CCCXXXII.—*The Chemistry of the Three-carbon System. Part XXIII. The Influence of Substituent Groups on the Tautomeric Change.*

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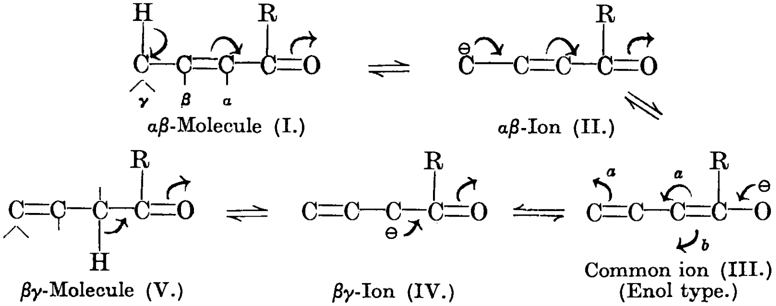
In the present paper a correlation is attempted of the more recent quantitative data on tautomerism in three-carbon systems (J., 1927, 362, 2579; 1928, 2343; this vol., pp. 1269, 2139, 2153; *et cet.*) and a further example of the change in unsaturated esters is described.

Accepting the hypothesis that tautomeric change in these as in other pseudo-acidic substances (Lapworth, J., 1901, **79**, 1265) takes place through dissociation (Ingold, Shoppee, and Thorpe, J., 1926, 2477), the three-carbon change may be considered as proceeding through the establishment of four equilibria, shown below for unsaturated ketones :

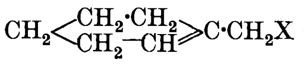


αβ-Molecule (I.) αβ-Ion (II.)

βγ-Molecule (V.) βγ-Ion (IV.) Common ion (III.) (Enol type.)

In these formulæ and in the subsequent discussion, the nomenclature and symbols are those used by Robinson and others and also in this connexion by Ingold (*loc. cit.*; *Ann. Reports*, 1927, 106, *et cet.*). The two "keto-ions" (II and IV) have been included to avoid creating an arbitrary distinction between substances such as these ketones and the much more inert but still mobile compounds in which there is no group capable of enolisation or similar reaction (*e.g.*, hydrocarbons). In the latter type there must be interchange between (II) and (IV), but the evidence is that the direct change is inappreciable in systems containing an activating group.

Substituents and Mobility.—(1) *Activating groups.* The existence of only one "cryptomeric" form can no longer be taken as proving (although it suggests) that the system is one possessing a high degree of mobility. More trustworthy is the evidence derived from a direct comparison of the rates of interchange of related substances under identical conditions. As an example, a study of the change



$$CH_2\!\left<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}\right>\!C\cdot CH_2X \rightleftharpoons \alpha\beta\text{-isomeride}$$

has yielded the following results (Kon and Linstead, this vol., p. 1269; Kandiah and Linstead, *ibid.*, p. 2139):

X	$-CO\cdot CH_3$.	$-CO_2Et$.	$-CN$.	$-CO\cdot\bar{O}$.
Mobility	800	8	920	0*

* There is no detectable change in the sodium salts of the carboxylic acids under the standard conditions used for the interconversion of the other substances—unpublished observation.

The results for the other series fall into line with these.

Ingold (*loc. cit.*) has connected the ability of a group to promote prototropic change with its attraction for electrons as shown by its *m*-orienting power in benzene substitution. Further, in substances activated by ^{-}COR, the promotion of mobility is correlated with the electron repulsion of the group R. On these grounds, the mobility sequence $^{-}CO\cdot CH_3 > {}^{-}CO_2Et > {}^{-}CO\cdot\bar{O}$ is deduced (part of a long sequence; Ingold, Shoppee, and Thorpe, J., 1926, 1482) in agreement with the experimental figures. Whilst, however, the broad connexion between the two phenomena seems clear, it would appear that too great emphasis has been laid on the agreement between the sequences : the figures for the *m*-directing power of the activating groups when themselves substituted in the benzene ring exhibit irregularities when compared with the mobility sequence.

Group (in order of mobility)	$-CN$.	$-CO\cdot CH_3$.	$-CO_2Et$.	$-CO\cdot\bar{O}$.
% *m*-Nitration at 0° (Holleman) ...	100	55	68	—

(2) *Alkyl groups.* The facts point to a depression of mobility with increasing alkyl substitution. This is in agreement with the prototropic theory, from which it would be expected that the mobility would fall as the three-carbon system acquired electron control from the surrounding groups. Part of the effect may, however, be due to steric factors, for, applying the argument of Flürscheim (J., 1909, **95**, 725) on the electrolytic dissociation of organic acids, the presence of bulky alkyl groups will inhibit the (bimolecular) recombination of the proton without affecting the (unimolecular) dissociation.

Substituents and Equilibrium.—In this discussion it will be assumed that the equilibrium represents a structural constant.

The constitutive influences of alkyl groups are those most readily studied. According to Ingold, terminal (α- and γ-) alkyl groups exercise their customary inductive effect, involving a repulsion of electrons. The experimental figures, notably those for equilibria of unsaturated acids, are in complete agreement with this view, a particularly striking fact being the exceptional stability of pyroterebic acid (VIII) to alkali. Ingold, Shoppee, and Thorpe (*loc. cit.*) have concluded from observations on citraconic and itaconic esters that the introduction of an electron-attracting group, such as carbethoxyl, in the β-position tends to stabilise the βγ-phase. The theoretical explanation they advance, however, cannot be accepted as a general one for groups in the β-position. Two disturbing factors in systems of this type are that the direction of tautomeric change may depend upon the configuration of the isomerides and that the effect of the introduction of a second unsaturated group varies according to its identity or otherwise with the activating group already present in the molecule (compare Fittig, *Annalen*, 1898, **304**, 117 ; 1903, **330**, 292 ; Fichter and Latzko, *J. pr. Chem.*, 1906, **74**, 327 ; Thiele, *Annalen*, 1901, **319**, 196). Whatever may be the explanation of the effect of such groups, it seems clearly unsatisfactory to generalise from them. Indeed, such generalisation would lead, to take a particular example, to a false inference as to the effect of β-alkyl groups. It is implied in the original theory that such groups, being opposite in effect to the acceptor groups, would stabilise the αβ-phase. Actually they have a marked influence favouring the βγ-position of the bond. This appears to be common to aliphatic and alicyclic compounds, the maximum effect being produced by the ethyl group (Goldberg and Linstead, J., 1928, 2343). From first principles this would seem to be the *expected effect* of a β-alkyl group, for in the common ion (III) the β-group, by increasing the negative nature of the β-carbon atom, will render it less ready to receive the tautomeric electron displacements from the negative pole in the activating group and to transmit these to the γ-carbon atom, *i.e.*, will inhibit process (*a*). This will result in preferential formation of the βγ-keto-ion (IV) and an increased amount of the βγ-form at equilibrium.

In conclusion, attention may be directed to three other factors affecting equilibrium.

(1) *Conjugation.* Whatever may be its nature, the *existence* of an additional non-polar element of stability associated with conjugated systems cannot be doubted (see Lapworth and Manske, J., 1928, 2535). In a three-carbon system this tends, apart from all other factors, to stabilise the αβ-ion (compare Birch, Kon, and Norris, J., 1923, **123**, 1367). It may be expected to be most evident when the activating group is most " unsaturated." A clear example of its effect is found in the preponderance of the αβ-form in all nitrile equilibria (Kandiah and Linstead, *loc. cit.*).

A similar effect controls the equilibria in three-carbon systems terminated by a phenyl group : there the double bond invariably approaches the phenyl group regardless of the polar character of the migrating group (Linstead and Williams, J., 1926, 2735 ; Burton and Ingold, J., 1928, 1904). Recognition of a distinct non-polar element of stability in such compounds makes it unnecessary to assume that the phenyl group has opposite polar effects in anionotropic and in prototropic change.

In systems possessing this " conjugated stability " there would appear to be some form of stable association between two electrons of the " double bond " and the electrons of the unsaturated centre of the activating group (compare Baker, Cooper, and Ingold, J., 1928, 122).

(2) *Steric effects.* In addition to any polar effect, a substituent group will exert a *resistance* to a mode of recombination by blocking the free space around a charged carbon atom. The application of this consideration is obvious and it may be deduced that a terminal alkyl group will have a steric effect supporting its polar effect. On the other hand, a β-alkyl group can have no steric effect on equilibrium, and this may account for the observed difference between the influence of similar groups in the β- and in the γ-position.

(3) *Strain.* A decrease of the strain in an alicyclic compound brought about by the movement of a double bond may alter the equilibrium in favour of the phase associated with the least strain. It is doubtful, however, whether this causes major effects of any importance and it would certainly appear undesirable to apply such considerations to *gem*-dialkyl compounds (Kon and May, J., 1927, 1549).

To amplify consideration of these factors or to assess their relative importance further would not be justified by the data available. They provide, however, a working basis for further investigation.

The experimental portion of this paper describes the examination of tautomeric change in *iso*hexenoic esters. As reversible movement of the double bond had previously been observed only in one pair of mono-olefinic esters (Linstead and May, J., 1927, 2565; Kon and Linstead, this vol., p. 1273), it was obviously desirable to obtain confirmatory evidence from a study of similar compounds. The iso*hexenoic* esters (VI and VII) were selected for this purpose, as it was thought that in them the $\beta\gamma$-phase (VII) would show considerable stability and that the change would be appreciably faster than in the esters already examined (the *cyclo*hexenylacetic esters).

(VI.) $CHMe_2-CH=CH\cdot CO_2Et$ $CMe_2=CH-CH_2\cdot CO_2Et$ (VII.)

As observed in the previous work on esters (*loc. cit.*), sodium ethoxide prepared from commercial "absolute" alcohol and the ethoxide prepared from the carefully dehydrated alcohol differ markedly in their action. Ethyl Δ^{α}-*iso*hexenoate (VI), treated with an equimolecular quantity of *N*-sodium ethoxide prepared from "absolute" alcohol, yielded the *ethoxy*-ester (IX) and a mixture of sodium salts composed mainly of that of the $\beta\gamma$-acid, pyroterebic acid (VIII).

(VIII.) $CMe_2=CH-CH_2\cdot CO_2H$ $CHMe_2\cdot CH(OEt)\cdot CH_2\cdot CO_2Et$ (IX.)

When carefully dried alcohol had been used in the preparation of the sodium ethoxide, hydrolysis of the ester (VI) was almost entirely prevented and the only reactions proceeding were those of equilibration ($VI \rightleftharpoons VII$) and of addition of alcohol to the $\alpha\beta$-ester. After treatment of the $\alpha\beta$-ester with an equivalent quantity of *N*-sodium ethoxide at 25° for 6 hours, the low-boiling fraction of the product showed a greatly increased affinity for iodine chloride and a change in physical properties indicating the formation of the $\beta\gamma$-isomeride. Hydrolysis of the equilibrated material under conditions precluding isomeric change yielded a product containing a large proportion of the βγ-acid. Ozonisation of the same material gave oxidation products of both the αβ- and the βγ-ester. There could be no doubt, therefore, of the essential change αβ⟶βγ-ester. These substances, however, differed from the *cyclo*hexenylacetic esters previously examined in the relatively high amount of addition compound formed, which is presumably to be attributed to the absence of a second β-substituent such as is present in the cyclic compounds. This rendered quantitative study of the change a matter of some difficulty, as the ethoxy-ester could not be readily separated from the unsaturated esters by fractionation. In any case an exact determination of mobility was invalidated by the considerable side reaction. An approximately quantitative examination was carried out by a method, described in the experimental portion, which takes advantage of the difference in properties of the three esters indicated below :

	B. p.	$d^{17°}_{4°}$.	$n^{17°}_{D}$.	% Iodine addition.*
Ethyl Δ^{α}-*iso*hexenoate (VI)	60°/13 mm.	0·8978	1·4341	0·9
Ethyl Δ^{β}-*iso*hexenoate (VII)	58°/11 mm.	0·9134	1·4329	91·2
Ethyl β-ethoxy*iso*hexoate (IX)	79°/ 8 mm.	0·9166	1·4197	4·9

* Iodine addition to esters refers throughout to the percentage addition in 30 minutes under the conditions of Linstead and May; *loc. cit.*, p. 2678.

The approximate figures given in Table I are calculated from the data in the experimental section and are expressed in simplified form as the proportions of the three esters present in the isolated product after definite periods of reaction.

TABLE I.

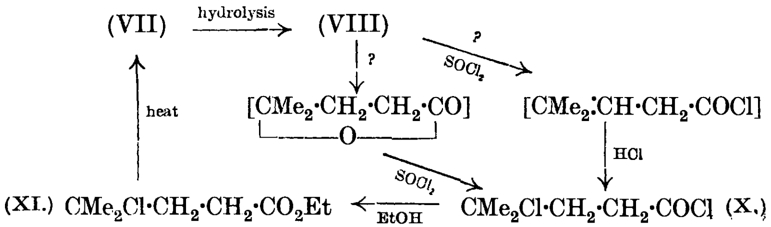
*iso*Hexenoic esters + 1 equiv. of *N*-NaOEt at 25°.

	Time of reaction	% Total product.			Ratio of
Initial material.	(hrs.).	αβ-.	βγ-.	β-(OEt).	αβ- to βγ-ester.
αβ-Ester	1	66	11	23	86 : 14
,,	2	55	21	24	72 : 28
,,	3	37	25	38	60 : 40
,,	4	23	29	48	44 : 56
,,	4	24	34	42	41 : 59
,,	8	— 40	—	60	—
βγ-Ester	2	0	97	3	0 : 100
,,	6	0	90	10	0 : 100

Addition is perceptibly faster than tautomeric change in this system, as is shown particularly by the fact that the αβ-ester produced from the βγ- adds on alcohol as fast as it is formed. There is, however, little change of any sort in the βγ-ester, which suggests that the equilibrium, as in the corresponding acids, is greatly on the βγ-side. It was not possible to follow the change of the αβ-ester for more than 4 hours, as continued treatment led to the extinction of the low fraction. An approximate value for the equilibrium was obtained by treating a mixture containing 88·4% of the βγ-ester for 4 hours under the standard conditions : the product contained 8% αβ-, 74% βγ-, and 18% ethoxy-ester, giving an αβ–βγ ratio of 10 : 90, which would therefore appear to represent the equilibrium in the tautomeric change. Although the mobility cannot be determined with accuracy, as the change is no longer a unimolecular reversible reaction, it is obviously much greater than that of the esters previously examined.

The addition of alcohol to the αβ-ester is reversible, and in this respect resembles the ordinary Michael addition of sodio-esters, the reversibility of which was first shown by Vorländer (*Ber.*, 1900, **33**, 3185; *Annalen*, 1906, **349**, 155; compare Ingold and Powell, J., 1921, **119**, 1976). Treated under the standard conditions for 4 hours, the ethoxy-ester gave a mixture of 10% of the αβ- and 29% of the βγ-ester together with 61% of unchanged material .

It was found impossible to prepare the βγ-ester (VII) from the corresponding acid through the acid chloride, as this acid (VIII) reacted with thionyl chloride. to give a mixture of its own acid chloride and that of the corresponding γ-chloro-acid (X). This mixture could not be separated completely, but the chloro-acid chloride was obtained almost pure and gave the corresponding *ethyl* ester and *anilide*. The tertiary chlorine in these compounds was very labile. The chloro-anilide lost hydrogen chloride even on recrystallisation from hydroxylic solvents, and the chloro-ester evolved hydrogen chloride freely on distillation. The product in the last decomposition was mainly the βγ-ester, which could not, however, be obtained pure by this method (compare Jones and Tattersall, J., 1904, **85**, 1693). The chloro-acid chloride might be formed in two ways : (1) the acid chloride of the βγ-acid may add on the hydrogen chloride liberated in the reaction of the acid with thionyl chloride, or (2) *iso*hexolactone may be formed from the βγ-acid and may react with thionyl chloride with the elimination of one molecule of sulphur dioxide. The lactonisation of the acid is known to be unusually facile (Fittig and Geisler, *Annalen*, 1881, **208**, 37 ; Perkin, J., 1902, **81**, 256) and the second explanation is perhaps the more probable. These reactions are illustrated below :



EXPERIMENTAL.

Δ^{α}-*iso*Hexenoic acid (Goldberg and Linstead, *loc. cit.*) prepared in five different experiments showed a close agreement in properties. A representative product had b. p. 115—116°/20 mm., $n_D^{20\cdot6°}$ 1·4489, $d_{4°}^{20\cdot6°}$ 0·9529, $[R_L]_D$ 33·11 (calc., 30·98). This sample had an iodine addition of 0·6% in 10 minutes, the value obtained in the previous work being 1·8% (*loc. cit.*, p. 2359). The acid gave the dibromide, m. p. 124—125°, isolated by previous workers, but the anilide, which forms well-defined needles from alcohol and water, has m. p. 142° and not 128° as previously recorded.

Ethyl Δ^{α}-iso*Hexenoate* (VI).—(a) *Through the acid chloride.* The $\alpha\beta$-acid (27 g.) on treatment with a slight excess of thionyl chloride gave 26·5 g. of the acid chloride, b. p. 58—59°/18 mm., which with 25% excess of ethyl alcohol gave the ester in good yield, 23 g. boiling at 76—77°/25 mm. This had $n_D^{20\cdot8°}$ 1·4328, $d_{4°}^{20\cdot8°}$ 0·9048, $[R_L]_D$ 40·80 (calc., 40·33), and an iodine addition of 0·4%. The abnormally low refractivity indicated the presence of impurity, and the ester was found to contain chlorine and was therefore unsuitable for the work in view. Alkaline hydrolysis of this material gave an acid product from which nearly 60% of $\alpha\beta$-acid free from chlorine could be distilled at 104—106°/9 mm. On further distillation, the residue exploded violently with the evolution of a gas (? hydrogen chloride).

(b) *Direct esterification.* The $\alpha\beta$-acid (52 g., b. p. 108°/9 mm., $n_D^{12\cdot5°}$ 1·4521, $d_{4°}^{12\cdot5°}$ 0·9617) was boiled with ethyl alcohol (120 c.c.) and concentrated sulphuric acid (10 g.) for 2½ hours. The neutral product yielded 51 g. (79%) of a fraction, b. p. 60°/13 mm., together with 5 g. (8%) of less pure material. As a test of homogeneity, the main fraction was collected in two portions, the physical properties of which were found to be almost identical and to be unchanged by further fractionation. This fraction was used as pure $\alpha\beta$-*ester* in this work. Its physical properties are recorded on p. 2503 (Found : C, 67·4; H, 9·8. $C_8H_{14}O_2$ requires C, 67·5; H, 9·9%).

Hydrolysis with two equivalents of $N/2$-alcoholic-aqueous potash in the cold yielded the pure $\alpha\beta$-acid (b. p. 108°/10 mm.; $n_D^{16\cdot2°}$ 1·4583; iodine addition, 0·4% in 5 minutes).

The ester (3·25 g.) in dry chloroform was treated with a current of ozonised air for 20 hours. Removal of the solvent and addition of water gave an aldehydic oil volatile in steam. This was distilled, separated, dried, and redistilled; 1·05 g. (64%) of a substance were then obtained boiling at 60—70° and having the general properties of *iso*butaldehyde, with which it was identified by the formation of the *p*-nitrophenylhydrazone, m. p. and mixed m. p. 127—128°. No acetone superoxide or formaldehyde could be detected. The aqueous residue after removal of the aldehyde was made alkaline and evaporated to small bulk. On acidification, oxalic acid separated; it was identified by m. p. (99°) and the usual tests.

Ethyl Pyroterebate (VII).—Pyroterebic acid was prepared from Δ^{α}-*iso*hexenoic acid by Goldberg and Linstead's method (*loc. cit.*). In this work the crude acid was distilled under reduced pressure without previous distillation in steam and was partly esterified under the conditions of Eccott and Linstead (this vol., p. 2153). In a typical series of experiments the αβ-acid (38 g.) yielded 29·5 g. of crude pyroterebic acid, of which 23 g. boiled at 103—106°/13 mm. This was kept in contact with 80 c.c. of N-alcoholic hydrogen chloride and 240 c.c. of absolute alcohol for 4¼ hours. The mixture was worked up in the manner already described (*loc. cit.*) and yielded 23 g. of ester, of which 20·7 g. boiled at 58—59°/11 mm. This fraction was pure *ethyl pyroterebate* and contained no chlorine. It had the normal molecular refractivity ($[R_L]_D$ 40·41) and high affinity for iodine (91·2%) expected from the βγ-structure. The freshly distilled material gave correct figures on analysis (Found: C, 67·3; H, 9·8. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%), but after a month there was distinct evidence of oxidation (Found : C, 64·5, 64·3; H, 9·6, 9·4%) and the material left a viscous residue on distillation.

Hydrolysis with 15% sodium hydroxide solution at room temperature gave pyroterebic acid, identified by the formation of the dibromide, m. p. 102° (Williams, *Ber.*, 1873, **6**, 1095), which did not depress the melting point of an authentic sample. A considerable amount of the isomeric *iso*hexolactone was also formed in this hydrolysis.

The ozonide of the ester was formed in the same way as that of the αβ-ester and on decomposition with water gave a white crystalline solid volatile in steam. This was identified as acetone superoxide by its decomposition with alkali to the ketone and subsequent conversion into iodoform (m. p. 119—121° decomp., mixed m. p.). No *iso*butaldehyde was formed by the action of water on the ozonide, but a pungent, intensely irritating vapour, apparently formaldehyde, was slowly evolved, probably owing to a secondary change (compare Briner and Meier, *Helv. Chim. Acta*, 1929, **12**, 529).

Mixtures of the αβ- and βγ-esters react with iodine chloride as follows :

% *αβ*-Ester	80	66·6	50	40	33·3	20
Mean % addition	20·0	32·0	47·7	56·9	63·1	75·5

Action of Alcoholic Sodium Ethoxide on the Esters.—(1) *Alcohol not specially dried.* The αβ-ester (6·61 g.) was left over-night with 1·05 N-alcoholic sodium ethoxide (1 equiv.) at room temperature.

After 14 hours, a white crystalline precipitate had formed, which was filtered off and washed with ether. On acidification the dry odourless solid (1·7 g.) gave an acid, $n_D^{20·1°}$ 1·443, $d_{4°}^{20·1°}$ 0·9705, $[R_L]_D$ 31·25; dibromide, m. p. 102°. The experiment was repeated with 11·7 g. of αβ-ester, the change being allowed to proceed for 68 hours. The semi-solid mixture was worked up by the method used in previous work (Kon and Linstead, this vol., p. 1278) and gave 3·2 g. of neutral fraction, b. p. 85—91°/19 mm. (27%—mainly ethoxy-ester), and a liquid acid (49%) which on distillation gave 3·1 g. of b. p. 110—121°/18 mm. and 1·0 g. of b. p. 121—130°/20 mm. The second of these was unsaturated to bromine and permanganate and was presumably mainly αβ-acid. The first fraction was freed from lactone and then had $n_D^{18·5°}$ 1·4434, $d_{4°}^{18·5°}$ 0·9746, $[R_L]_D$ 31·06 and gave the βγ-dibromide, m. p. 102°.

(2) N-*Anhydrous sodium ethoxide at* 25°. These experiments were carried out in exactly the same way as those with the *cyclo*hexane esters (*loc. cit.*). The acid fraction was negligible in every case. The neutral fraction was divided into an "unsaturated ester" fraction and a "high fraction" boiling below and above 70°/18 mm. respectively. The results of these experiments are shown below.

Expt.	Initial ester.	Amount used, g.	Time of treatment (hours).	% Yield of unsaturated fraction.	% High fraction.	Undistilled residue, %.
1	αβ	1·94	1	41·2	12·9	3
2	,,	5·47	2	59·4	27·4	—
3	,,	3·87	3	45·1	25·8	2
4	,,	3·87	4	30·9	37·4	2
5	,,	9·77	4	32·8	43·0	8
6	,,	9·29	8	Nil	76·0	5
7	βγ	4·92	2	61·0	1·0	6
8	,,	2·58	6	32·9	15·5	8

The physical properties and iodine additions of the various unsaturated fractions are given below. These were determined at temperatures between 16° and 19°, but have been adjusted to 17° for convenience in comparison, the corrections $\delta(n) = -0·0004$ and $\delta(d) = -0·0008$ per degree rise being used.

Expt.	1	2	3	4	5	7	8
$n_D^{17°}$	1·4323	1·4311	1·4300	1·4390	1·4313	1·4325	1·4318
$d_{4°}^{17°}$	0·9019	0·8993	0·9058	0·9062	0·9051	0·9095	0·9101
% Iodine addition	13·1	24·3	29·4	36·5	—	89·5	83·9

The ethoxy-ester in the low fraction was estimated from the refractive index, a linear relationship being assumed between $n_D^{17°}$ 1·4197 for the ethoxy-ester and $n_D^{17°}$ 1·4335 for the unsaturated esters. The βγ-ester was estimated from the iodine addition, the action of the feebly reactive ethoxy-ester being neglected. In calculating the figures already given (p. 2503), it has been assumed that in each case the fraction boiling above 70°/18 mm. contains 60% of the ethoxy-ester (see below) and that, as the two unsaturated esters have virtually the same boiling point, the 40% of unsaturated esters in the high fraction are present in the ratio in which they occur in the low fraction from the same experiment.

The two fractions obtained in experiment (5) were further examined. The low fraction had C, 66·7; H, 9·9%, equivalent to an ethoxy-ester content of 18%, whereas the corresponding figure calculated from the refractive index was 20%. On ozonisation and decomposition in the manner already described, this fraction gave : *iso*butaldehyde, identified as the *p*-nitrophenylhydrazone; acetone superoxide, converted into the ketone and thence into iodoform; oxalic acid, and the irritating vapour (? formaldehyde) previously observed. The high fraction from this experiment (b. p. 70—86°/13 mm.) had $d_{4^\circ}^{17^\circ}$ 0·9106, $n_D^{17^\circ}$ 1·4252, whence the ethoxy-ester content is 60% (Found : C, 65·1; H, 10·2%. A mixture of 40% of $C_8H_{14}O_2$ and 60% of $C_{10}H_{18}O_3$ requires C, 65·3; H, 10·2%). Its iodine addition was 23·3%, equivalent to 23% of the βγ-ester. The other high fractions were not examined in detail but were used in the preparation of the ethoxy-ester.

A mixture of 0·684 g. of the αβ-ester and 5·205 g. of the βγ-ester (88·4% βγ-), after treatment under the standard conditions for 4 hours, gave 2·6 g. of unsaturated fraction (44%), 20% of high fraction, and 9% of residue. The low fraction had $n_D^{19\cdot7^\circ}$ 1·4316, $d_{4^\circ}^{19\cdot7^\circ}$ 0·9079, and an iodine addition of 82·8%, and hence the approximate composition of the whole was 8% αβ-, 74% βγ-, and 18% ethoxy-ester, the αβ–βγ ratio being substantially unaltered.

To confirm the change αβ⟶βγ-ester, a sample of the αβ-ester was equilibrated in the usual way for 6 hours and the low fraction of the product (b. p. 60—68°/8 mm., 4 g.) was hydrolysed with 10% sodium hydroxide solution at room temperature. The acid product was freed from lactone and distilled (3 g.) under reduced pressure. The low-boiling fraction (99—104°/8 mm., 1·05 g.) had $n_D^{15\cdot8^\circ}$ 1·4465, $d_{4^\circ}^{15\cdot8^\circ}$ 0·9764, and an iodine addition of 67·5% in 5 minutes, corresponding to a βγ-content of 87%. The pure βγ-acid has $n_D^{16\cdot7^\circ}$ 1·4474, $d_{4^\circ}^{16\cdot7^\circ}$ 0·9757, and adds 76·6% of iodine in 10 minutes. Further, the low fraction gave the dibromide of the βγ-acid, m. p. 101—102°, unchanged by admixture with an authentic specimen.

The high fractions from the equilibrations were united and fractionated three times, the fractions boiling above 75°/10 mm. being redistilled. In the third distillation nothing came over below

75°/8 mm. and a final distillation gave *ethyl* β-*ethoxy*iso*hexoate* (IX) as a colourless oil, less mobile and less odorous than the corresponding unsaturated esters, and having the physical properties already mentioned (Found: C, 63·8; H, 10·5. $C_{10}H_{20}O_3$ requires C, 63·8; H, 10·7%). From 15·2 g. of the αβ-ester, 1·25 g. of the pure ethoxy-ester were isolated, and more was obtained by further treatment of the various intermediate fractions with sodium ethoxide. The ethoxy-ester has no action on bromine in chloroform and a slow action on permanganate in acetone, whereas the αβ-ester immediately decolorises the latter reagent.

On treatment with one equivalent of sodium ethoxide in the usual manner for 4 hours the pure ethoxy-ester (1·535 g.) gave 0·85 g. of neutral product, b. p. 65—83°/8 mm., 0·25 g. of which boiled below 70°/8 mm. The united distillates had $n_D^{19·0°}$ 1·4239, $d_{4°}^{19·0°}$ 0·9108, and an iodine addition of 28·2%, indicating the production of unsaturated material.

Action of Thionyl Chloride on Pyroterebic Acid.—Pyroterebic acid (25 g.), purified by distillation in steam and under reduced pressure, was treated with thionyl chloride (28 c.c.), the action being completed on the steam-bath. After removal of the excess of reagent the product was fractionated; it boiled indefinitely at 50—90°/20 mm. and appeared to consist of two substances, b. p. about 60° and 85°/20 mm. respectively. The same result was obtained when the acid chloride was made in two stages, more thionyl chloride being added to the high-boiling product from the first stage to ensure that no acid was escaping reaction. The low fractions of these preparations on treatment with aniline gave anilides, which formed masses of felted needles from dilute alcohol, m. p. 90—100°. With ethyl alcohol, esters were obtained, b. p. 66—85°/15 mm., and as there seemed to be no prospect of preparing a pure pyroterebic ester directly, the high-boiling impurity was further examined.

The high-boiling acid chloride fractions gave anilides which formed fairly well-defined crystals, m. p. about 125°, from benzene and light petroleum. They were united and fractionated a number of times, a substance being obtained, b. p. 89—90°/18 mm., with the characteristic properties of an acid chloride. This appeared to be almost pure γ-chloro*iso*hexoyl chloride (X), although analyses (of derivatives) gave rather low values for the chlorine content. With aniline in ether, a well-defined *anilide* was obtained which after one crystallisation from light petroleum gave bold clusters of needles, m. p. 132°. A mixture with the αβ-anilide (m. p. 142°) melted at 129°. On crystallisation from hydroxylic solvents the melting point of the product fell and a substance with an indefinite

m. p. of 90—100° was eventually obtained apparently identical with that formed from the low-boiling acid chloride. The chloro-anilide (m. p. 132°) also appeared to be decomposed slightly by continued crystallisation from benzene and light petroleum (Found : Cl, 13·2. $C_{12}H_{16}ONCl$ requires Cl, 15·7%).

With ethyl alcohol, the chloro-acid chloride gave the corresponding *ethyl* ester (XI), which boiled with little or no decomposition at 85—92°/13 mm. in the crude state and at 89—92°/13 mm. on refractionation (Found : Cl, 17·4, 16·7. $C_8H_{15}O_2Cl$ requires Cl, 19·9%). On being heated at atmospheric pressure, it lost hydrogen chloride freely and after two distillations at atmospheric pressure the elimination of chlorine was complete. In this way 7·3 g. of chloro-ester gave 5 g. of an unsaturated ester, b. p. 171°/751 mm., which was mainly ethyl pyroterebate, but the iodine addition was only 64·3% as compared with 91·2% for the pure ester. On hydrolysis it yielded an acid sufficiently pure to give the dibromide, m. p. 100° (mixed m. p. 101—102°), and the chloro-anilide, m. p. 130° (mixed m. p. 130°).

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