# CCCXLIII.—*The Chemistry of the Three-carbon System. Part XXVII. Homomesitones,* $C_{10}H_{18}O$ *and* $C_8H_{14}O$.

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It has been shown by Abbott, Kon, and Satchell (J., 1928, 2514) that two molecules of methyl ethyl ketone condense to unsaturated ketones, $C_8H_{14}O$, in two different ways. Straight-chain ketones of the type (I) are produced with alkaline condensing agents, whilst acids lead to branched-chain products of the type (II), the corresponding $\beta\gamma$-ketones being also formed in each case :

(I.) $CMeEt{:}CH{\cdot}COEt$ $CMeEt{:}CMe{\cdot}COMe$ (II.)

Both types were found to form equilibrium mixtures with their $\beta\gamma$-isomerides under the influence of suitable catalysts, and an additional interest attaches to them because definite indications were obtained of their existence in *cis*- and *trans*-modifications.

The higher homologues, $C_{10}H_{18}O$, derived from diethyl and methyl propyl ketone, have now been prepared.

The intermolecular condensation of diethyl ketone can give rise to only two homomesitones, *viz.*, (III) and (IV), whilst methyl propyl ketone can give four products; of these, (V) and (VI) should be formed with alkaline, and (VII) and (VIII) with acid condensing agents :

(III.) $CH_2Me{\cdot}CEt{:}CMe{\cdot}COEt$ $CHMe{:}CEt{\cdot}CHMe{\cdot}COEt$ (IV.)
(V.) $CH_2Et{\cdot}CMe{:}CH{\cdot}COPr^{\alpha}$ $CHEt{:}CMe{\cdot}CH_2{\cdot}COPr^{\alpha}$ (VI.)
(VII.) $CH_2Et{\cdot}CMe{:}CEt{\cdot}COMe$ $CHEt{:}CMe{\cdot}CHEt{\cdot}COMe$ (VIII.)
(IX.) $CH_2Me{\cdot}CEt{:}CH{\cdot}COMe$ $CHMe{:}CEt{\cdot}CH_2{\cdot}COMe$ (X.)

The behaviour of these compounds with sodium ethoxide has been examined, and for the sake of quantitative comparison the equilibration of the similarly constituted ketones (IX) and (X) (Kon and Linstead, J., 1925, **127**, 815) and of the homomesitones described by Abbott, Kon, and Satchell has been repeated under the standard conditions developed by Kon and Linstead (J., 1929, 1269).

*Homomesitones* (III) *and* (IV).—The action of alkaline condensing agents on diethyl ketone has been studied by Franke and Köhler (*Annalen*, 1923, **438**, 314), who state that they were unable to obtain a pure homomesitone; the only definite substance isolated had a b. p. (247°) and composition suggesting a different structure. Ekeley and Scott Carpenter (*J. Amer. Chem. Soc.*, 1924, **46**, 446) claim to have isolated a small amount of a homomesitone which gave " an odour of diethyl ketone " and acetic acid on oxidation; finally, Grignard and Fluchaire (*Ann. Chim.*, 1928, **9**, 5) obtained a small amount of unsaturated ketone ( ?) by the dehydration of the corresponding ketol; the properties of this substance, which did not yield a semicarbazone, differ from those of Ekeley and Scott Carpenter's ketone, notably in being practically odourless.

In our hands, the action of sodium ethoxide on diethyl ketone did not yield a trace of homomesitone, although a fair amount of a higher-boiling oil, evidently identical with Franke and Köhler's compound, was formed; its properties point to its being a *cyclic* ketone, $C_{11}H_{18}O$.

The action of acid condensing agents on diethyl ketone was equally unsatisfactory, and we were therefore obliged to resort to synthesis for the preparation of the ketones (III) and (IV). These were readily obtained pure by standard methods; both formed characteristic semicarbazones and possessed a strong camphoraceous odour. In this and other properties they differ appreciably from Grignard and Fluchaire's compound, and it appears improbable that the latter can have the constitution (III) assigned to it. The same remark applies also to Ekeley and Scott Carpenter's product, more especially as in the presence of sodium ethoxide the compound (III) passes completely into its βγ-isomeride (IV) (see below), which cannot yield diethyl ketone on oxidation.

On the other hand, methyl propyl ketone readily undergoes intermolecular condensation with both alkaline and acid condensing agents. Thus, with sodium ethoxide a fair yield of homomesitone is obtained (compare Franke and Köhler, *loc. cit.*), quite analogous to that obtained from methyl ethyl ketone and possessing a similar rather unpleasant odour. Its physical properties closely resemble those of the ketone prepared by Grignard and Fluchaire (*loc. cit.*) by the dehydration of the corresponding ketol, to which the structure (V) was assigned. Although the homomesitone has a high molecular refraction, which denotes a considerable proportion of the αβ-form (V), it has an appreciable affinity for iodine chloride and is evidently an equilibrium mixture of the two isomerides (V) and (VI). This conclusion is readily confirmed by treating the mixture with aluminium amalgam, whereby the αβ-ketone is converted into a bimolecular reduction product, leaving the pure βγ-ketone (VI) which is readily recognised by its high iodine addition. The proportion of these two products is 3 to 1, in good agreement with the composition of the equilibrium mixture (73% αβ) as estimated by the iodometric method.

It was not possible to isolate the αβ-ketone in a pure state. Both ketones were synthesised, but although a pure βγ-ketone was readily obtained, the αβ-ketone afforded by the Blaise–Maire reaction was contaminated with impurities which raised its density, whilst that prepared by Darzens and Rost's method (*Compt. rend.*, 1911, **153**, 772) contained much of the isomeric βγ-ketone; neither specimen gave a semicarbazone. The identity of the synthetic αβ-ketone with that contained in the equilibrium mixture was readily established by the preparation of the same solid dihydroresorcinol derivative from each.

The action of acid condensing agents on methyl propyl ketone has been examined by Grignard and Colonge* (*Compt. rend.*, 1930, **190**, 1349), who used halogen acids, and by Descudé (*Ann. Chim. Phys.*, 1903, **29**, 486), who employed acetyl chloride and zinc chloride; these authors did not, however, characterise the products obtained.

We have found that Descudé's method gives a good yield of crude homomesitone, which is appreciably denser than that described above and possesses a strong camphoraceous odour, quite different from that of the ketones (V) and (VI). Unfortunately, it is difficult to isolate a pure ketone from it although a small quantity of a semicarbazone, m. p. 154°, can usually be obtained.

We were therefore again obliged to resort to synthesis and readily obtained the two ketones (VII) and (VIII) pure; the second of these ($\beta\gamma$) gave a semicarbazone, m. p. 154°, identical with that obtained by Descude's method, proving that the intermolecular condensation of methyl propyl ketone with acids gives a product with a *branched* chain. Moreover, the properties of the pure $\alpha\beta$-ketone (VII) proved to be very similar to those of the crude ketone obtained by Descudé's method, although it could not be isolated; this, however, is not surprising in view of the great solubility of the semicarbazone of (VII).

It should be stated that no definite indications have been obtained of the existence in stereoisomeric forms of any of the new ketones now described, although the very intractable nature of the compounds (V) and (VI) may perhaps be due to this cause.

*Tautomerism of the Homomesitones.*—The equilibria and mobilities determined in the course of the present work can be summarised as follows:

| Ketone ($\alpha\beta$-form). | % $\alpha\beta$ at equilibrium. | Mobility. | Half-change period (mins.). |
|---|---|---|---|
| (I) | 67* | 1100 | 4 |
| (IX) | 44 | 930 | 6 |
| (V) | 73 | 268 | 12 |
| (II) | 17* | 2·9 | 3,700 |
| (III) | 0(?) | 0·95 | 7,300 |
| (VII) | 0(?) | 0·32 | 21,500 |

* Determined by Abbott, Kon, and Satchell (*loc. cit.*).

The extremely slow equilibration of the $\alpha$-substituted ketones (II), (III), and (VII) is at once apparent, and illustrates the profound retarding effect of the $\alpha$-substituent already observed in several other cases (compare this vol., p. 1411); it is noteworthy that the change is remarkably free from side reactions (addition of alcohol, etc.).

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* *Added in proof.*—Colonge (*Bull. Soc. chim.*, 1931, **49**, 426) has given further details of this work and concludes that the same homomesitone is produced both by acid and by alkaline reagents. The synthesis now described show that this view is incorrect.

Again, the great effect of the α-group on the equilibrium, favouring the βγ-form, is also noteworthy; this agrees with the observations of Kon and Thakur (J., 1930, 2217) and of Abbott, Kon, and Satchell on ketones; there can be no doubt that the effect of an α-alkyl group on ketone equilibria is precisely the opposite to that in acids.

Finally, attention is directed to the equilibration of the ketone (II) and its βγ-isomeride, on which additional information has now been obtained. It is clear that the change is less simple than hitherto believed, and that *cis-trans*-isomerism plays a considerable part in it. For instance, it has now been found that the two stereoisomeric forms of the βγ-ketone, although very similar in physical properties, have widely different reactivities towards iodine chloride; that derived from the semicarbazone, m. p. 203—204°, has an addition of only 43% (ketone *a*), whilst that corresponding to the commoner, more soluble, semicarbazone, m. p. 163°, has an addition of 95% (ketone *b*). Mixtures of the two semicarbazones melt at intermediate temperatures; as a rule, preparations melting at about 180° or higher were employed in the previous work (Abbott, Kon, and Satchell) and these give a ketone with an addition of 80—85%. The pure αβ-ketone and the pure ketone *b* give, on treatment with sodium ethoxide, equilibrium mixtures with an addition of about 81%, a value distinctly higher than that previously found; the difference may be due to the prolonged treatment with sodium methoxide which was employed in the earlier work and has since been shown to favour side reactions.

The equilibrium mixtures obtained in this way contain appreciable quantities of the ketone *a* which can be easily recognised. Unfortunately, we have not been able to obtain enough of this substance for a thorough investigation; a single experiment on the equilibration of the pure ketone *a* suggests that the αβ–βγ equilibrium is established much more rapidly than the equilibrium between the *cis*- and *trans*-forms of the βγ-ketone; this, therefore, most probably proceeds through the intermediate formation of the αβ-ketone, the relationship being somewhat similar to that observed by Linstead and Mann (this vol., p. 726) in the equilibration of citraconic acid.

The presence of both forms of the βγ-ketone in the equilibrium mixture makes the actual point of equilibrium uncertain, but the value previously found appears to be at least of the right order, and has been used in calculating the mobility given on p. 2499.

## EXPERIMENTAL.

The preparation of the new substances obtained is given below. The equilibrations were, unless otherwise stated, carried out exactly as described by Kon and Linstead (*loc. cit.*), the products being analysed iodometrically by the method of Linstead and May (J., 1927, 2565). For this purpose reference curves were constructed for the iodine additions of each pair of ketones, the number *J* representing the addition in 10 minutes in chloroform solution.

*ε-Methyl-*$\Delta^{\epsilon}$*-hepten-γ-one.*—The equilibration data of this ketone were determined by Mr. R. D. Satchell on the specimen described by Abbott, Kon, and Satchell (*loc. cit.*), and analysed with the aid of the reference curve already given.

| Time (mins.) | 10 | 20 | 30 | 60 | 120 |
|---|---|---|---|---|---|
| *J*, % | 50·1 | 43·8 | 39·1 | 36·9 | 36·5 |
| αβ-Ketone, % | 48·3 | 57·0 | 63·0 | 65·8 | 66·3 |

*δ-Ethylhexen-γ-ones.*—The ketones were prepared as described by Kon and Linstead (*loc. cit.*), but the regeneration from the semicarbazone was carried out by Kon's method (J., 1930, 1616). The pure ketones had the following properties: αβ, b. p. 74°/29 mm., $d_{4^\circ}^{18 \cdot 0^\circ}$ 0·85621, $n_{D}^{18 \cdot 0^\circ}$ 1·45373, $[R_L]_D$ 39·90; βγ, b. p. 70°/26 mm., $d_{4^\circ}^{15 \cdot 6^\circ}$ 0·85453, $n_{D}^{15 \cdot 6^\circ}$ 1·44271, $[R_L]_D$ 39·10.

*Reference curve:*

| Mixture (% αβ) | 100 | 90 | 75 | 50 | 25 | 10 | 0 |
|---|---|---|---|---|---|---|---|
| *J*, % | 4·2 | 13·5 | 26·1 | 41·8 | 52·6 | 57·9 | 60·5 |

The following results were obtained with the αβ-ketone:

| Time (mins.) | 10 | 20 | 40 | 80 |
|---|---|---|---|---|
| *J*, % | 35·9 | 41·4 | 43·9 | 44·8 |
| αβ-Ketone, % | 62·5 | 51·5 | 47·0 | 44·0 |

The recovered samples were then combined and again treated with sodium ethoxide for 2 hours; the product had b. p. 71—73°/26—27 mm., $d_{4^\circ}^{18^\circ}$ 0·85918, $n_{D}^{18^\circ}$ 1·44773, *J* 45·2 (= 43·5% αβ). A specimen of the βγ-ketone similarly treated gave a product, b. p. 68—72°/25 mm., $d_{4^\circ}^{18^\circ}$ 0·85510, $n_{D}^{18^\circ}$ 1·44622, *J* 44·3 (= 44·5% αβ).

The combined equilibrium mixtures of ketone obtained above were treated with aluminium amalgam (compare Abbott, Kon, and Satchell, *loc. cit.*); the low fraction was isolated readily from the semicarbazone of the βγ-ketone, m. p. 144°, after one crystallisation.

*γδ-Dimethylhexene-β-ones* (*Homomesitones*).—The αβ-ketone was prepared as described by Abbott, Kon, and Satchell (*loc. cit.*), and had the properties and iodine additions recorded there.

The stereoisomeric βγ-ketones were prepared by several methods. Synthesis leads to a mixture, as previously found (*loc. cit.*), and so does treatment of the αβ-ketone with sodium ethoxide, followed by reduction with aluminium amalgam, although only one form is present in some cases. The semicarbazones prepared from these mixtures contain mostly the low-melting form, whilst the high-melting one, although very sparingly soluble, is only obtained pure with the greatest difficulty. A specimen of it, m. p. 200—201°, gave on regeneration by Kon's method, the *a* ketone, b. p. 47°/14 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·8520, $n_{\mathrm{D}}^{20\cdot0^\circ}$ 1·43818, $[R_L]_{\mathrm{D}}$ 38·81 (Calc., 38·72), *J* 43·2% (Found : C, 76·4; H, 11·2. $C_8H_{14}O$ requires C, 76·2; H, 11·1%); on recombination with semicarbazide, it gave a product, m. p. 201° without purification. The pure low-melting form gave the *b* ketone, b. p. 47°/11 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·85187, $n_{\mathrm{D}}^{20\cdot0^\circ}$ 1·43748, $[R_L]_{\mathrm{D}}$ 38·74, *J* 94·9%. There is thus a remarkable difference in the iodine addition of the two forms, although their physical properties are very similar; there is quite an appreciable difference in smell, the ketone *a* having a slightly mouldy odour reminiscent of some camphor derivatives. Mixtures of the semicarbazones, m. p. 163° and 203—204°, melt at intermediate temperatures, but *both* m. p.'s are depressed by the addition of the αβ-semicarbazone.

*Equilibrations.* The reference curve given by Abbott, Kon, and Satchell has been constructed by using the pure αβ-ketone and a βγ-ketone regenerated from a semicarbazone melting at about 180°, and therefore containing both *a* and *b* forms. A similar curve has now been constructed for mixtures of pure αβ- and pure *b* ketone from the following values :

| Mixture, % *αβ* ...... | 100 | 90 | 75 | 50 | 25 | 10 | 0 |
|---|---|---|---|---|---|---|---|
| *J*, % .................. | 3·4 | 16·1 | 34·2 | 63·2 | 82·1 | 90·2 | 94·9 |

This curve gives maximum values for the αβ-content of a given mixture because it is assumed that all the addition is due to the very additive *b* ketone, whilst actually some of it is due to the inert form *a*. The pure αβ-ketone was equilibrated with the following results :

| Time (hrs.) .......................... | 24 | 48 | 72 | 118 |
|---|---|---|---|---|
| *J*, % .................................... | 32·0 | 55·7 | 66·4 | 69·7 |
| Maximum, % ....................... | 76·5 | 57·0 | 46·0 | 41·0 |

The mobility calculated from these figures is about 2·9, Abbott, Kon, and Satchell's value for the point of equilibrium being assumed. The combined samples (5 g.) were warmed on the steam-bath with 1 g. of sodium dissolved in 20 c.c. of *iso*propyl alcohol for an hour. The ketone isolated, b. p. 42—45°/9 mm., had $d_{4^\circ}^{20\cdot0^\circ}$ 0·8574, $n_{\mathrm{D}}^{20\cdot0^\circ}$ 1·44321, *J* 80·8%; it gave a semicarbazone, m. p. 163°, after one crystallisation.

Pure specimens of αβ-ketone and *b* ketone were each warmed on the steam-bath with sodium ethoxide for 2 hours. The recovered ketones had *J* 80·9 and 81·7% respectively, and these therefore appear to represent the equilibrium value. The specimen derived from *b* was converted into the semicarbazone, which after one crystallisation from methyl alcohol formed characteristic rhombic crystals, m. p. 178—180°, so that the production of the *a* ketone was evident.

A similar experiment was performed with the pure ketone *a*, of which only a very small amount was available. The recovered ketone showed very little change in iodine addition (*J* 45%); this can be taken to mean that the production of the highly additive form *b* is slow as compared with the three-carbon change.

The pure αβ-ketone (10 g.) was then treated with sodium ethoxide as above; the product had the unusually high addition of 84·1% (= 22% αβ from the latest curve). It was treated with a large excess of aluminium amalgam after which it had b. p. 50°/14 mm., *J* 94·8%; it formed the more soluble semicarbazone, m. p. 163°, and thus appeared to be the pure ketone *b*. Quite an appreciable residue of high-boiling bimolecular by-product was also obtained in this experiment, showing that some αβ-ketone was present in the equilibrium mixture.

A similar large-scale experiment was performed with the pure ketone *b*. The equilibrated ketone had an addition of 83·3% before and 91·5% after reduction. On treatment with semicarbazide, it gave a mixture of semicarbazones melting after one crystallisation at 173—175°, thus confirming the presence of the ketone *a*; the iodine addition of the product points to the presence of some 15% of *a* in the mixture.

From these results it can be concluded that although the proportion of the *a* and the *b* form of the βγ-ketone varies in the equilibrium mixture, *b* predominates largely. The point of equilibrium becomes uncertain, but the value previously found (17% αβ) appears to be of the right order.

δ-*Methyl*-ε-*ethylheptenones*, (III) *and* (IV).—Diethyl ketone (340 g.) was kept in the cold with alcohol-free sodium ethoxide prepared from 40 g. of sodium for 6 days. The resulting oil was isolated by means of ether, washed, dried, and carefully fractionated, but practically the whole boiled below 35°/25 mm. (diethyl ketone) and some 20 g. at 126—130°/16 mm. In another experiment the mixture was kept for 12 days, and 65 g. of high-boiling fraction were obtained from 170 g. of diethyl ketone; no trace of ketone boiling at the correct temperature for the latter appeared to be formed. The high-boiling fraction had b. p. 124—128°/12—18 mm., $d_{4^\circ}^{20^\circ}$ 0·9312, $n_{\mathrm{D}}^{20^\circ}$ 1·48917, and was evidently a cyclic *compound* (Found: C, 79·5; H, 11·1. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%).

Diethyl ketone was saturated with hydrogen bromide at 0° (Grignard and Colonge, *loc. cit.*), and kept for 2 days, after which it was taken up in ether, washed, dried, and the ether evaporated. No high-boiling fraction (homomesitone) was formed. Descudé's method of condensation was also tried, but a homomesitone fraction was not isolated.

δ-*Methyl*-ε-*ethyl*-$\Delta^{\delta}$-*hepten*-γ-*one* (III).—α-Methyl-ββ-diethylacrylic acid (this vol., p. 1416) was converted into its chloride, b. p. 84°/12 mm., by means of thionyl chloride, and this was added to ethylzinc iodide (Blaise and Maire, *Ann. Chim. Phys.*, 1908, **15**, 556; compare Dickins, Hugh, and Kon, J., 1928, 1630), a 50% yield of ketone, b. p. 94°/23—21 mm., being obtained. This was converted into the *semicarbazone*, which crystallised from methyl alcohol in pearly plates, m. p. 153° (Found: C, 62·4; H, 9·9. $C_{11}H_{21}ON_3$ requires C, 62·5; H, 10·0%). The ketone regenerated from it with the aid of oxalic acid, b. p. 80°/10 mm., $d_{4^\circ}^{19\cdot0^\circ}$ 0·86218, $n_{D}^{19\cdot0^\circ}$ 1·45453, $[R_L]_D$ 48·45 (Calc., 47·96), had a powerful camphoraceous odour; in all these properties it differs appreciably from the substance described by Grignard and Fluchaire (*loc. cit.*).

δ-*Methyl*-ε-*ethyl*-$\Delta^{\epsilon}$-*hepten*-γ-*one* (IV).—α-Methyl-β-ethyl-$\Delta^{\beta}$-pentenoic acid (this vol., p. 1416) was converted into the chloride, b. p. 74°/15 mm., and this treated in ethereal solution with ethylmagnesium iodide (Darzens and Rost, *loc. cit.*; Abbott, Kon, and Satchell, *loc. cit.*), a 50% yield of ketonic fraction, b. p. 83—88°/18 mm., being obtained. The *semicarbazone* was readily formed, and crystallised from methyl alcohol or acetone in clusters of needles, m. p. 109° (Found: C, 62·5; H, 10·3. $C_{11}H_{21}ON_3$ requires C, 62·5; H, 10·0%). The ketone regenerated from it had a pleasant camphoraceous odour, less intense than that of the αβ-ketone; b. p. 74°/10 mm., $d_{4^\circ}^{21\cdot0^\circ}$ 0·85640, $n_{D}^{21\cdot0^\circ}$ 1·44522, $[R_L]_D$ 47·96 (Calc. 47·96).

*Equilibrations. Reference Curve :*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mixture (% αβ) ...... | 100 | 90 | 75 | 50 | 25 | 10 | 0 |
| *J*, % ................. | 4·3 | 22·2 | 51·7 | 82·5 | 91·3 | 94·3 | 95·0 |

The high addition of the βγ-ketone and mixtures containing up to 25% of αβ-ketone was a source of difficulty. The pure ketone can absorb more than the theoretical quantity of halogen, so at the end of 10 mins. it is colourless; on the addition of potassium iodide, some of the halogen is liberated. Similarly, there is a marked "back reaction" at the end of the titration. These difficulties can be partly overcome by working with more dilute solutions, but Kon and Thakur's method (*loc. cit.*) is the most satisfactory.

| Expt. | Ketone. | Time (hrs.). | *J*, %. | % αβ-. |
|---|---|---|---|---|
| (1) | αβ | 4 | 5·9 | 97·5 |
| (1) | ,, | 21½ | 18·5 | 89·5 |
| (2) | Recovered material from (1) | 168 | 95·0 | 0 |
| (3) | βγ | 168 | 94·9 | 0 |

The material from Expt. (2) was analysed, and it was found that no measurable addition of alcohol had occurred (Found: C, 77·7; H, 11·7. Calc., C, 77·9; H, 11·8%); on treatment with semicarbazide, the βγ-semicarbazone, melting correctly at 109° after two crystallisations, was obtained.

*ζ-Methylnonen-δ-ones*, (V) *and* (VI).—Methyl propyl ketone (100 g.) was treated with ice-cold, alcohol-free, sodium ethoxide from 12 g. of sodium as described on p. 2503, and the products isolated and fractionated after 2—3 days. Unchanged ketone (25 g.) was recovered, and also the following fractions : (1) 55—92°/17 mm., 5 g.; (2) 92—94°/17 mm., 13 g.; (3) 94—105°/17 mm., 5 g.; some 20 g. of higher-boiling oil being neglected. The second fraction on redistillation had b. p. 88—89°/15 mm., and contained the required homomesitones, $d_{4^\circ}^{17\cdot5^\circ}$ 0·84917, $n_D^{17\cdot5^\circ}$ 1·45163, $[R_L]_D$ 48·93 (Calc., 47·96), $J$ 32·4% (Found : C, 77·9; H, 11·8. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). It had a characteristic, rather unpleasant odour. No semicarbazone could be obtained from it.

In another experiment, the yield of redistilled homomesitone fraction was 18 g., with $J$ 33·4%; this value did not alter after 3 hours' treatment with sodium ethoxide, and therefore represents the equilibrium value.

On treatment with aluminium amalgam the homomesitone gave about 75% of a viscous bimolecular reduction product, b. p. 140—145°/2 mm., and 25% of pure βγ-ketone (VI); this had b. p. 89°/19 mm., $d_{4^\circ}^{21\cdot9^\circ}$ 0·84444, $n_D^{21\cdot9^\circ}$ 1·44191, $[R_L]_D$ 48·40, $J$ 84·6%, and was used for equilibrations. Another specimen obtained in the same way also had $J$ 84·6%.

1-*Methyl*-4-*ethyl*-1-*propyl*cyclo*hexane*-3 : 5-*dione*.—The homomesitone (5·4 g.) was added to ethyl malonate (5·3 g.) and sodium (0·8 g.) in 20 c.c. of alcohol, and the mixture refluxed over-night. It was then cooled, poured into water, neutral impurities were removed with ether, and the aqueous layer strongly acidified and repeatedly extracted with ether. The extract was evaporated, and the residue refluxed for 3 hours with an excess of 20% potassium hydroxide. The cooled product was extracted with ether, strongly acidified, and again thoroughly extracted. On removal of the ether, an oil was obtained which solidified and, after two crystallisations from dilute alcohol, formed needles, m. p. 106° (Found : C, 73·3; H, 10·2. $C_{12}H_{20}O_2$ requires C, 73·5; H, 10·2%). The 1-*methyl*-4-*ethyl*-1-*propyl*cyclo*hexane*-3 : 5-*dione* rapidly decomposes on keeping.

*ζ-Methyl-Δ^ε-nonen-δ-one* (V).—Liquid β-methyl-β-propylacrylic acid (this vol., p. 1414) was converted into the chloride, b. p. 100°/26 mm., and this on treatment with propylzinc iodide gave a moderate yield of the ketonic fraction, which on redistillation boiled at 90—92°/16 mm., $d_{4^\circ}^{20^\circ}$ 0·8608, $n_D^{20^\circ}$ 1·45183, $[R_L]_D$ 48·3, $J$ 8·6. The low molecular refraction suggests the presence of impurities (esters) which raise the density. A semicarbazone could not be obtained.

The action of propylmagnesium iodide in β-methyl-β-propyl·acrylyl chloride gave a 60% yield of a product, b. p. 90—96°/16 mm., $d_{4°}^{20·7°}$ 0·84118, $n_{D}^{20·7°}$ 1·45053; this had a much higher iodine addition (55%), and evidently contained a considerable quantity of the βγ-isomeride. It was used for condensation with ethyl sodiomalonate as described on p. 2505, the compound, m. p. 106°, being obtained in good yield.

*ξ-Methyl-Δ^η-nonen-δ-one* (VI).—β-Methyl-$\Delta^{\beta}$-hexenoic acid (this vol., p. 1415) was converted into the chloride, b. p. 68°/16 mm., which on treatment with propylmagnesium iodide gave a 65% yield of a fraction, b. p. 94°/17 mm., *J* 73·6. As a semicarbazone could not be obtained from it, this was treated in ethereal solution with aluminium amalgam; the product then had b. p. 94°/18 mm., $d_{4°}^{21·5°}$ 0·84130, $n_{D}^{21·5°}$ 1·44291, $[R_L]_D$ 48·56 (Calc., 47·96), *J* 85·3% (Found: C, 77·6; H, 11·6. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). The *ketone* is thus in every way similar to the βγ-ketone isolated from the equilibrium mixture.

*Equilibrations. Reference Curve:*

| Mixture (% αβ) ...... | 100 | 90 | 66·7 | 50 | 33·3 | 10 | 0 |
|---|---|---|---|---|---|---|---|
| *J*, % .................. | 8·6 | 17·5 | 38·3 | 52·6 | 64·2 | 74·4 | 85·3 |

| Ketone. | Time (mins.). | *J*, %. | % αβ. |
|---|---|---|---|
| αβ | 10 | 16·3 | 91·0 |
| " | 20 | 19·0 | 89·0 |
| " | 40 | 51·2 | 86·0 |
| βγ | 10 | 65·4 | 31·5 |
| " | 20 | 56·0 | 46·0 |
| " | 40 | 45·7 | 58·0 |

The combined fractions from the equilibration of the βγ-ketone were treated with sodium ethoxide, and then had b. p. 95°/22 mm., *J* 34·5 (71% αβ), in good agreement with the equilibrium value already obtained. The equilibration of the αβ-ketone clearly shows that it contains some inert impurity, but this should not materially affect the accuracy of the reference curve.

*γ-Ethyl-δ-methylhepten-β-ones.*—300 G. of methyl propyl ketone were treated with acetyl chloride and zinc chloride by Descudé's method (*loc. cit.*). About 100 g. were recovered unchanged, whilst on progressive refractionation of the residue, a portion, b. p. 74—76°/11 mm., $d_{4°}^{20·0°}$ 0·8681, $n_{D}^{20·0°}$ 1·45023 was obtained. After prolonged treatment with semicarbazide, the semicarbazone, m. p. 154°, identical with that described below, was isolated from it in small amount. Efforts to obtain a further quantity of this ketone, by treating the higher chlorine-containing fraction of the reaction product with alcoholic alkali or sodium ethoxide, were unsuccessful, as no semicarbazone could be obtained from the products. For the same reason, the αβ-ketone was not identified in any of the fractions obtained, probably owing to the great solubility of its semicarbazone.

The action of hydrobromic acid on methyl propyl ketone also leads to the formation of a homomesitone fraction very similar in properties to that described above, and evidently containing ketones with a branched chain because its iodine addition rose to 75% after treatment with sodium ethoxide : we have so far failed to isolate a pure compound from it.

*γ-Ethyl-δ-methyl-*$\Delta^{\gamma}$*-hepten-β-one* (VII). — The *αβ-ketone* was obtained in 50% yield by treating methylzinc iodide with the chloride of β-methyl-α-ethyl-β-propylacrylic acid (this vol., p. 1417), b. p. 82—83°/10 mm. ; it was purified by redistillation, and boiled at 83°/14 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·85589, $n_{D}^{20\cdot0^\circ}$ 1·45353, $[R_L]_D$ 48·72 (Calc., 47·96); it had a strong camphoraceous odour (Found : C, 77·6; H, 11·5. $C_{10}H_{18}O$ requires C, 77·8; H, 11·8%). The *semicarbazone* was formed with difficulty, and was very soluble; it crystallised from light petroleum (b. p. 60—80°) in plates, m. p. 123° (Found : C, 62·7; H, 9·9. $C_{11}H_{21}ON_3$ requires C, 62·6; H, 9·9%).

*δ-Methyl-γ-ethyl-*$\Delta^{\delta}$*-hepten-β-one* (VIII). The isomeric βγ-ketone was obtained in 56—60% yield from the chloride of β-methyl-α-ethyl-$\Delta^{\beta}$-hexenoic acid (this vol., p. 1417), b. p. 80°/15 mm., with either zinc or magnesium methyl iodide. It was converted into the *semicarbazone*, which formed needles, m. p. 154°, after two crystallisations from methyl alcohol or, better, acetone containing a little ammonia to prevent possible decomposition (this solvent has been very successfully employed in these laboratories for a number of semicarbazones) (Found : C, 62·6; H, 10·0. $C_{11}H_{21}ON_3$ requires C, 62·6; H, 9·9%). The ketone regenerated from it by Kon's method had b. p. 69°/11 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·84503, $n_{D}^{20\cdot0^\circ}$ 1·44050, $[R_L]_D$ 48·10 (Calc., 47·96); it possessed a pleasant camphoraceous odour.

*Equilibrations. Reference Curve :*

| Mixture (% αβ) …… | 100 | 90 | 75 | 50 | 25 | 10 | 0 |
|---|---|---|---|---|---|---|---|
| *J*, % ……………… | 7·4 | 29·3 | 53·5 | 77·7 | 92·2 | 95·5 | 97·0 |

The same difficulties were encountered as in the previous case and were overcome in the same way.

| Expt. | Ketone. | Time (hrs.). | *J*, %. | % αβ-Ketone. |
|---|---|---|---|---|
| (1) | αβ | 48 | 28·4 | 90·5 |
| (1) | ,, | 117 | 48·7 | 79·0 |
| (1) | ,, | 290 | 66·7 | 62·5 |
| (2) | 45% αβ | 6 (at b. p.) | 98·5 | 0 |
| (3) | αβ | 6 (at b. p. with sodium *iso*propoxide) | 97·0 | 0 |

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