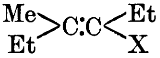
CCIII.—*The Chemistry of the Three-carbon System. Part XII. The Effect of Positive Substituents in the α-Position on the Tautomerism.*

By George Armand Robert Kon and Bindigawavale Tirumalachar Narayanan.

In studying the influence of substituents on three-carbon tautomerism, we examined first the effect produced by a group in the α-position, that is, attached to the carbon atom bearing the negative activating group. The effect of introducing a negative or activating group in this position has been discussed (Kon and Speight, J., 1926, 2727); the effect of a positive group on the mobility and point of equilibrium of three-carbon systems is described below.

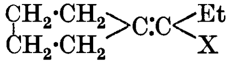
Theoretically, the effect of a positive substituent in the α-position should be a general diminution of the mobility of the system—a phenomenon frequently observed in keto-enol systems, glutaconic esters, etc. The effect on the position of equilibrium is less easy to forecast, because it is probably made up of more than one factor, both polar and steric in nature. It must be assumed that the polar effect diminishes that due to the activating group; and as this favours the αβ-phase, it is to be expected that the βγ-phase will be favoured by the presence of an α-alkyl group. A phenyl group should behave in the same way from the electronic point of view, but the strong tendency to conjugation exhibited by this group (Linstead and Williams, J., 1926, 2735; Johnson and Kon, *ibid.*,

p. 2748) would probably neutralise this tendency, and it would be expected that the αβ-phase in α-phenylated systems would possess considerable stability. We were not able to study this case owing to difficulty in preparing suitable material for investigation; we have, however, examined a number of systems bearing an ethyl group on the α-carbon atom and belonging to several representative types, namely, acids, ketones, and nitriles of the general types (I), (II), and (III).



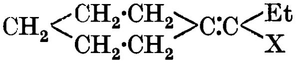
$\begin{matrix}Me\\Et\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}Et\\X\end{matrix}$

(I.)



$\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}Et\\X\end{matrix}$

(II.)



$CH_2\!<\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}Et\\X\end{matrix}$

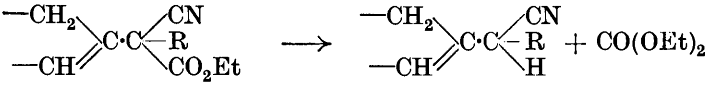
(III.)

$X = CO_2H, COMe, \text{or } CN.$

The properties of the first two groups of compounds are in full agreement with theoretical considerations. The mobility of the systems appears to be less than that of the parent substances; indeed, Birch, Kon, and Norris (J., 1923, **123**, 1361) had failed to condense α-ethyl-Δ^1-*cyclo*hexenylacetone with ethyl sodiomalonate and concluded that this ketone did not react in the αβ-phase. That statement requires revision, for the condensation does proceed, although it requires a considerable time for completion. The mobility of the system in ketones of this series is, however, still considerable, because only one substance, having in every case the βγ-structure, is obtained under the conditions of the Blaise–Maire synthesis from either the αβ- or the βγ-acid; the conversion of αβ-acids into their βγ-isomerides on treatment with alkali is actually unexpectedly rapid. These facts indicate that the βγ-forms of the compounds in question are even more favoured than those of the parent (unsubstituted) compounds and that the mobility of the system is not very greatly affected.

It is, therefore, all the more surprising to find that the α-substituted nitriles, of which several have been prepared by Birch and Kon (J., 1923, **123**, 2440), constitute a sharp contrast to the acids and ketones just mentioned. They are invariably obtained in the αβ-form, and no direct evidence had until lately been obtained of the existence of a βγ-phase, although it is abundantly proved that unsubstituted nitriles, such as *cyclo*hexenylacetonitrile, exist in the βγ-form, but can also react in the αβ-form (compare Birch and Kon, *loc. cit.*). Whilst this difference appears at first to be in contradiction with theoretical considerations, it is capable of a ready explanation. The reaction by which α-substituted nitriles are produced involves the elimination of ethyl carbonate from the corresponding cyano-esters under the influence of alcoholic sodium ethoxide and it has been shown by Ingold and Thorpe (J., 1919,

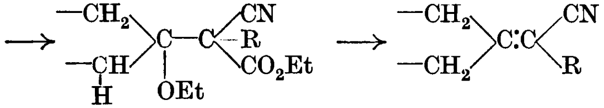
115, 143) to proceed in many cases in the presence of very small amounts of the reagent. The cyano-esters from which they are produced have necessarily a βγ-unsaturated structure (IV) and it has been assumed hitherto that the βγ-form (V) of the nitrile would be produced at first :



(IV.) (V.)

This view of the mechanism is, however, incorrect; the only way in which the system can reacquire its mobile hydrogen atom, and one which at the same time explains the ready occurrence of such reactions, consists in the addition of the elements of alcohol to the double bond, the hydrogen becoming attached to the γ-carbon atom; the system then loses ethyl carbonate with the formation of an αβ-double bond :

(IV.)



This possibility was overlooked in the original paper (Birch and Kon, *loc. cit.*), but it would appear that the scheme now suggested is of general application and that αβ-unsaturated compounds are always produced by the elimination of ethyl carbonate from fully substituted but potentially tautomeric systems (compare Thole and Thorpe, J., 1911, **99**, 2191; Thorpe, J., 1912, **101**, 871; Feist, *Annalen*, 1922, **428**, 25).

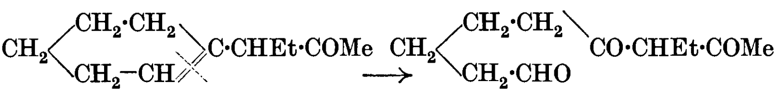
The αβ-compounds so produced can, of course, pass into the βγ-forms if they are sufficiently mobile under the conditions of the experiment; this is, apparently, not the case for the nitriles under discussion. The probable reason for this lack of mobility was suggested by Prof. R. Robinson (private communication), who pointed out that the retarding effect of the α-alkyl group on the mobility of the system was likely to be greater the weaker the activating group on which mobility ultimately depends; it would be greatest in a system activated by a weak group such as CN (compare Bradley and Robinson, J., 1926, 2356). For this reason, α-substituted nitriles are probably static or nearly so and are therefore isolated in the αβ-form, although this may not be the most stable. Experiments have been undertaken to confirm this view: the βγ-isomeride of *cyclo*hexylidenebutyronitrile has already been prepared and found to differ from the αβ-compound; its properties are now under investigation.

The α-substituted nitriles can be hydrolysed by means of alcoholic sulphuric acid to the corresponding αβ-unsaturated esters (or ester containing a high proportion of the αβ-compound), but these cannot be further hydrolysed to the acids without undergoing conversion into the βγ-form.

Some experiments were carried out to ascertain the positions of equilibrium between the αβ- and βγ-acids in the presence of alkali of various concentrations, but an exact estimate was impossible owing to the insufficient analytical methods available at the time. Conversion of the acids into their amides shows, however, that the equilibrium is so much on the side of the βγ-compound that the presence of the αβ-isomeride cannot be recognised with certainty. The acids are mostly liquids and extremely difficult to purify, and therefore do not lend themselves well to investigation by the analytical methods recently developed by Linstead (this vol., p. 355).

The semicarbazones of the α-substituted ketones are isolated in only one form in the ordinary way; a small amount of a second form can, however, be obtained in all cases by previously treating the ketone with cold sodium ethoxide for 40 hours.

The oxidation of ketones of this group is always difficult. Ozonisation, however, gives definite evidence of the βγ-form of these substances; in every case an oil, giving a deep colour with ferric chloride, is formed, evidently according to the scheme



We have, moreover, succeeded in oxidising one of the ketones to the corresponding acid by means of hypobromite, the βγ-acid being the sole product obtained.

EXPERIMENTAL.

1-*Hydroxy-α-ethyl*cyclo*hexaneacetic Acid.*—The ester was obtained by the Reformatski reaction as described by Wallach (*Annalen*, 1908, **360**, 44); the yield (55%) was slightly improved by adding the magnesium in several portions. The hydrolysis of the ester was difficult and considerable fission into ketone and butyric acid always occurred. The best method was as follows: 100 G. of the ester were added to a hot solution of 100 g. of potassium hydroxide in 100 c.c. of water; 100 c.c. of methyl alcohol were then added gradually and the mixture was refluxed for 2—3 hours. The solution was freed from alcohol under reduced pressure, diluted, extracted with ether, and acidified with ice-cold 30% sulphuric acid. The *acid* thus liberated was extracted with ether, dried, and distilled under reduced pressure, some 24 g. boiling at 167—170°/16 mm. This fraction was a viscous oil with a strong odour of butyric acid; $d_4^{18.8°}$ 1·0010, $n_D^{18.8°}$ 1·46798 (Found: C, 64·7; H, 10·05. $C_{10}H_{18}O_3$ requires C, 64·5; H, 9·7%. Found for the *silver* salt: Ag, 36·9. $C_{10}H_{17}O_3Ag$ requires Ag, 36·9%).

*α-Ethyl-Δ¹-*cyclo*hexenylacetic Acid.*—The hydroxy-ester on dehydration with phosphorus oxychloride or potassium hydrogen sulphate yielded ethyl α-ethyl*cyclo*hexenylacetate (Wallach, *loc. cit.*), b. p. 112—116°/15—18 mm., $d_4^{18.2°}$ 0·862624, n_D 1·45593; $[R_L]_D$ 57·09 (Calc., 56·72) (Found: C, 63·8; H, 9·9. Calc.: C, 63·5; H, 10·2%). The acid obtained from it on alkaline hydrolysis had b. p. 154—156°/20 mm., $d_4^{20.6°}$ 1·01528, $n_D^{20.6°}$ 1·47014 (Found: Ag in silver salt, 39·2. Calc.: Ag, 39·3%). Wallach's hydrobromide, m. p. 106—107°, was readily obtained. The *amide*, prepared by leading dry ammonia into a benzene solution of the acid chloride, was recrystallised from dilute methyl alcohol and had m. p. 115—116° (Found: C, 71·3; H, 10·4. $C_{10}H_{17}ON$ requires C, 71·8; H, 10·2%). The p-*toluidide* was similarly obtained and had m. p. 115° after crystallisation from alcohol (Found: N, 5·6. $C_{17}H_{23}ON$ requires N, 5·4%).

A small quantity of the acid was ozonised in dry chloroform solution, and the ozonide shaken with cold water for 20 minutes. The aqueous solution gave a deep violet colour with ferric chloride; 20% sulphuric acid was then added and the product steam-distilled. Adipic acid was identified in the residue in the flask.

*α-Ethyl*cyclo*hexylideneacetic Acid.*—This acid was prepared by treating the hydroxy-acid with acetic anhydride in the usual manner and isolated from the steam distillate by means of ether. On distillation, some hydrocarbon, a fraction, b.p. up to 160°/20 mm., and one, b. p. 164—166°/20 mm., were obtained, the last being the almost pure αβ-acid. This had $d_4^{19.0°}$ 1·01831 and n_D 1·47977 (Found in the silver salt: Ag, 39·3. Calc.: Ag, 39·3%). The yield was poor (20%).

An attempt was also made to prepare the acid from the ester obtained by hydrolysis of α-*cyclo*hexylidenebutyronitrile, b. p. 129°/20 mm.* (Farrow and Kon, J., 1926, 2128), as described by Harding, Haworth, and Perkin (J., 1908, **93**, 1949); the crude ester had b. p. 120—124°/20—23 mm., $d_4^{18.8°}$ 0·936298, $n_D^{18.8°}$ 1·46827, $[R_L]_D$ 58·22 (Calc., 56·72). The ester on careful alkaline hydrolysis gave a mixture of acids in which the βγ-acid predominated.

The *chloride*, prepared by the action of thionyl chloride, boiled

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* The b. p. of this substance was omitted in the original description (*loc. cit.*).

at 110—112°/20 mm. and gave an *amide*, m. p. 104—105° after crystallisation from dilute alcohol, in which it is more soluble than the βγ-amide; a mixture of the two amides melted at 94—98° (Found: C, 71·3; H, 10·6%). The p-*toluidide* melted at 104°.

The acid did not give well-defined oxidation products with permanganate; on treatment with ozone in chloroform solution, traces of *cyclo*hexanone and some adipic acid were obtained. The product obtained by treating the ozonide with cold water did not give a colour with ferric chloride.

Equilibration Experiments.—3·36 G. of α-ethyl*cyclo*hexylideneacetic acid (the αβ-acid) were boiled with a large excess of 20% sodium hydroxide solution for ½ hour. The product was isolated in the usual way and separated into a neutral and an acid portion by means of sodium hydrogen carbonate. The neutral compound (0·5—0·7 g.) was evidently a lactone; it was converted into the silver salt of the corresponding hydroxy-acid (Found: Ag, 37·0. Calc. for $C_{10}H_{17}O_3Ag$: Ag, 36·9%). The acid recovered from the bicarbonate solution was converted into the amide, which melted at 106—108° (mixed m. p. with the βγ-amide, 106—110°) in the crude state and at 114° after two crystallisations.

The experiment was repeated with 50% alkali. A larger quantity (1—1·2 g.) of the lactone was obtained, the amide of the acid melted at a lower temperature, and by repeated crystallisation some 10% of the αβ-amide could be isolated from it, in addition to the βγ-amide, m. p. 114°.

α-Ethyl-Δ^1-*cyclo*hexenylacetic acid (the βγ-acid) also was treated with 20% potassium hydroxide solution. About 0·5 g. of the lactone was isolated; the amide obtained melted at 113—114° after two crystallisations; the αβ-amide was present only in traces.

α-*Ethyl*cyclo*hexenylacetone.*—This ketone was obtained in 50—55% yield by the action of zinc methyl iodide on the chloride of *either* the αβ- or the βγ-acid; the latter reaction has already been carried out by Birch, Kon, and Norris (*loc. cit.*). It is most conveniently prepared by the ethylation of *cyclo*hexenylacetone in the presence of sodium (Kon, J., 1926, 1792) or sodium ethoxide. The semicarbazone has m. p. 177—182° (crude) and 185° after crystallisation (Found: C, 64·1; H, 9·3; N, 19·0. Calc.: C, 64·6; H, 9·4; N, 18·8%). The ketone regenerated from it had $d_{4^\circ}^{18\cdot6^\circ}$ 0·92011 and n_D 1·46798 and gave the same semicarbazone on treatment with semicarbazide.

The ketone (3·32 g.) was kept for 40 hours in a solution of 0·46 g. of sodium in 10 c.c. of alcohol. The ketone was recovered (2·6 g.) and converted into the semicarbazone (1·2 g.), which melted at 167—180°. On recrystallisation from alcohol, this gave 0·9 g.,

m. p. 185°; the mother-liquor on dilution gave a crop, m. p. 172—176°. After two more crystallisations, 0·1 g. was obtained, m. p. 175—176° (mixed m. p. with compound of m. p. 185°, 167—172°).

A solution of the ketone (2·24g.) in acetic acid at — 4° was saturated with hydrogen bromide and poured into water after 15 minutes. The brown oil obtained was isolated by means of ether, the ether removed, and the bromo-ketone warmed on the steam-bath with aqueous sodium carbonate for 15 minutes. The regenerated ketone was converted into the semicarbazone, which melted at 185° after one crystallisation; no other semicarbazone appeared to be formed.

Attempts were made to alkylate the ketone in the presence of "molecular" sodium or sodium ethoxide, but no trace of alkylation product was obtained.

The ketone (5·4 g.) was heated over-night with ethyl malonate (5·2 g.) and sodium (0·82 g.) in 20 c.c. of alcohol. The product was cooled and poured into water, neutral impurities were removed with ether, and the aqueous layer was strongly acidified and again thoroughly extracted with ether. On removing the ether, a solid (6·5 g.) was obtained which gave a blood-red colour with ferric chloride, and melted at 76—77° after crystallisation from benzene and petroleum; it was hydrolysed by boiling it for 3 hours with 20% potassium hydroxide solution. The product was acidified, warmed for another hour, and shaken with ether. The dried extract gave on evaporation a solid, which was recrystallised from acidified water and again from dilute alcohol; lustrous needles, m. p. 159—160°, of cyclo*hexane*spiro-2-*ethyl*cyclo*hexane*-3 : 5-*dione* were thus obtained (Found: C, 74·8; H, 9·9. $C_{13}H_{20}O_2$ requires C, 75·0; H, 9·6%).

*Oxidation of α-Ethyl*cyclo*hexenylacetone.*—The ketone (2·5 g.) was suspended in a solution of 1·2 g. of potassium hydroxide in 10 c.c. of water and kept at 0° while 0·8 c.c. of bromine was gradually added with shaking; the mixture was kept at 0° over-night. A part of the ketone remained unchanged; from the alkaline liquid an acid was obtained (1 g.) which was converted into the amide (m. p. 108—112°; 113—114° after crystallisation); this was identified as the βγ-amide (α-ethyl-Δ^1-*cyclo*hexenylacetamide) by direct comparison.

No definite products were obtained on oxidation of the ketone with potassium permanganate; with ozone, an ozonide was formed which decomposed when shaken with cold water. The product, which gave a deep violet colour with ferric chloride, was mixed with 20% sulphuric acid and distilled in steam, but no definite products except adipic acid could be identified.

Ethyl 1-*Hydroxy-α-ethyl*cyclo*pentaneacetate.*—This ester was prepared from *cyclo*pentanone as was its higher homologue from *cyclo*-

hexanone, some 40 g., b. p. 127—137°/20—25 mm., being obtained from 1 g.-mol., in addition to 20 g. each of high and low fractions (Found: C, 66·5; H, 9·8. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%). The *acid* was obtained in 42% yield, b. p. 157—160°/23 mm., $d_{4^\circ}^{20\cdot5^\circ}$ 1·01232, $n_D^{20\cdot5^\circ}$ 1·43869, $[R_L]_D$ 44·55 (Calc., 44·65) (Found: C, 62·6; H, 9·5. $C_9H_{16}O_3$ requires C, 62·8; H, 9·3%. Found in silver salt: Ag, 38·8. $C_9H_{15}O_3Ag$ requires Ag, 38·7%) .

α-*Ethyl*-Δ¹-cyclo*pentenylacetic Acid*.—This βγ-acid could not be prepared by the usual method involving the dehydration of ethyl 1-hydroxy-α-ethyl*cyclo*pentaneacetate and hydrolysis, because the hydroxy-ester remained practically unchanged after treatment with potassium hydrogen sulphate and with anhydrous oxalic acid, whilst phosphorus oxychloride gave a very small yield of an impure ester accompanied by tarry by-products. Thionyl chloride also was unsatisfactory. The hydroxy-acid (44 g.) was boiled with 250 c.c. of 20% sulphuric acid for 2 hours, the product distilled in steam, and the distillate extracted with ether and divided into neutral (8 g.) and acid (15 g.) constituents. The latter consisted of an oil, b. p. 138—142°/15 mm., in addition to about 1 g. of a solid acid, m. p. 80—81° (the αβ-acid). The oily βγ-acid has a strong odour of butyric acid, $d_{4^\circ}^{17\cdot4^\circ}$ 1·01909, $n_D^{17\cdot4^\circ}$ 1·47525, $[R_L]_D$ 42·65 (Calc., 42·75) (Found: C, 70·5; H, 8·7. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%. Found in the silver salt: Ag, 41·4. $C_9H_{13}O_2Ag$ requires Ag, 41·3%). The *chloride*, prepared by means of thionyl chloride, has b. p. 96—98°/20 mm.; the *amide* obtained from it was appreciably soluble in water and formed lustrous needles, m. p. 102—103°, from dilute alcohol (Found: C, 70·2; H, 10·1. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%).

The acid readily adds on bromine in ether or acetic acid, but the *bromide* is unstable; the *hydrobromide* also was prepared in acetic acid solution, but could not be obtained solid.

α-*Ethyl*cyclo*pentylideneacetic Acid*.—This αβ-acid was prepared from the hydroxy-acid (70 g.) by the method described on p. 1540. The first runnings were liquid; thereafter 14 g. of a solid, m. p. 80—81° after crystallisation from ether–petroleum, were obtained (Found: C, 70·4; H, 9·2. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%). The liquid by-product gave three fractions on distillation; 4 g. boiled below 100°/16 mm., 6 g. up to 158°, and 8 g. at 158—162°. The *chloride* had b. p. 102—106°/16—18 mm.; the *amide* formed pearly plates, m. p. 97° (mixed m. p. with the βγ-amide, 78—82°), from aqueous alcohol, and was less soluble than the βγ-isomeride (Found: C, 70·7; H, 10·1. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%). The *bromide* was unstable; the *hydrobromide* could not be obtained solid.

The *nitrile* was obtained in the same way as the higher homologue (Farrow and Kon, *loc. cit.*), the yield being 65%. It had b. p. 116—118°/20 mm., $d_{4^\circ}^{21\cdot7^\circ}$ 0·923586, $n_D^{21\cdot7^\circ}$ 1·47555, $[R_L]_D$ 41·22 (Calc., 40·90). The nitrile was hydrolysed to the *ethyl* ester, which had b. p. 116—118°/25 mm., $d_{4^\circ}^{19\cdot5^\circ}$ 0·936298, $n_D^{19\cdot5^\circ}$ 1·47417, $[R_L]_D$ 54·65 (Calc., 52·10). Both ester and nitrile gave *cyclo*pentanone on oxidation with ozone. Hydrolysis of the ester led to a mixture of acids in which the βγ-acid predominated.

α-Ethyl-Δ^1-cyclo*pentenylacetone.*—This βγ-ketone was obtained in about 60% yield by the action of zinc methyl iodide on α-ethyl*cyclo*pentenylacetyl chloride; the yield from the αβ-chloride was much lower (40%). The semicarbazone formed plates, m. p. 166—167°, from dilute alcohol, and was identical with that prepared from the ethylated parent ketone (Kon and Linstead, J., 1925, **127**, 821). The ketone regenerated from it had b. p. 94°/15 mm., $d_{4^\circ}^{19\cdot5^\circ}$ 0·917685, $n_D^{19\cdot5^\circ}$ 1·45942, $[R_L]_D$ 45·32 (Calc., 45·72).

The ketone was treated with sodium ethoxide exactly as described on p. 1541; the semicarbazone obtained from the product contained about 10% of a more soluble form, m. p. 143—145°.

Addition and removal of hydrogen bromide produced no change, and attempts to introduce another alkyl group failed.

The ketone condensed readily with ethyl sodiomalonate, the reaction being complete in 3 hours, but neither the dihydroresorcinol ester nor its hydrolysis product could be obtained solid; the liquid products showed the usual reactions of their class with ferric chloride, etc. A small amount of the diketone was oxidised with hypobromite and the resulting dibasic acid (*α-ethyl*cyclo*pentane-*1 : 1*-diacetic acid*) was analysed in the form of its *silver* salt (Found: Ag, 50·8. $C_{11}H_{16}O_4Ag_2$ requires Ag, 50·5%).

The ketone formed an ozonide, which was decomposed by cold water to an oil giving an intense colour with ferric chloride but from which no definite compounds could be obtained on hydrolysis. Oxidation with permanganate also was inconclusive.

β-Hydroxy-β-methyl-α-ethylpentanoic Acid.—The ester was prepared from methyl ethyl ketone as before; the reaction started very slowly, but the yield was good, being 127 g., b. p. 106—108°/18 mm., together with 20 g. of a lower fraction which can be used for preparing the βγ-ester (Found: C, 63·4; H, 10·9. $C_{10}H_{20}O_3$ requires C, 63·8; H, 10·8%). On hydrolysis, a 50% yield of the *acid* was obtained as an oil, b. p. 132—136°/20 mm. (Found for the *silver* salt: Ag, 40·6. $C_8H_{15}O_3Ag$ requires Ag, 40·5%).

β-Methyl-α-ethyl-Δ^{β}*-pentenoic Acid.*—The preceding hydroxy-ester gave a 70% yield of ethyl β-methyl-α-ethyl-Δ^{β}-pentenoate, b. p. 84—88°/20 mm., $d_{4^\circ}^{19\cdot2^\circ}$ 0·93160, $n_D^{19\cdot2^\circ}$ 1·43618, $[R_L]_D$ 48·67 (Calc., 49·34) on dehydration with phosphorus oxychloride, and about a 50% yield with potassium hydrogen sulphate. The *acid*, obtained on hydrolysis in 66% yield, was a liquid with a penetrating smell, b. p. 122—126°/20 mm., $d_{4^\circ}^{20\cdot4^\circ}$ 0·95884, $n_{D}^{20\cdot4^\circ}$ 1·45113, $[R_L]_D$ 39·90 (Calc., 40·23) (Found for the *silver* salt: Ag, 43·3. $C_8H_{13}O_2Ag$ requires Ag, 43·4%). The *chloride* had b. p. 76—78°/18—20 mm.; the p-*toluidide* formed needles, m. p. 102—104°, from methyl alcohol.

The acid in dry chloroform was treated with ozone, and the ozonide decomposed with water; acetaldehyde was formed in quantity and was identified by means of β-naphthol as usual (compare Kon and Linstead, J., 1925, **127**, 616).

β-*Methyl*-αβ-*diethyl*-Δ^α^-*pentenoic Acid*.—This acid, prepared in poor yield from β-hydroxy-β-methyl-αβ-diethylpentanoic acid by means of acetic anhydride, had b. p. 126—130°/15—18 mm., $d_{4^\circ}^{20\cdot4^\circ}$ 0·95930, $n_{D}^{20\cdot4^\circ}$ 1·45193, $[R_L]_D$ 39·94, and was probably still contaminated with some of the hydroxy-acid, although the silver salt gave correct figures on analysis (Found: Ag, 43·3. Calc.: Ag, 43·4%). The *chloride* had b. p. 86—90°/20 mm.; a small lower fraction (b. p. 72—76°) also was obtained. The p-*toluidide* crystallised from methyl alcohol, in which it is more soluble than the βγ-toluidide, in plates, m. p. 112—113° (mixed m. p. 87—89°). The *hydrobromide* was unstable.

δ-*Methyl*-γ-*ethyl*-Δ^{δ}-*hexen*-β-*one*.—This ketone was obtained in good yield from β-methyl-α-ethyl-Δ^{β}-pentenoyl chloride. The *semicarbazone* formed lustrous needles or plates, m. p. 163—164°, from methyl or ethyl alcohol (Found: C, 61·3; H, 9·3. $C_{10}H_{19}ON_3$ requires C, 60·9; H, 9·6%). The *ketone* regenerated from it had b. p. 72—74°/16 mm., $d_{4^\circ}^{19\cdot7^\circ}$ 0·85068, $n_{D}^{19\cdot7^\circ}$ 1·43908, $[R_L]_D$ 43·30 (Calc., 43·38). The *same* ketone was also obtained, although in poorer yield, from the αβ-chloride. The ketone was oxidised in dry chloroform solution with ozone; the ozonide on decomposition gave acetaldehyde, which was identified as before.

The ketone was treated with cold sodium ethoxide for 48 hours (p. 1541). The semicarbazones prepared from the product consisted for the most part of δ-methyl-γ-ethyl-Δ^{δ}-hexen-β-one semicarbazone, m. p. 163—164°, but contained also about 7% of a semicarbazone which melted, after repeated crystallisation, at 151—152°. A mixture of the two semicarbazones melted at 138—149°. After treatment with hydrogen bromide, the original ketone also gave a very small amount of a semicarbazone, m. p. 148—149°.

Attempts to alkylate the ketone were unsuccessful. The ketone condensed readily with ethyl sodiomalonate to a liquid ester which gave an intense colour with ferric chloride; the dihydroresorcinol obtained on hydrolysis of the ester did not solidify and was not further examined.

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