresponding acids in caustic alkali solution (Linstead, this vol., p. 2579). It would appear probable that the esters of mono-olefinic acids undergo a reaction analogous to the Fittig change. This does not seem to have been observed previously, although many examples of changes in unsaturated esters containing a second negative group have been recorded (compare Thorpe, J., 1905, **87**, 1670; Vorländer, *Annalen*, 1906, **345**, 244; Farmer, J., 1923, **123**, 3324). This branch of the work is being further investigated.

The iodine chloride addition method has now been used in a study of the pulegone $\rightleftharpoons$ *iso*pulegone change and is being used in that of other tautomeric ketones.

EXPERIMENTAL.

Materials.—The Δ^1-*cyclo*hexenyl- and *cyclo*hexylidene-acetic acids satisfied the usual criteria of purity. The $\beta\beta$-dipropylacrylic acid, ββ-di*iso*butylacrylic acid, and their isomerides were the original materials prepared by Kon and May (*loc. cit.*). The isomeric ethylhexen-β-ones (III and IV) were prepared by Kon and Linstead's method (*loc. cit.*) and had the following properties: βγ-Ketone, b. p. 70°/20 mm.; semicarbazone, m. p. 141° after one crystallisation. αβ-Ketone, b. p. 71°/18 mm.; semicarbazone, m. p. 156° without crystallisation. Ethyl styrylacetate, prepared by esterification of the pure acid, had b. p. 162°/24 mm. This ester underwent slow fission to benzaldehyde on standing and was redistilled immediately before use. Ethyl *cyclo*hexylideneacetate, prepared from the pure acid through the acid chloride (b. p. 104°/11 mm.), had b. p. 111°/16 mm. Ethyl Δ^1-*cyclo*hexenylacetate, made from the pure solid acid through the acid chloride (b. p. 86°/13 mm.), had b. p. 95°/14 mm. The iodine used was of analytical purity.

Reaction of the Isomeric cyclo*Hexenylacetic Acids with Iodine.*—(1) *Qualitative.* Excess of iodine in aqueous potassium iodide was added to a solution of the βγ-acid in aqueous sodium bicarbonate. A resinous oil was formed almost immediately, and after 5 minutes this was extracted with ether; the extract was washed with solutions of sodium thiosulphate and sodium carbonate and dried. The ether was removed cautiously, the last traces in a good vacuum; the residue slowly solidified. Subsequent preparations were readily induced to crystallise by seeding. The crude product was pressed on a porous tile and then boiled in ether with the addition of animal charcoal. The purified lactone, obtained by filtration and evaporation, was recrystallised from light petroleum, the *γ-lactone* of 1-*iodo*-2-*hydroxy*cyclo*hexylacetic acid*,  $C_6H_9I<\substack{CH_2\\O}>CO$, separating in white prisms, m. p. 58° (Found: C, 36·0; H, 4·3; I, 46·3. $C_8H_{11}O_2I$ requires C, 36·1; H, 4·2; I, 47·7%). It is soluble in organic solvents except cold light petroleum, insoluble in water and in alkali carbonate solutions, but soluble in caustic alkalis. The crude material has a strong characteristic smell, which is diminished by purification. Hot petroleum solutions develop a characteristic pink colour which is not due to the liberation of iodine. The liquefied lactone decomposes vigorously at 80—100° with the formation of free iodine.

When treated with iodine under similar conditions, the isomeric αβ-acid slowly formed an insoluble resin, which had a strong smell quite different from that of the preceding lactone and could not be obtained in a pure condition. The rate of reaction of the αβ-acid under these conditions was determined in the following experiments.

i. 0·4986 G. of the acid in 25 c.c. of saturated aqueous sodium bicarbonate was treated with 25 c.c. of iodine solution of Bougault's concentration (25 g. I_2, 40 g. KI, water to 125 c.c.). % Addition found: (in 2 hrs. 10 mins.) 7; (in 24 hrs.) 30, 34.

ii. $0{\cdot}7140 \times 10^{-3}$ G.-mol. of the acid in 10 c.c. of the bicarbonate solution was treated with $0{\cdot}6435 \times 10^{-3}$ g.-mol. of iodine in potassium iodide solution. % Addition found: (in 1 hr.) 1; (in 2 hrs.) 1·9; (in 2 hrs. 30 mins.) 2·7.

(2) *Quantitative.* When mixtures of the acids were treated under the analytical conditions described below, the product was a mixture of the 1-iodo-γ-lactone and the unchanged αβ-acid. The following experiments indicate the degree of completion of the separation. The mixed acids in known proportion (1—2 g.) were dissolved in some 15 c.c. of saturated sodium bicarbonate solution, and iodine (3 g.-atoms to 1 of acid) was added in potassium iodide solution of Bougault's concentration. After 1—2 hours, 4 c.c. of saturated sodium carbonate solution were added and the lactone was isolated in the manner already described. The αβ-acid was separated from the carbonate solution in the usual way and weighed. The weight of βγ-acid present in the mixture was calculated from the weight of crude lactone.

Mixture 1. Found: αβ-acid, 81·8; βγ, 19·6% (= 101·4%). Actual αβ-acid, 85%.

Mixture 2. Found: αβ-acid, 48·5; βγ, 47·7% (= 96·2%) Actual αβ-acid, 52·6%.

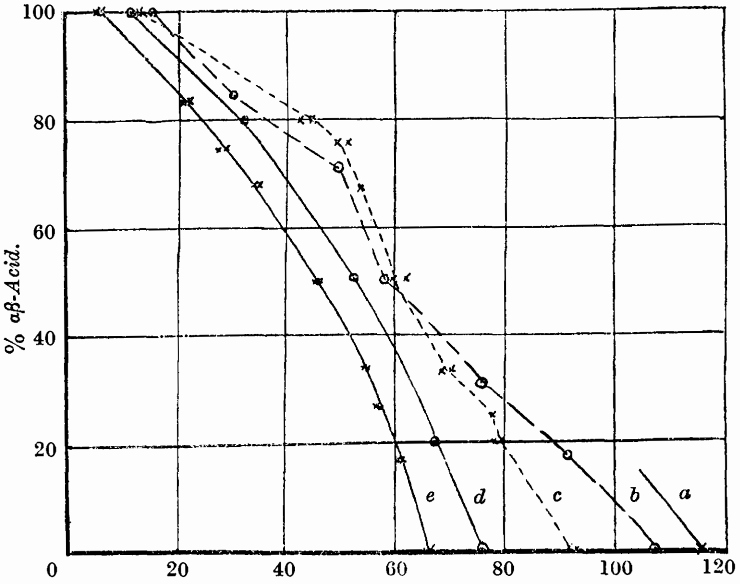
Mixture 3. Found: αβ-acid, 80·7; βγ, 24·3% (= 105%). Actual αβ-acid, 76·3%.

Titration Methods of Analysis.—(1) *By interpolation.* To find the most satisfactory conditions of reaction, various concentrations of the reagents were tried. The results are shown in Fig. 1. Curves *a*, *b*, and *c* were obtained on using 500, 250, and 100% excess of iodine respectively, and curves *d* and *e* on using the reagents in exactly equivalent proportion. The high addition values in series *a* and *b* are due to side reactions still under investigation. Some reaction of the iodine with traces of carbonate present certainly occurs. Curve *e* is the standard reference curve, obtained by using 0·033 g.-mol. of each reagent per litre.

In carrying out a determination, the acid (1/60th g.-mol.) is dissolved in a little saturated sodium bicarbonate solution without heating, and the mixture is then made up to 250 c.c. with the bicarbonate solution. To 10 c.c. of the solution, contained in a stoppered bottle, the theoretical quantity (about 28 c.c.) of approximately $N/20$-iodine (in potassium iodide solution) is added, and the reaction is allowed to proceed for 10 minutes in the dark; 10 c.c. of chloroform and about 200 c.c. of water are then added, the solution is acidified with hydrochloric acid, and the unchanged iodine immediately titrated with $N/20$-sodium thiosulphate.*

The time of reaction can be altered to bring out the difference in reactivity of any pair of isomerides, provided that the time taken in analyses of unknown mixtures of the isomerides is the same as that taken in the analyses from which the reference curve is constructed. Exact thermostatic control of temperature is unnecessary, but large temperature changes obviously introduce a source of error and are to be avoided.

FIG. 1.



By plotting % addition of iodine against composition a smooth curve is obtained (curve *e*, Fig. 1) which can be used for the analysis of unknown mixtures of these acids.

(2) *By extrapolation.* The titrations were carried out as in the preceding method.

---

* The acidification is desirable, as traces of carbonate present in the bicarbonate react with hypoiodous acid as follows (Bougault, *Compt. rend.*, 1917, **164**, 949):

$$I_2 + H_2O \rightleftharpoons HIO + HI; \quad 2HIO + Na_2CO_3 \longrightarrow NaIO;$$
$$4NaIO + Na_2S_2O_3 + H_2O \longrightarrow 2NaHSO_4 + 4NaI.$$

The last reaction proceeds concurrently with the ordinary titration reaction and requires only 1/8th of the normal amount of thiosulphate per g.-mol. of free iodine. In the early work described above, this precaution was omitted and there is therefore a slight absolute error.

TABLE I.

Mixtures of Δ^1-*cyclo*Hexenyl- and *cyclo*Hexylidene-acetic Acids.

% αβ-Acid	100	83·7	75·0	66·7
% Addition	5·9, 4·9, 6·3	21·0, 22·4	28·5, 26·8	34·7, 33·3
% αβ-Acid	50	33·3	25·0	16·7
% Addition	43·5, 43·7	53·6, 53·1	56·7, 56·2	60·2, 60·5
% αβ-Acid	0			
% Addition	66·4, 65·5, 65·5			

TABLE II.

Test Mixtures of Δ^1-*cyclo*Hexenyl- and *cyclo*Hexylidene-acetic Acids (see Fig. 2).

Mixture.	Acid in 10 c.c. (g.-mol. × 10^3).	Iodine added (g.-mol. × 10^3).	Iodine solution.	% βγ-Acid.	
				Actual.*	Found.
A	0·7140	0·6435	25 c.c. aq.	0	−0·1
B	0·5897	0·6451	,,	8·7	9·4
C	0·5508	0·6470	,,	23·7	24·7
D	0·7012	0·6451	,,	40·1	40·5
E	0·7226	0·7280	,,	60·9	61·3
F	0·4936	0·5170	15 c.c. alc.	81·4	82·5
G	0·7106	0·8413	32·5 c.c. alc.	100	103

* These points are shown in Fig. 2, marked ⊙, where the ordinates represent % βγ-acid for this purpose.

The iodine solutions in aqueous potassium iodide were similar to those used in the previous method. The solution in alcohol which was used in all the determinations described in this paper had the composition : iodine 6·35 g., 95% ethyl alcohol 600 c.c., water to 1 litre.

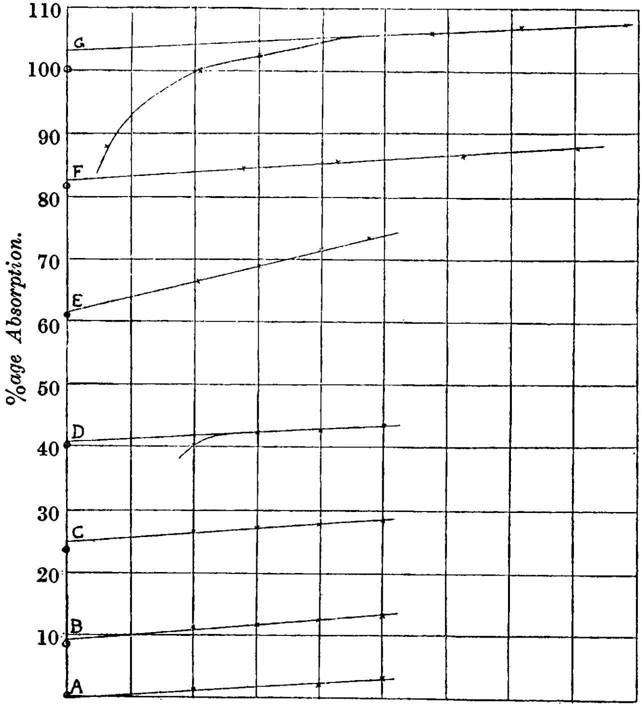
The accuracy of the method will not, in most cases, exceed ± 5%, as we consider the *cyclo*hexenylacetic acids to be an exceptionally favourable pair. The method, however, is the only one capable of giving trustworthy results for acids which cannot be completely separated from their isomerides. As such it has been applied in the two cases studied by Kon and May (*loc. cit.*).

Equilibrations.—1. *Dipropyl-acids.* ββ-Dipropylacrylic acid and its $\Delta^{\beta\gamma}$-isomeride were heated with aqueous potash under the following conditions :

a.	βγ-Acid	heated with excess	60%	potash for	24 hours.
b.	βγ- ,,	,, ,, ,,	60%	,,	24 ,,
		then with	20%	,,	24 ,,
c.	αβ- ,,	,, ,, ,,	60%	,,	48 ,,
d.	αβ- ,,	,, ,, ,,	20%	,,	48 ,,

The results of iodine absorption by the products (Table III) show that equilibration is slow in 60% potash, probably owing to the sparing solubility of the potassium salts of the acids at this concentration. The effect on the result of an increase in iodine concentration is shown by the two analyses (cA and cB) of the product in experiment c.

FIG. 2.



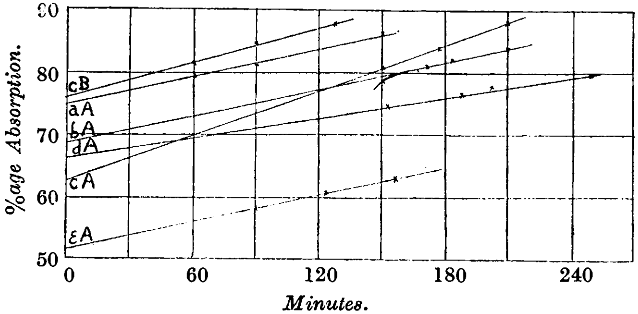


FIG. 3.

2. *Di*iso*butyl-acids.*—Only one accurate determination has been carried out, on a mixture of ββ-di*iso*butylacrylic acid and its $\Delta^{\beta\gamma}$-isomeride which was heated with 60% potash for 24 hours. The result obtained (51·5% of βγ-acid) by the iodine absorption method

agrees with that to be expected from the physical properties of the mixture (Kon and May, *loc. cit.*).

TABLE III.

ββ-Dipropyl- and ββ-Di*iso*butyl-acrylic Acids (see Fig. 3).

Mixture.	Acid in 10 c.c. (g.-mol. × 10^3).	Iodine in 25 c.c. alcoholic solution (g.-mol. × 10^3).	% βγ-Acid found.
Dipropyl.			
aA	0·5720	0·6182	(74·9)
bA	0·6810	0·6458	68·6
cA	0·6298	0·6458	62·5
cB	0·5530	0·7350	(76·2)
dA	0·4238	0·4125	66·3
			Mean 65·8
Di*iso*butyl.			
eA	0·6380	0·6265	51·5

Addition of Bromine to the Isomeric Ethylhexenones.—The reaction with bromine was studied by the method given in Part I (this vol., p. 355). The reaction of the αβ-ketone with an equimolecular quantity of bromine was approximately bimolecular; the mean velocity coefficients obtained under various conditions are in Table IV, where *c* is the concentration (g.-mol. per l.) of each reagent.

TABLE IV.

Solvent.	*c.*	Temp.	Mean *k*.
CCl_4	1/60	25°	0·0141±0·0059
CS_2	,,	,,	0·0151±0·0094
$CHCl_3$	,,	,,	0·0024±0·0008
$CHCl_3$	,,	0	0·195 ±0·035
CCl_4	1/120	25	0·0052±0·0004

The order for the rates of reaction in the various solvents at 25° is the same as that found by Herz and Mylius for cinnamic acid (*Ber.*, 1906, **39**, 3817), namely, $CS_2 > CCl_4 > CHCl_3$. Under all the above conditions the βγ-ketone reacted completely (within the limits of experimental error).

Experiments at 25° with concentrations of the reagents each 1/300 g.-mol. per litre of carbon tetrachloride (a bromine solution at this dilution retained its strength during the necessary interval of time) showed that the βγ-ketone reacted completely in 6—7 minutes, whereas the reaction of the αβ-ketone was quite slow. The addition figures over a 2-minute interval were determined and compared with those obtained for the equilibrated ketones (prepared in the usual way from the parent ketones by the action of cold sodium ethoxide solution). The figures given in Table V are subject to considerable experimental error owing to the small differences measured.

TABLE V.

Ketone.	Treatment.	Mean % addition of bromine in 2 mins.
$\alpha\beta$	Pure.	$37{\cdot}9 \pm 0{\cdot}6$
$\alpha\beta$	NaOEt, 24 hrs.	83·3
$\alpha\beta$	NaOEt, 48 hrs.	89·3
$\beta\gamma$	NaOEt, 48 hrs.	89·2
$\beta\gamma$	Pure.	$97{\cdot}3 \pm 1{\cdot}9$

By interpolation the equilibrium is found to be approximately 14% $\alpha\beta$-ketone $\rightleftharpoons$ 86% $\beta\gamma$-ketone. In confirmation, the semicarbazone of the equilibrium mixture was prepared and was found to be mainly that of the $\beta\gamma$-ketone.

Use of Iodine Chloride.—The two standard solutions required in this method contain respectively 3·384 g. of iodine and 5·076 g. of mercuric chloride per 100 c.c. of 95% ethyl alcohol. These solutions are mixed in equal parts 24 hours before use; the mixture does not retain its strength. 10 C.c. are approximately equivalent to 1/1500 g.-mol. of a mono-olefinic substance.

An analysis is carried out by weighing out 1/300 g.-mol. of the unsaturated substance into a graduated flask and dissolving it in 50 c.c. of pure carbon tetrachloride. 10 C.c. of this solution are pipetted into a stoppered bottle. The iodine chloride solution prepared as described above is standardised against $N/20$-sodium thiosulphate and the exact theoretical amount is run into the solution of the unsaturated substance from a burette.* The reaction is allowed to proceed in the dark. At the end of a convenient time, determined by preliminary experiments, the mixture is treated with some 30 c.c. of 10% potassium iodide solution and 300 c.c. of water, and the unchanged iodine chloride is determined by back titration. The isomeric ethyl *cyclo*hexenylacetates showed the expected large difference in reaction; the figures for these esters and for ethyl styrylacetate under these conditions are in Table VI.

TABLE VI.

		Time (mins.).		
		10.	20.	60.
% Addition to ethyl	*cyclo*hexylideneacetate ($\alpha\beta$)	0·2	2·2	4·2
	Δ^1-*cyclo*hexenylacetate ($\beta\gamma$)	56·0, 56·1	62·0	69·8
	styrylacetate ($\beta\gamma$)	34·2	46·4	62·7, 61·8

---

* If M is the mol. wt. in g. of the substance, t is the titre of 10 c.c. of iodine chloride solution, and F the factor of the thiosulphate (1 c.c. $= F$ g. of iodine), then the volume of iodine chloride solution (J) required by 10 c.c. of a solution containing x g. per 50 c.c. is given by (i) $J = 507{\cdot}6x/MtF$, and the % of unchanged substance at the end of the reaction period by (ii) $1000T/tJ$, where T is the back titre. Expression (i) allows for small discrepancies in weighing the unsaturated material; x/M should equal 1/300 to the nearest milligram.

There was no back reaction with the αβ-ester after titration, but a slow liberation of iodine occurred in the case of the two βγ-esters.

Artificial mixtures of known amounts of the two *cyclo*hexenylacetates reacted as follows in 1 hour :

% αβ-Ester......	100	75·1	50·2	33·5	25·1	0
% Addition ...	4·2 ± 0·5	23·5 ± 0·05	43·3 ± 0·05	54·5 ± 0·3	59·7	69·8

The smooth composition–addition curve given by these figures was then used to determine the compositions of equilibrated mixtures of the esters. The pure esters were refluxed at 60° with an equimolecular amount of alcoholic sodium ethoxide for 43 hours. The product was in each case poured into water and extracted with ether. After drying and removal of the ether the residue was fractionated. Some 15—20% of liquid was isolated (b. p. 134°/12 mm., probably β-ethoxy-ester), but the bulk of the material was recovered as unsaturated ester, which had the following properties :

Parent ester.	B. p. of product.	% Addition of iodine chloride in 60 mins.	% αβ-Ester (calc.).
αβ	94—102°/12 mm.	68·4 ± 0·1	6
βγ	102—107°/17 mm.	63·8 ± 0·05	16

The equilibrium appears to be of the order of 10% αβ-ester $\rightleftharpoons$ 90% βγ-ester.

The equilibrated ester from the αβ-ester was hydrolysed under conditions precluding isomeric change in the acids, namely, at room temperature with 10% alcoholic-aqueous sodium hydroxide for 4 days. The acid isolated in the usual way was found to consist of Δ^1-*cyclo*hexenylacetic acid [plates, m. p. (crude) 33—34°], contaminated with an oily mixture which deposited more βγ-acid but no αβ-acid on standing.

The authors wish to express their thanks to Professor J. F. Thorpe, F.R.S., and Dr. G. A. R. Kon for their interest in this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.
[*Received, August 22nd,* 1927.]