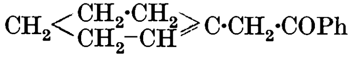
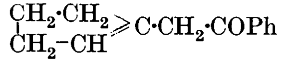
CCLXXXII.—*The Chemistry of the Three-carbon System. Part VI. Some Systems containing the Benzoyl Group.*

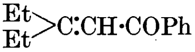
By Maurice Duncan Farrow and George Armand Robert Kon.

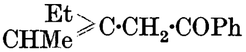
From the analogy existing between compounds containing the keto-enol and the three-carbon system (J., 1923, **123**, 1361) it is possible to predict a similarity in the behaviour of the compounds under the influence of factors affecting the mobility or point of equilibrium of such systems. For example, the introduction of a benzoyl group in the place of acetyl in various diacylmethanes produces a greater tendency to enolisation and enhances the acidity of the compound (K. H. Meyer, *Ber.*, 1912, **45**, 2843; Dieckmann, *Ber.*, 1922, **55**, 2470); the phenylated compounds also show a greater tendency to crystallise and therefore are more readily separated into the pure keto and enol forms by freezing, etc. The introduction of benzoyl as an activating group in compounds which owe their mobility to the three-carbon system should give rise to a series of ketones possessing considerable mobility, since this property is clearly connected with the acidity or "enolising efficiency" of the activating group (compare Meyer, *loc. cit.*). The enhanced tendency to enolisation should be detectable in the more ready formation of alkyl derivatives, particularly in view of the results already obtained (Kon, this vol., p. 1792). Moreover, it was hoped that the new ketones would prove useful in the separation of the two constituents of an equilibrium mixture of the nature of *cyclo*hexenylacetone; pending further work on this problem, it is proposed to describe the general properties of ketones of the new series.

The compounds prepared include α-Δ^1-*cyclo*hexenylacetophenone (I), α-Δ^1-*cyclo*pentenylacetophenone (II), and the corresponding ketones of the *gem*-diethyl series (III and IV).

(I.)

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}\geqslant C\cdot CH_2\cdot COPh$$


$$\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}\geqslant C\cdot CH_2\cdot COPh$$
(II.)

(III.)

$$\begin{matrix}Et\\ Et\end{matrix}>C:CH\cdot COPh$$

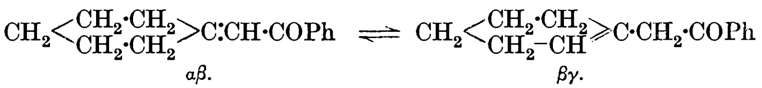

$$\begin{matrix}Et\\ CHMe\end{matrix}\geqslant C\cdot CH_2\cdot COPh$$
(IV.)

Except for a few minor differences attributable to the effect of the phenyl group, the properties of these compounds closely resemble those of the corresponding methyl ketones, in accordance with theoretical considerations; the compounds (III) and (IV) exhibit what was described as retarded mobility (Kon and Linstead, J., 1925, **127**, 815).

The effect of the phenyl group is apparent in the optical properties of the ketones, which all show exaltation of the molecular refraction; this must be due to the fact that the double bond of the keto-group is conjugated with those of the phenyl group. A similar if less pronounced exaltation is observed in acetophenone, from which these compounds may be considered to be derived. The unsatisfactory agreement of the observed and calculated figures for the refraction does not affect the value of the optical method, because comparisons can be made between the optical properties of a series of closely related compounds which agree amongst themselves, thus eliminating the theoretical figures altogether. As regards the tendency to enolisation, there is evidence to show that here again the phenyl group exercises an influence, for the yield of α-ethyl derivatives from the ketones (I) and (II) is much higher than in the case of *cyclo*hexenylacetone. In view of the high enolising efficiency of the group —COPh, it might have been expected that the ketones (I) and (II) could be methylated in the presence of methyl alcohol (compare Kon, *loc. cit.*), but this was not the case.

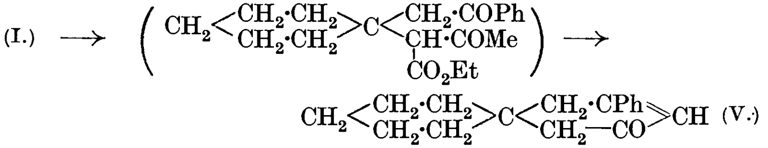
As already stated, these differences are of a minor character; the most striking characteristics of this series of compounds are due to the three-carbon system which they contain and in this respect they differ but little from the corresponding methyl ketones.

The reactions of the compound (I) make it clear that, although it has only been obtained in one form, to which the βγ-structure has been assigned, it functions as an equilibrium mixture of the αβ- and the βγ-phases :



$$\underset{\alpha\beta.}{CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C{:}CH\cdot COPh} \rightleftharpoons \underset{\beta\gamma.}{CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}>C\cdot CH_2\cdot COPh}$$

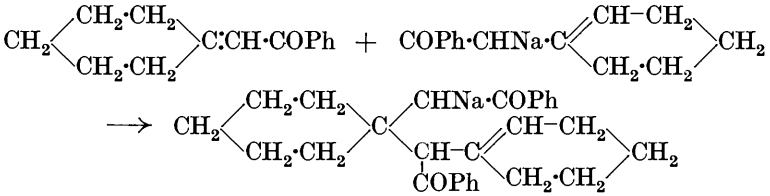
The compound (I) was readily prepared by the direct condensation of *cyclo*hexanone with acetophenone; it could also be obtained by the action of magnesium phenyl bromide or, better, its double compound with zinc chloride (Blaise, *Bull. Soc. chim.*, 1911, 9, 9) on either Δ^1-*cyclo*hexenylacetyl chloride or *cyclo*hexylideneacetyl chloride. In spite of careful manipulation, no difference could be detected between the products of these two reactions; and it has been previously shown that the two solid acids (m. p. 38° and 92°, respectively) can be regenerated from these acid chlorides. The same semicarbazone, m. p. 120—121°, was obtained in good yield from the ketone derived from each of these sources; exhaustive fractional crystallisation of the semicarbazone failed to reveal the existence of a second modification such as was isolated from *cyclo*hexenyl- and from *cyclo*pentenyl-acetone. Oxidation with ozone led to an acidic oil having the properties of an aldehyde and giving a quantitative yield of benzoic acid on hydrolysis; unfortunately no other definite fission-products could be isolated. No *cyclo*-hexanone, which would result from the oxidation of the αβ-phase of the compound, could be detected. The ketone did not react smoothly with ethyl sodiomalonate, whilst the reaction with ethyl sodiocyanoacetate was followed by fission, acetophenone being one of the products isolated; the existence of the αβ-phase of the ketone was, however, definitely proved by the reaction with ethyl sodioacetoacetate, a compound (V) analogous to *iso*phorone being obtained:



$$\text{(I.)} \longrightarrow \left(CH_2{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}C{<}{\substack{CH_2\cdot COPh\\ CH\cdot COMe\\ CO_2Et}} \right) \longrightarrow CH_2{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}C{<}{\substack{CH_2\cdot CPh\\ CH_2-CO}}{\gg}CH \quad \text{(V.)}$$

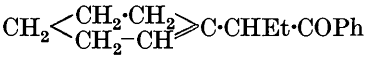
The reaction takes a long time to complete and the yield never exceeds 50%, but the ketone recovered from the operation can be condensed again with the same result.

Another interesting reaction is brought about by the agency of cold sodium ethoxide; only a tenth of the ketone remains unchanged after 24 hours, the remainder being changed to a solid, $C_{28}H_{32}O_2$, m. p. 201°, which readily loses a molecule of water, giving another solid, m. p. 106°. It would appear that the first substance was formed by the condensation of the αβ-phase of the ketone (I) with the sodio-derivative of the βγ-phase, the reaction being



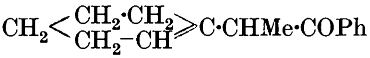
$$CH_2{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}C{:}CH\cdot COPh + COPh\cdot CHNa\cdot C{\ll}{\substack{CH-CH_2\\ CH_2\cdot CH_2}}{>}CH_2 \longrightarrow CH_2{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}C{<}{\substack{CHNa\cdot COPh\\ CH(COPh)-C{\ll}{\substack{CH-CH_2\\ CH_2\cdot CH_2}}{>}CH_2}}$$

analogous to that observed with ethyl α-cyanodimethylacrylate (Birch and Kon, J., 1923, **123**, 2440); the compound can then lose a molecule of water by forming another ring. The ketone (I) gives a very good yield of the ethyl derivative (VI) by the action of ethyl iodide in the presence of sodium ethoxide, although, as already mentioned, no trace of the corresponding methyl derivative



$$CH_2{<}{\substack{CH_2\cdot CH_2\\ CH_2-CH}}{\gg}C\cdot CHEt\cdot COPh$$

(VI.)



$$CH_2{<}{\substack{CH_2\cdot CH_2\\ CH_2-CH}}{\gg}C\cdot CHMe\cdot COPh$$

(VII.)

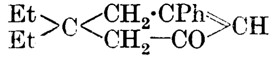
(VII) is formed in the presence of sodium methoxide; methylation proceeds readily in a neutral solvent. The alkyl derivatives cannot be further alkylated and no longer give a colour with ferric chloride or sodium ethoxide. They show a slight exaltation of the molecular refraction comparable with that found in the parent substance (see p. 2129); they are, however, concordant amongst themselves.

Attempts were made to condense the ketone (I) with benzaldehyde and piperonal, but without success.

*cyclo*Pentanone could not be condensed with acetophenone to give the ketone (II); this was, however, prepared in the same way as the higher homologue. from α-Δ^1-*cyclo*pentenyl- and *cyclo*pentylidene-acetyl chlorides (compare Kon and Linstead, *loc. cit.*), the same substance being obtained in each case. The compound resembles the higher homologue in every respect: it gives a similar product on treatment with ozone, condenses with ethyl sodioacetoacetate, and gives an α-ethyl derivative, though in poorer yield. These reactions show that the compound is mobile like the higher homologue.

When the Blaise reaction was applied to the chlorides of diethylacrylic acid and its βγ-isomeride, two *different* ketones (III and IV) were obtained. The αβ-ketone showed a considerable exaltation of the molecular refraction and was characterised by the formation of an *oximino-oxime*. It also condensed with ethyl sodioacetoacetate to give the cylic compound (VIII).

(III.) ⟶



$$\begin{matrix}Et\\Et\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CPh\\CH_2-CO\end{matrix}\!>\!CH$$

(VIII.)

The ketone (IV) had a normal molecular refraction and did not form an oximino-oxime; when treated with ethyl sodioacetoacetate, it gave the compound (VIII) in about the same yield as its isomeride; it is clear, therefore, that in the presence of sodium ethoxide the βγ-ketone is partly converted into the αβ. The actual equilibrium in the presence of sodium ethoxide was not investigated, because the semicarbazone of the ketone (III) is an extremely intractable substance and the separation of a mixture of the two ketones is practically impossible. The action of 25% sulphuric acid on the αβ-ketone causes conversion into the βγ-isomeride (in addition to some hydrolysis), to the extent of roughly 25% in 4 hours, whilst the βγ-ketone is not affected by this treatment.

The ketones (III) and (IV) are therefore analogous to the pair of ketones investigated by Kon and Linstead, and exhibit retarded mobility in the same way, that is, they can be prepared in a pure state and are stable in the absence of reagents, but form an equilibrium mixture in the presence of sodium ethoxide.

All the ketones here described undergo hydrolytic fission on prolonged boiling with acids or alkalis, being split into acetophenone and *cyclo*hexanone, *cyclo*pentanone and diethyl ketone, respectively. *cyclo*Hexenylacetone undergoes a similar fission.

This reaction cannot safely be employed as a guide to the structure of a ketone, since both (III) and (IV) give the same products. It is probable that water is first added to the double linking of the ketone, the hydroxyl attaching itself in each case to the β-carbon atom; the hydroxy-ketone can then undergo the reversed aldol reaction (compare J., 1923, **123**, 1717):

$$\begin{array}{rcl} \mathrm{CEt_2{:}CH{\cdot}COPh + H_2O} & \searrow & \\ & & \mathrm{CEt_2(OH){\cdot}CH_2{\cdot}COPh.} \\ \mathrm{CHMe{:}CEt{\cdot}CH_2{\cdot}COPh + H_2O} & \nearrow & \end{array}$$

EXPERIMENTAL.

α-Δ^1-cyclo*Hexenylacetophenone* (I).

A mixture of 5% sodium ethoxide (1000 c.c.), *cyclo*hexanone (200 g.), and acetophenone (275 g.) was kept ice-cold for a few hours and at room temperature for 3 days; water was then added. The oil produced, isolated and dried in ether, was distilled, the fraction, b. p. 172—178°/14 mm., being almost pure α-Δ^1-cyclo*hexenylacetophenone*; more was obtained by redistillation of the higher fractions, the total yield being about 40% (Found: C, 83·9; H, 8·1. $C_{14}H_{16}O$ requires C, 84·0; H, 8·1%). The ketone is a somewhat viscous, pale yellow oil, $d_{4^\circ}^{21^\circ}$ 1·04157, $n_D^{21\cdot0^\circ}$ 1·55630, $[R_L]_D$ 61·78 (calc., 61·39*); it gives an orange colour with alcoholic ferric chloride. It is not very volatile in steam and therefore the usual method of purification could not be applied.

The *semicarbazone*, prepared by keeping the components in warm methyl-alcoholic solution for an hour, gradually separated as a crystalline cake during 2 days. It crystallised from methyl alcohol in large, transparent, rhombic crystals, m. p. 115—117°, which contained about half a molecule of methyl alcohol; after drying at 100°, the crystals became opaque and melted at 120—121° (Found: C, 70·0; H, 7·4. $C_{15}H_{19}ON_3$ requires C, 70·0; H, 7·4%). This form is obtained direct by crystallisation from dilute methyl alcohol, whilst from benzene a product of indefinite melting point (94—115°) is obtained; only one definite form of the semicarbazone has been isolated up to the present.

The semicarbazone was only slowly decomposed by oxalic acid, but was completely hydrolysed by boiling 5% sulphuric acid in 1

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* This and all subsequent theoretical values were calculated from the observed molecular refraction of acetophenone (Auwers and Eisenlohr, *J. pr. Chem.*, 1910, 82, 65).

hour. The ketone obtained had b. p. 176—178°/17 mm., $d_{4°}^{18\cdot0°}$ 1·04414, $n_{\mathrm{D}}^{18\cdot0°}$ 1·55886, $[R_L]_{\mathrm{D}}$ 61·87.

The *oxime*, prepared in the presence of potassium hydroxide, was an oil which readily solidified on rubbing with petroleum and separated from dilute alcohol in long needles, m. p. 101—102° (Found : C, 78·0; H, 7·8. $C_{14}H_{17}ON$ requires C, 78·1; H, 7·9%).

Oxidation of α-cyclo*Hexenylacetophenone with Ozone.*—The ketone (5 g. at a time) was ozonised in dry chloroform; the ozonide was freed from chloroform under reduced pressure and decomposed by warming with water. The product was a viscous oil with a smell reminiscent of hexahydrobenzaldehyde; it gave a mirror with ammoniacal silver nitrate and a red colour with alcoholic ferric chloride. On distilling it in steam no trace of *cyclo*hexanone was obtained, the only volatile product being benzoic acid. The residue from one experiment was treated with 10% sulphuric acid and again distilled in steam; a further quantity of benzoic acid (total yield 60%) was then obtained together with a little acetophenone, doubtless derived from the hydrolysis of some of the initial material (see p. 2135); no other products could be identified.

Synthesis of α-cyclo*Hexenylacetophenone.*—To a Grignard reagent. prepared from 26 g. of bromobenzene and cooled in ice, was added as rapidly as possible a solution of zinc chloride (1 mol.) in ether (prepared by allowing freshly fused zinc chloride to stand with 2 mols. of dry ether for 24 hours). Dry toluene (250 c.c.) was added and the mixture vigorously shaken; a suspension of the organometallic complex was produced which was freed from ether below 30° under reduced pressure. The suspension was cooled in ice and 13 g. ($\frac{1}{2}$ mol.) of α-Δ^1-*cyclo*hexenylacetyl chloride (b. p. 92—93°/17 mm., prepared from the solid acid, m. p. 38°), diluted with toluene, were slowly run in with vigorous agitation. After 1 hour the ketone was isolated in the usual way (see Part I) and purified by fractionation. A small low fraction consisting of diphenyl was obtained, and 11 g. (67%), b. p. 165—180°/17 mm.; the latter gave on redistillation 10 g., b. p. 168—174°/14 mm., $d_{4°}^{18\cdot0}$ 1·0422, $n_{\mathrm{D}}^{18\cdot0°}$ 1·55870, $[R_L]_{\mathrm{D}}$ 61·84, which readily formed the semicarbazone, m. p. 120—121° after rubbing with ether but without recrystallisation; this was identical in every respect with that previously obtained.

The experiment was repeated starting with the chloride of *cyclo*hexylideneacetic acid (b. p. 104°/13 mm.; the b. p. given by Birch, Kon, and Norris is too high). The ketone (yield about 64%) had b. p. 168—170°/12 mm., $d_{4°}^{20\cdot5°}$ 1·04209, $n_{\mathrm{D}}^{20\cdot5°}$ 1·55710, $[R_L]_{\mathrm{D}}$ 61·80, and readily gave a semicarbazone identical with that of the ketone obtained from the βγ-acid or prepared by direct condensation.

The ketone can also be obtained by the action of magnesium phenyl bromide on either of the above acid chlorides in ice-cold ether; the yield, however, seldom reaches 30%, the main portion of the product being an oil, b. p. 200—220°/20 mm., probably consisting of a tertiary alcohol.

Alkylation of α-cyclo*Hexenylacetophenone.*—The ketone was methylated in ether as described in Part V (this vol., p. 1792); the new ketone was then isolated in about 50% yield; no trace of unchanged parent substance appeared to be present, but a certain amount of high-boiling by-product was found. The ketone had b. p. 168—170°/15 mm., $d_{4°}^{18·5°}$ 0·99896, $n_{D}^{18·5°}$ 1·54314, $[R_L]_D$ 66·36 (calc., 66·11). The *semicarbazone* is very sparingly soluble and separates from methyl alcohol in minute plates, m. p. 191—192° (Found : C, 70·7; H, 8·1. $C_{16}H_{21}ON_3$ requires C, 70·8; H, 7·8%).

The ketone (I) was treated with sodium ethoxide and ethyl iodide as described in Part I. The ethylated ketone was isolated in approximately 90% yield and converted into the *semicarbazone*, which was formed very slowly; at the end of 3 weeks a yield of about 60% was obtained, the crude substance melting above 200°. It crystallised from much ethyl alcohol in minute, iridescent plates, m. p. 212° (Found : C, 71·1; H, 8·1; N, 14·7. $C_{17}H_{23}ON_3$ requires C, 71·6; H, 8·1; N, 14·7%). No trace of the semicarbazone of the parent ketone appeared to be present. The ketone regenerated by means of sulphuric acid was almost odourless; it had b. p. 184—185°/19 mm., $d_{4°}^{21·0°}$ 1·01155, $n_{D}^{21·0°}$ 1·54077, $[R_L]_D$ 70·85 (calc., 70·63).

An attempt was made to synthesise the ethylated ketone by the method of Haworth and Fife (J., 1914, **105**, 1665). Ethyl α-cyano-*cyclo*hexylideneacetate was ethylated, and the new ester kept for 4 hours with sodium ethoxide at 40° without previous purification (compare Birch and Kon, *loc. cit.*). α-cyclo*Hexylidenebutyronitrile* was isolated from the product in 67% yield and had $d_{4°}^{21·0°}$ 0·92283, $n_{D}^{21·0°}$ 1·48917, $[R_L]_D$ 46·67 (calc., 45·53). Magnesium phenyl bromide in ether had, however, no action on the nitrile, which was isolated unchanged.

Action of Ethyl Sodiocyanoacetate.—The ketone was treated on the steam-bath with ethyl cyanoacetate and sodium ethoxide for 6 hours. The product was divided into neutral and acid portions; the neutral portion contained, in addition to unchanged initial material, a considerable quantity of acetophenone, evidently formed as the result of fission; no definite compounds were isolated from the acid fraction, as they were uncrystallisable and could not be distilled.

Action of Ethyl Sodioacetoacetate.—The ketone, ethyl acetoacetate, and alcoholic sodium ethoxide in molecular proportions were heated under reflux or left in the cold; water and a little acid were then added, the oil was taken up in ether and distilled under reduced pressure, much carbon dioxide being evolved; the low fraction obtained consisted of initial material, whilst the fraction, b. p. 200—240°/20 mm., gave on redistillation a thick oil, b. p. 210—220°/20 mm., which solidified on cooling and formed stout needles, m. p. 69—70°, from dilute alcohol, consisting of the ketone (V) (Found: C, 84·8; H, 8·3. $C_{17}H_{20}O$ requires C, 85·0; H, 8·3%). The best yield of this (about 48%) was obtained when the reaction mixture was kept on the steam-bath for a week, whilst about 25% was obtained in the cold. The compound readily gave a highly insoluble *semicarbazone*, which formed small needles, m. p. 219°, from alcohol; these on exposure to sunlight assumed a bright yellow colour which disappeared on recrystallisation (Found: C, 72·5; H, 7·8; N, 14·4. $C_{18}H_{23}ON_3$ requires C, 72·7; H, 7·8; N, 14·1%).

Action of Sodium Ethoxide.—A mixture of the ketone (I) and alcoholic sodium ethoxide was kept for 4 days at room temperature and was then diluted with water and extracted with much ether. The extract on evaporation deposited a crystalline solid (35% yield) together with a small amount of unchanged ketone, which was removed by means of ether. The solid crystallised from benzene and petroleum in short needles, m. p. 201° (Found: C, 83·8; H, 8·1. *M*, cryoscopic in benzene, 389. $C_{28}H_{32}O_2$ requires C, 84·0; H, 8·1%; *M*, 400). The compound was sparingly soluble in ether, alcohol, or acetone, readily in benzene, ethyl acetate, or chloroform. It dissolved in hot acetic acid, but on diluting and cooling the solution a new compound, crystallising from dilute alcohol in felted needles, m. p. 106°, was precipitated (Found: C, 87·9; H, 7·9. $C_{28}H_{30}O$ requires C, 87·9; H, 7·9%). The compound is very soluble in alcohol and in ether.

Hydrolysis.—The ketone (10 g.) was boiled with an equal weight of potassium hydroxide in 70 c.c. of water for 36 hours; 4·3 g. remained unchanged, whilst *cyclo*hexanone and acetophenone were isolated from the lower-boiling fraction and identified by their semicarbazones. In 96 hours the hydrolysis was practically complete, a 95% yield of acetophenone-semicarbazone being isolated. In addition to a small amount of benzoic acid, a 70% yield of acetophenone was obtained in 24 hours by the agency of methyl-alcoholic potassium hydroxide (12 g. in 10 c.c. of water and 10 c.c. of alcohol). 25% Sulphuric acid (by vol.) produced about 50% fission in 36 hours.

α-Δ^1-cyclo*Pentenylacetophenone* (II).

Attempts to effect the direct condensation of *cyclo*pentanone with acetophenone were fruitless, the only ketone contained in the high fraction of the reaction product being *cyclo*pentylidene*cyclo*pentanone (Wallach, *Ber.*, 1896, **29**, 2963). The new ketone was therefore prepared synthetically by Blaise's method, exactly as described for the higher homologue, starting with the two pure acids, m. p. 51—52° and 63—64°, respectively (Kon and Linstead, J., 1925, **127**, 616). A 65% yield of the same ketone giving the same semicarbazone was obtained in either case (that prepared from the αβ-acid had b. p. 160—165°/16 mm., $d_{4^\circ}^{18\cdot0^\circ}$ 1·0542, $n_D^{18\cdot0^\circ}$ 1·56740; that from the βγ-acid had b. p. 164—165°/16 mm., $d_{4^\circ}^{18\cdot5^\circ}$ 1·05251, $n_D^{18\cdot5^\circ}$ 1·56637). The *semicarbazone* is less soluble than that of the ketone (I) and forms stellate clusters of needles, m. p. 157°, from methyl alcohol (Found : C, 69·0; H, 7·2. $C_{14}H_{17}ON_3$ requires C, 69·1; H, 7·0%). A second form of the semicarbazone could not be isolated. The *ketone* regenerated from it had b. p. 163—165°/16 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·04982, $n_D^{20\cdot0^\circ}$ 1·56437, $[R_L]_D$ 57·69 (calc., 56·77); it gave a deep orange colour with alcoholic ferric chloride.

Oxidation.—The product obtained by treating the ketone with ozone was exactly analogous to that obtained from the higher homologue; a 67% yield of benzoic acid was isolated after hydrolysis of the ozonide with sulphuric acid; no other recognisable product was isolated.

Alkylation.—The ketone was treated with ethyl iodide in the presence of sodium ethoxide as described on p. 2134. About 80% of ethylation product was obtained, the remainder being a high-boiling oil. On treatment with semicarbazide, a crystalline *semicarbazone* formed slowly (yield 37%); it separated from much alcohol in small plates, m. p. 196·5° (Found : C, 70·7; H, 7·8. $C_{16}H_{21}ON_3$ requires C, 70·8; H, 7·8%). The ketone regenerated from it was odourless and had b. p. 162°/11 mm., $d_{4^\circ}^{18\cdot5^\circ}$ 1·01725, $n_D^{18\cdot5^\circ}$ 1·54191, $[R_L]_D$ 66·25 (calc., 65·46).

Action of Ethyl Sodioacetoacetate.—The condensation was carried out as described on p. 2134. The product did not solidify and was therefore isolated in the form of its *semicarbazone*, which was obtained in about 60% yield; the actual yield of condensation product is doubtless higher. The semicarbazone separates from alcohol in small prisms, m. p. 193°, and turns yellow on exposure to light (Found : C, 72·2; H, 7·8. $C_{17}H_{21}ON_3$ requires C, 72·0; H, 7·5%).

Action of Sodium Ethoxide.—The reaction was complete after 48 hours in the cold; the product was, however, an uncrystallisable gum.

Hydrolysis.—This was carried out by means of aqueous potassium hydroxide; a yield of 50% of acetophenone was obtained after 36 hours' boiling.

α-Phenyl-γ-ethyl-Δ^{β}-penten-α-one (III).

Diethyl ketone could not be condensed with acetophenone. The ketone was therefore prepared by the Blaise reaction from the chloride of ββ-diethylacrylic acid, obtained as described by Kon and Linstead (*loc. cit.*); the acid had b. p. 117—119°/14 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·9693, $n_D^{20^\circ}$ 1·46539, $[R_L]_D$ 36·56. The yield of ketone was nearly 80%; it had b. p. 146—148°/13 mm., $d_{4^\circ}^{21\cdot6^\circ}$ 0·98716, $n_D^{21\cdot6}$ 1·54372, $[R_L]_D$ 60·14 (calc., 58·96). The *semicarbazone* was not easily formed and remained oily for several weeks; eventually a very small amount of solid was isolated which melted, after repeated crystallisation from methyl alcohol, at 90° (Found: C, 68·7; H, 8·0. $C_{14}H_{19}ON_3$ requires C, 68·5; H, 7·8%). The oily semicarbazone was purified by distillation in steam, after which oxalic acid was added and the distillation repeated; the pure *ketone* so obtained had b. p. 138°/8 mm., $d_{4^\circ}^{18\cdot0^\circ}$ 0·98638, $n_D^{18\cdot0^\circ}$ 1·54353, $[R_L]_D$ 60·10.

Oxime.—The ketone was heated for 4 hours with hydroxylamine hydrochloride (2 mols.) and potassium hydroxide in alcoholic solution. The *oximino-oxime* so obtained crystallised from benzene and petroleum in short needles, m. p. 158° (Found: C, 66·2; H, 8·7. $C_{13}H_{20}O_2N_2$ requires C, 66·0; H, 8·5%). If only one molecule of the reagent was used and the mixture kept in the cold for 24 hours, the *compound* obtained on dilution consisted of fine needles, m. p. 101—102° after crystallisation from petroleum (Found: C, 70·7; H, 8·7. $C_{13}H_{19}O_2N$ requires C, 70·5; H, 8·7%). It has the composition of the monoxime plus one molecule of water and is probably formed by the addition of hydroxylamine to the double bond of the ketone.

Hydrolysis.—The action of aqueous potassium hydroxide for 36 hours led to the formation of 45% of acetophenone; in addition, a high fraction (about 40%) was obtained which did not consist of the unchanged ketone but of the βγ-isomeride (IV, see below), which was identified by its semicarbazone. The ketone (III) was also boiled with 25% sulphuric acid for 4 hours; the high-boiling fraction obtained was a mixture of the initial material with the βγ-isomeride; judging from the optical properties ($[R_L]_D$), about 30% conversion had taken place, but it is difficult to estimate this. A small amount of the βγ-semicarbazone was isolated from the mixture.

Action of Ethyl Sodioacetoacetate.—The condensation was carried out as before, the mixture being heated for 48 hours, then left in the cold for 24 hours. About one-third of the ketone was recovered, and this appeared to have undergone partial conversion to the βγ-ketone. The high-boiling fraction did not solidify, but a *semicarbazone*, crystallising from alcohol in rosettes of needles, m. p. 178—179°, was obtained from it. It was identical with that obtained from the βγ-ketone (*q.v.*).

α-Phenyl-γ-ethyl-Δ^{γ}-penten-α-one (IV).

This ketone was obtained, in 83% yield, exactly like its αβ-isomeride from the chloride of γ-ethyl-Δ^{γ}-pentenoic acid (Kon and Linstead, *loc. cit.*). The latter was prepared by boiling β-hydroxy-ββ-diethylpropionic acid with dilute sulphuric acid (1 : 4) for 1½ hours; when freed from a small quantity of lactone, it had b. p. 113—115°/13 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·96597, $n_{\mathrm{D}}^{20\cdot0^\circ}$ 1·45113, $[R_L]_{\mathrm{D}}$ 35·71. The yield was only 40%, but the product was more easily obtained pure than by the process originally used.* The ketone prepared from it had b. p. 135—136°/10 mm., $d_{4^\circ}^{18\cdot0^\circ}$ 0·98945, $n_{\mathrm{D}}^{18\cdot0^\circ}$ 1·53679, $[R_L]_{\mathrm{D}}$59·33 (calc., 58·96). The *semicarbazone* separated from ethyl acetate in small plates, m. p. 171° (Found: C, 68·4; H, 7·9. $C_{14}H_{19}ON_3$ requires C, 68·5; H, 7·8%). The *ketone* regenerated from it had b. p. 146°/17 mm., $d_{4^\circ}^{19\cdot5^\circ}$ 0·98513, $n_{\mathrm{D}}^{19\cdot5^\circ}$ 1·53372, $[R_L]_{\mathrm{D}}$ 59·34. A crystalline oxime was not obtained.

Hydrolysis.—The ketone was boiled with aqueous potassium hydroxide for 36 hours. Diethyl ketone was identified in the product by its *p*-nitrophenylhydrazone, m. p. 138°; about 60% of acetophenonesemicarbazone was also obtained, whilst the high fraction (about 20%) consisted of initial material. The hydrolysis was also carried out with dilute sulphuric acid; two-thirds of the ketone remained unattacked, and this was the βγ-ketone, no conversion into the isomeride having taken place. It is therefore clear that only the αβ-ketone (III) is isomerised by boiling with sulphuric acid.

Action of Ethyl Sodioacetoacetate.—The condensation proceeds precisely as in the case of the αβ-ketone, the same yield of condensation product being obtained. It was identified by means of the semicarbazone, m. p. 178—179° (Found: C, 71·7; H, 8·0. Calc.: C, 71·6; H, 8·1%).

Hydrolysis of Δ^1-cyclo*Hexenylacetone.*—The ketone was boiled with aqueous potassium hydroxide for 36 hours. The product gave a low fraction in which acetone could be identified; *cyclo*hexanone was separated in the form of its semicarbazone, the yield being about 60%. The remainder consisted of the unchanged ketone with a quantity of gummy impurity.

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