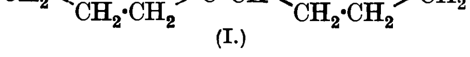
CCCCXVII.—*The Chemistry of the Three-carbon System. Part X. The Mobility of Some Cyclic Ketones.*

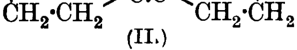
By George Armand Robert Kon and John Henry Nutland.

In our studies on compounds containing a potentially mobile three-carbon system we have investigated a group of ketones analogous to *cyclo*hexenylacetone (Part I, J., 1923, **123**, 1363) in which the ketone group forms part of a ring of five or six carbon atoms. The compounds examined include *cyclo*hexenyl*cyclo*hexanone (I), *cyclo*pentylidene*cyclo*pentanone (II), *iso*propylidene*cyclo*pentanone (III), camphorphorone (IV), pulegone (V), and *iso*pulegone (VI).



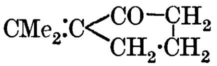
$CH_2<\begin{matrix}CH_2\text{-}CH\\CH_2\cdot CH_2\end{matrix}\gg C\text{-}CH<\begin{matrix}CO-CH_2\\CH_2\cdot CH_2\end{matrix}>CH_2$

(I.)

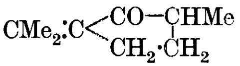


$\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C:C<\begin{matrix}CO-CH_2\\CH_2\cdot CH_2\end{matrix}$

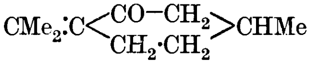
(II.)

(III.) 

$\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{CO-CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}$

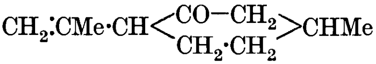
 (IV.)

$\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{CO-CHMe}\\ \mathrm{CH_2\cdot CH_2}\end{array}$



$\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{CO-CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{CHMe}$

(V.)



$\mathrm{CH_2{:}CMe\cdot CH}<\begin{array}{l}\mathrm{CO-CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{CHMe}$

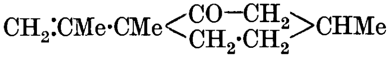
(VI.)

From theoretical considerations, it was to be expected that the chemistry of these compounds would not differ fundamentally from that of the corresponding methyl ketones. This is so; *e.g.*, all the ketones can react in the αβ-form because they condense with ethyl sodiocyanoacetate; on the other hand, they can be alkylated on the α-carbon atom through their sodio-derivatives, which are necessarily derived from the βγ-phase.

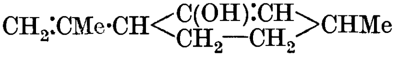
There are, however, several points of interest in their chemistry. The first is the characteristic difference in the point of equilibrium of the compounds (I) and (II). The former has ordinarily the βγ-structure as shown by its normal molecular refraction and its behaviour on oxidation (compare Wallach, *Annalen*, 1911, **381**, 95), whereas the latter is stable in the αβ-form—it shows an exaltation of the molecular refraction and gives *cyclo*pentanone on oxidation. The difference is undoubtedly connected with the greater tendency of the six-membered ring to acquire a double bond, which stabilises the βγ-form. A similar difference has already been recorded in another series (Kon and Speight, this vol., 2727).

Another important feature is the ready conversion of the compounds (III) and (IV) into alkyl derivatives, the double bond moving into the βγ-position with the production of the group $\mathrm{CH_2{:}CMe\cdot CR}<$. Up to the present, great difficulty had been experienced in obtaining βγ-derivatives from potentially mobile compounds in which the γ-carbon atom was not substituted, such as mesityl oxide (Kon, this vol., p. 1574) and dimethylacrylic acid (Kon and Linstead, J., 1925, **127**, 616). All the alkylated ketones have a lower density than the parent ketones (compare also Farrow and Kon, this vol., p. 2128).

The most interesting observation relates to pulegone and *iso*pulegone. Like the ketones (III) and (IV), both are readily methylated giving the same ketone (VII), which is a derivative of *iso*pulegone :

 (VII.)

$\mathrm{CH_2{:}CMe\cdot CMe}<\begin{array}{l}\mathrm{CO-CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{CHMe}$

 (VIII.)

$\mathrm{CH_2{:}CMe\cdot CH}<\begin{array}{l}\mathrm{C(OH){:}CH}\\ \mathrm{CH_2-CH_2}\end{array}>\mathrm{CHMe}$

The sodio-derivative is not derived from either of the enols of the type (VIII) prepared by Grignard (*Compt. rend.*, 1926, **182**, 422) from both pulegone and *iso*pulegone; otherwise the methyl group would enter the position 6 and two *different* ketones would be produced.

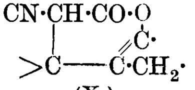
This conclusion is supported by the observation that the dextrorotatory pulegone and the dextro- or lævo-rotatory *iso*pulegone (according as the natural or the synthetic ketone is employed) give the same strongly lævorotatory methyl or ethyl derivative. The latter is formed from a sodio-derivative common to both ketones and containing only *one* asymmetric carbon atom. The varying optical activity of *iso*pulegone is presumably due to the second asymmetric carbon atom which it contains. On the other hand, both pulegone and *iso*pulegone condense with ethyl cyanoacetate with equal readiness to give the same condensation product, so that these ketones are analogous to the two ketones described by Kon and Linstead (J., 1925, **127**, 815) in exhibiting retarded mobility; that is, whilst they are quite distinct and give rise to distinct derivatives, they become interconvertible in the presence of a reagent such as sodium ethoxide. The observation is of even greater interest when it is remembered that both pulegone and *iso*pulegone occur in nature. Indeed, there can be little doubt that tautomerism of the three-carbon or ring-chain type accounts for many of the changes observed in the terpene group.

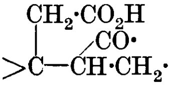
The semicarbazones of the compounds (I) and (II), like those of *cyclo*pentenyl- and *cyclo*hexenyl-acetone, occur in two forms; they probably differ in the position of the double bond, *i.e.*, represent the two individuals composing the liquid equilibrium mixture of ketones. The amount of the second form is generally small except in the case of *cyclo*pentenylacetone (Kon, J., 1921, **119**, 810). In this ketone the αβ-form should be favoured for the reason given on p. 3102 and the liquid equilibrium mixture should contain an appreciable quantity of it. This would account, not only for the comparable quantities of the two semicarbazones obtained, but also for the unusually high molecular refraction observed. The ketones regenerated from the pure semicarbazones (which, being crystalline solids, must have definite structures) again give a mixture on recombining with semicarbazide. Ketones such as camphorphorone, which give only one semicarbazone, may consist of one form only, like Kon and Linstead's ketones and pulegone and *iso*pulegone; or the equilibrium may be very much on one side.

The condensation of three compounds of this series with ethyl sodiocyanoacetate is abnormal: Vorländer (*Annalen*, 1906, **345**, 158) found that pulegone gave an unsaturated cyano-lactone (X), formed by loss of alcohol from the expected cyano-ester (IX);

the same substance has now been obtained in equally good yield from *iso*pulegone, and with the ketone (I) an analogous reaction takes place. It is remarkable that the cyano-esters of type (IX) derived from the other ketones (all belonging to the *cyclo*pentane series) do not undergo internal ring formation and can be readily converted into the corresponding acetic acids (XI) on alkaline hydrolysis. The reason for this difference must be sought in the spatial effect of the *cyclo*hexane ring.


(IX.)


(X.)


(XI.)

EXPERIMENTAL.

2-Δ^1-cyclo*Hexenyl*cyclo*hexanone* (I).

The ketone was prepared in 80% yield as described by Wallach (*Ber.*, 1907, **40**, 70) and was purified by steam distillation before the final distillation under reduced pressure.

Semicarbazone. The recorded m. p.'s differ considerably; indeed, Brown and Ritter (*Ber.*, 1922, **55**, 3798), who isolated a semicarbazone, m. p. 191°, considered that their ketone was an isomeride of Wallach's, the semicarbazone of which melted at 179—181°. We have found that preparations of varying melting point were obtained owing to the presence, although in small amount, of a second form of the semicarbazone. The crude semicarbazone was prepared by adding 24 g. of the ketone in 200 c.c. of alcohol to a hot solution of 22 g. of semicarbazide hydrochloride and 35 g. of sodium acetate in 50 c.c. of water; the solid was collected after 12 hours, and a further quantity obtained by adding water to the mother-liquor. The dried solid was ground with light petroleum and extracted with boiling benzene. The residue, m. p. about 194°, was sparingly soluble in ethyl or methyl alcohol, benzene, acetone, or ethyl acetate and was best crystallised from the first or the last, being thus obtained in sparkling plates of constant m. p. 200—201° (Found : C, 66·7; H, 8·8. Calc. for $C_{13}H_{21}ON_3$: C, 66·4; H, 8·9%).

The benzene extract, on cooling, deposited a solid from which a certain amount of the semicarbazone, m. p. 200—201°, could be isolated; in addition, it contained a more soluble compound (about 2% of the total semicarbazone isolated) which crystallised from benzene and had m. p. 172° (Found : C, 66·5; H, 9·0%).

The ketone regenerated from the pure, high-melting semicarbazone by means of oxalic acid (this was used throughout this work) had b. p. 145°/17 mm., $d_{4^\circ}^{15\cdot1^\circ}$ 1·00404, $n_{D}^{15\cdot1^\circ}$ 1·50692, $[R_L]_D$ 52·81 (calc., 52·92). On reconverting it into the semicarbazone a mixture of the two forms, m. p. 200—201° and 172°, was once more obtained which could be separated as described above.

Oxidation. The pure ketone dissolved in dry chloroform was treated with ozone until absorption ceased. The ozonide was freed from chloroform under reduced pressure and boiled with water; on distillation in steam no volatile products were obtained. From the product, ether extracted adipic acid, which melted at 151° after two crystallisations from hydrochloric acid (yield, 3 g. from 5 g. of ketone). A better yield (4·5 g.) was obtained by conducting the ozonisation in the presence of water; no other products were isolated, although a special search was made for *cyclo*hexanone which could have resulted from the oxidation of the $\alpha\beta$-form of the ketone.

Methylation. The ketone was treated with methyl iodide and "molecular" sodium in ether (Kon, this vol., p. 1572). The ketone isolated boiled in part somewhat higher (146—152°/15 mm.) than the original ketone. The higher fraction was converted into the *semicarbazone*, which was ground with petroleum and thrice crystallised from alcohol; it then melted constantly at 204° and depressed the m. p. of the semicarbazone of the parent ketone (Found: C, 67·3; H, 9·4; N, 16·6. $C_{14}H_{23}ON_3$ requires C, 67·4; H, 9·3; N, 16·8%). The yield was about 15%.

2-*Methyl*-2-Δ^1-cyclo*hexenyl*cyclo*hexanone* regenerated from the semicarbazone had b. p. 150°/18 mm., $d_4^{19\cdot4^\circ}$ 0·98804, $n_D^{19\cdot4^\circ}$ 1·50320, $[R_L]_D$ 57·51 (calc., 57·52). Its constitution was confirmed by oxidation with ozone. The ozonide was warmed with water for an hour and the oily product was isolated by means of ether and treated with semicarbazide. After 12 hours, the semicarbazone was collected and recrystallised twice from alcohol; it had m. p. 145—146° and was evidently derived from δ-acetylvaleric acid (Found: C, 47·7; H, 7·4. Calc.: C, 47·8; H, 7·5%). The filtrate from this semicarbazone contained adipic acid.

Ethylation. Attempts to ethylate *cyclo*hexenyl*cyclo*hexanone under various conditions failed.

Condensation with ethyl sodiocyanoacetate. No condensation product could be obtained with ethyl sodiomalonate, and only a very small quantity of the nitrile (see below) with ethyl sodiocyanoacetate in alcoholic solution. The ketone (18 g.) was then heated for 24 hours with ethyl sodiocyanoacetate (1/10 mol.) prepared from "molecular" sodium in 100 c.c. of benzene. The cold mixture was poured into water and extracted with ether. The extract was distilled, 10 g. of the original ketone and 2 g. of a fraction, b. p. 200—260°(decomp.)/60—70 mm., being obtained; this fraction solidified on cooling. A further 4 g. of the same substance were obtained on acidifying the aqueous solution obtained above and allowing it to stand for some time. The solid (27% yield) crystallised from alcohol or from benzene–petroleum in cubes, m. p. 112°, and was the *cyanolactone* of type (X) (Found : C, 73·7; H, 8·1; N, 5·9. $C_{15}H_{19}O_2N$ requires C, 73·4; H, 7·8; N, 5·7%). The same yield of the cyanolactone was obtained from the ketone recovered from a previous condensation and from the ketone regenerated from the pure semicarbazone. The compound resembles Vorländer's pulegone derivative (*q.v.*) in every respect. It dissolves in alkalis on warming and the solution rapidly becomes cloudy with the regeneration of *cyclo*hexenyl*cyclo*hexanone.

It was recovered unchanged after boiling for 2—3 hours with 60% sulphuric acid. A solution of it in excess of the concentrated acid was warmed to about 50°, left for 3 days, and poured into ice-water. The precipitate was collected, dried, and recrystallised alternately from benzene and dilute alcohol, being finally obtained in long needles, m. p. 166°; the compound was nitrogenous and appeared to be an *imide* (Found : C, 67·4; H, 9·5; N, 6·3. $C_{14}H_{21}ON$ requires C, 67·7; H, 9·7; N, 6·4%).

2-cyclo*Pentylidene*cyclo*pentanone* (II).

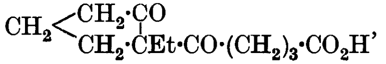
The ketone can be prepared in about 30% yield by either of the methods used by Wallach (*Ber.*, 1896, **29**, 2963); a 38% yield is obtained by using sodium ethoxide freed from alcohol under reduced pressure.

Semicarbazone. This compound was prepared and separated into two forms exactly as described on p. 3104. The less soluble form, after repeated crystallisation from ethyl and methyl alcohol, benzene, acetone, and ethyl acetate, formed plates, m. p. 223°, but darkening below this temperature (Found : C, 63·5; H, 8·2. $C_{11}H_{17}ON_3$ requires C, 63·8; H, 8·2%). The more soluble form had m. p. 207° (Found : C, 63·7; H, 8·2%). The proportion of the higher- and the lower-melting form isolated was about 20 : 1.

The ketone regenerated from the pure, high-melting form had b. p. 135°/25 mm., $d_{4^\circ}^{18\cdot9^\circ}$ 1·01787, $n_{D}^{18\cdot9^\circ}$ 1·52145, $[R_L]_D$ 44·95, in good agreement with Wallach's figures. The pure ketone gave a mixture of the same two semicarbazones, in the proportion of 20 : 1, when treated with semicarbazide.

Oxidation. This was carried out by means of ozone as before. The steam distillate contained a considerable quantity of *cyclo*pentanone, which was isolated by means of ether and identified in the form of its semicarbazone. The residue from the steam distillation contained glutaric acid, m. p. 97°, which was identified by direct comparison with a genuine specimen. These two products establish the αβ-formula of the ketone.

Ethylation. Attempts to ethylate the ketone in the presence of sodium ethoxide were unsuccessful, but the reaction proceeded well with " molecular " sodium. The sodio-derivative was usually prepared in ethereal solution so as to avoid polymerisation; the ether was then distilled off and replaced by benzene before the addition of ethyl iodide. A considerable amount of the ketone isolated boiled at 140—150°/25 mm. The *semicarbazone* prepared from this fraction melted, after crystallising successively from alcohol, acetone, and alcohol, at 202°; it depressed the melting points of the semicarbazones of the parent ketone (Found : C, 66·4; H, 8·9; N, 17·6. $C_{13}H_{21}ON_3$ requires C, 66·4; H, 8·9; N, 17·9%). The yield was 35%.

The ketone, 2-*ethyl*-2-Δ^1-cyclo*pentenyl*cyclo*pentanone*, regenerated from it had b. p. 140°/22 mm., $d_{4°}^{22·4°}$ 0·983385, $n_D^{22·4°}$ 1·49756, $[R_L]_D$ 53·07 (calc., 52·92). It was oxidised with ozone in chloroform solution, the ozonide decomposed with hot water, and the product distilled in steam. The residue contained glutaric acid (m. p. 97° after recrystallisation), whilst the volatile fraction contained 2-ethyl*cyclo*pentanone, which was identified by means of its semicarbazone, m. p. 177° (Best and Thorpe, J., 1909, **95**, 713) (Found : C, 56·6; H, 8·8; N, 24·6. Calc.: C, 56·8; H, 8·9; N, 24·9%). These products were not those primarily formed, and if the ozonide was decomposed by means of cold water the greater part was converted into an oily *aldehyde* which was readily oxidised to the corresponding *acid* by silver oxide. This acid doubtless had the structure  $CH_2{<}\begin{matrix}CH_2{\cdot}CO\\ |\\ CH_2{\cdot}CEt{\cdot}CO{\cdot}(CH_2)_3{\cdot}CO_2H\end{matrix}$, as it broke up into 2-ethyl*cyclo*pentanone and glutaric acid on merely boiling with water; it was too unstable to isolate in a pure state.

The ethylation of *cyclo*pentylidene*cyclo*pentanone was repeated with a specimen of the ketone regenerated from the semicarbazone; the same yield of the ethylation product was obtained.

Condensation with ethyl sodiocyanoacetate. This was carried out as described on p. 3105. The neutral reaction product contained, in addition to higher-boiling oils which were not investigated, a fraction, b. p. 164—165°/20 mm., consisting of a cyano-ester of the type (X) which was isolated in 10% yield (Found : C, 68·9, 68·8; H, 8·1, 8·1. $C_{15}H_{21}O_3N$ requires C, 68·4; H, 8·0%). Only a small quantity of acid material was produced in this reaction and this could not be purified.

The cyano-ester (3 g.) was boiled with baryta (15 g. in 75 c.c. of water) for 2 hours and the sparingly soluble barium salt produced was collected and decomposed with ice-cold hydrochloric acid. The *acid* (type XI), isolated by means of ether, formed octahedral prisms, m. p. 135°, from acetone-benzene (Found : C, 68·4; H, 8·6. $C_{12}H_{18}O_3$ requires C, 68·6; H, 8·6%). The *semicarbazone* formed needles, m. p. 197°, from alcohol (Found: C, 61·0; H, 8·1. $C_{13}H_{21}O_3N_3$ requires C, 61·2; H, 8·2%).

2-iso*Propylidene*cyclo*pentanone* (III).

The ketone was prepared as described by Wallach (*Annalen*, 1912, **394**, 362); the use of dry sodium ethoxide was not found advantageous.

Semicarbazone. This was prepared and treated as before, but in spite of a careful search only one form was obtained, crystallising from methyl alcohol in large plates which became opaque on keeping; m. p. 217—218°. The ketone regenerated from it had b. p. 92°/20 mm., $d_4^{18·4°}$ 0·96704, $n_D^{18·4°}$ 1·49680, $[R_L]_D$ 37·70 (calc., 36·61).

Oxidation. The ozonide of this ketone gave, on decomposition, acetone (semicarbazone, m. p. 187°) and glutaric acid, m. p. 97°, which were identified in the usual ways.

Ethylation. This was carried out as described on p. 3107. Almost the whole of the ketone isolated boiled at 98—102°/22 mm., the yield of the new ketone being 90%. The *semicarbazone* formed stellate clusters of needles, m. p. 199°, from alcohol (Found : C, 63·3; H, 9·0. $C_{11}H_{19}ON_3$ requires C, 63·2; H, 9·1%). The ketone, 2-*ethyl*-2-iso*propenyl*cyclo*pentanone*, regenerated from it had b. p. 97—98°/20 mm., $d_4^{19·7°}$ 0·94132, $n_D^{19·7°}$ 1·47892, $[R_L]_D$ 45·84 (calc., 45·85). The structure of the ethylated ketone was established by oxidation with ozone in acetic acid solution by the method of Grignard (*Compt. rend.*, 1923, **177**, 669); the formation of formic acid was confirmed by the usual tests. The acetic acid solution was concentrated in a vacuum and then treated with semicarbazide, the *semicarbazone* of a ketonic *acid* being obtained; after three crystallisations from alcohol, it formed plates, m. p. 141—142° (Found : C, 52·3; H, 8·4. $C_{10}H_{19}O_3N_3$ requires C, 52·4; H, 8·3%). The acid was doubtless δ-acetylheptoic acid (Blaise and Köhler, *Compt. rend.*, 1909, **148**, 1403).

Condensation with ethyl sodiocyanoacetate. This was carried out as before. The *cyano*-ester, formed in 15% yield, had b. p. 135°/20 mm. (Found: C, 65·3; H, 8·0. $C_{13}H_{19}O_3N$ requires C, 65·8; H, 8·0%). On hydrolysis with baryta the ester yielded an *acid* (type XI) which crystallised from acetone–petroleum in long needles, m. p. 133° (Found : C, 65·4; H, 8·6. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%).

Camphorphorone.

The ketone was prepared in 40% yield by the method of Wallach and Collman (*Annalen*, 1904, **331**, 320) in the apparatus described by Day, Kon, and Stevenson (J., 1920, **117**, 639).

Semicarbazone. This derivative was formed very slowly, the mixture of ketone and semicarbazide being kept for 2 weeks before the first crop of semicarbazone was collected; further quantities separated when the mother-liquor was gradually diluted. The semicarbazone appears to exist in one form only, plates, m. p. 197—198° (Wallach and Collman, *loc. cit.*). The pure ketone regenerated from it had b. p. 87—88°/14 mm., $d_4^{18.8^\circ}$ 0·93722, $n_D^{18.8^\circ}$ 1·48511, $[R_L]_D$ 42·28 (calc., 41·23). The *pure* ketone combines rapidly with semicarbazide.

Oxidation. Oxidation with ozone gave acetone (semicarbazone, m. p. 187°) and α-methylglutaric acid, m. p. 77—78° (Found : C, 46·1 ; H, 6·5. Calc. : C, 46·1 ; H, 6·4%).

Ethylation. This operation was carried out as described on p. 3107. The semicarbazone of the ethylated ketone was obtained in 50% yield; the yield of ketone was doubtless higher. The *semicarbazone* crystallised from alcohol in stellate clusters of needles, m. p. 184° (Found : C, 64·4 ; H, 9·3. $C_{12}H_{21}ON_3$ requires C, 64·6 ; H, 9·4%). The ketone, 5-*methyl*-2-*ethyl*-2-iso*propenyl*cyclo*pentanone*, regenerated from it had b. p. 95—96°/16 mm., $d_4^{18.7^\circ}$ 0·91131, $n_D^{18.7^\circ}$ 1·46533, $[R_L]_D$ 50·46 (calc., 50·47). The ketone was oxidised with ozone in acetic acid in the same way as the lower homologue. Formic acid was isolated, and a ketonic *acid* in the form of its *semicarbazone*, which crystallised from alcohol in plates, m. p. 147—148° (Found : C, 54·2 ; H, 8·7. $C_{11}H_{21}O_3N_3$ requires C, 54·4 ; H, 8·7%). The parent acid was doubtless δ-*acetyl*-α-*methylheptoic acid.*

Condensation with ethyl sodiocyanoacetate. Camphorphorone does not condense with ethyl sodiomalonate according to Vorländer (*loc. cit.*). The reaction with ethyl sodiocyanoacetate proceeded normally; the cyano-ester was not purified, the fractions 96—140°/15 mm. and 140—200°/15 mm. being directly hydrolysed with baryta to the nitrogen-free *acid* (type XI), which formed long needles, m. p. 135°, from acetone–benzene (Found : C, 66·5 ; H, 9·2. $C_{11}H_{18}O_3$ requires C, 66·7 ; H, 9·1%). The total quantity of acid obtained represented a 30% yield of condensation product.

Pulegone.

The ketone isolated from oil of pennyroyal by the bisulphite process had b. p. 99°/14 mm. and $[\alpha]_D + 20·8°$.

The semicarbazone prepared from it consisted of one substance only and formed clusters of needles, m. p. 172°, after two crystallisations from alcohol. A specimen of the ketone regenerated from it had b. p. 99°/14 mm., $d_{4^\circ}^{19\cdot2^\circ}$ 0·93712, $n_{D}^{19\cdot2^\circ}$ 1·48803, $[R_L]_D$ 46·78 (calc., 45·81) and $[\alpha]_D + 22\cdot1^\circ$. On oxidation with ozone in chloroform solution, acetone and β-methyladipic acid, m. p. 94°, were obtained.

Methylation. This operation was carried out in ethereal solution with "molecular sodium," and a yield of about 50% of an oil, b. p. about 109°/20 mm., obtained after two distillations. The *semicarbazone* separated from alcohol in fine needles, m. p. 203—204° (Found: C, 64·5; H, 9·5. $C_{12}H_{21}ON_3$ requires C, 64·5; H, 9·5%). The ketone, 2:5-*dimethyl*-2-iso*propenyl*cyclo*hexanone* (2-*methyl*iso*pulegone*) (VII), had b. p. 108°/19 mm., $d_{4^\circ}^{18\cdot8^\circ}$ 0·92081, $n_{D}^{18\cdot8^\circ}$ 1·47163, $[R_L]_D$ 50·51 (calc., 50·47), and $[\alpha]_D$ (in alcohol) $-122\cdot1^\circ$.

The ketone was oxidised with ozone in acetic acid solution, formic acid and ε-acetyl-β-methylheptoic acid (Léser, *Bull. Soc. chim.*, 1901, **25**, 199) being obtained; the latter was isolated as its *semicarbazone*, which formed plates, m. p. 166—168° from dilute alcohol (Found: C, 54·2; H, 8·7. $C_{11}H_{21}O_3N_3$ requires C, 54·3; H, 8·7%).

Ethylation. This was carried out as before; the yield appeared to be about 40%. The *semicarbazone* of the new ketone was obtained in clusters of needles, m. p. 207—208° (Found: C, 65·7; H, 9·8. $C_{13}H_{23}ON_3$ requires C, 65·9; H, 9·7%). The ketone, 5-*methyl*-2-*ethyl*-2-iso*propenyl*cyclo*hexanone*, regenerated from it had b. p. 110°/15 mm., $d_{15^\circ}^{19\cdot1^\circ}$ 0·90362, $n_{D}^{19\cdot1^\circ}$ 1·46433, $[R_L]_D$ 55·05 (calc., 55·09), and $[\alpha]_D$ (in alcohol) $-174\cdot0^\circ$.

Condensation with ethyl sodiocyanoacetate. This operation was carried out as before; both the neutral and the acid portion of the condensation product gave, on distillation, Vorländer's compound, m. p. 78°, the total yield being 42% (Found: C, 70·9; H, 7·8. Calc.: C, 71·2; H, 7·8%). Like the compound described on p. 3106, it forms, on treatment with sulphuric acid, an *imide* which forms needles, m. p. 129°, from alcohol and appears to be isomeric with the compound prepared by Vorländer (*loc. cit.*, p. 196) (Found: C, 74·5; H, 9·9; N, 7·2. $C_{12}H_{19}ON$ requires C, 74·6; H, 9·9; N, 7·2%).

iso*Pulegone.*

This ketone was prepared both from oil of pennyroyal and from pulegone hydrobromide. The crude ketone obtained from the latter source had b. p. 102—103°/16 mm., $d_{4^\circ}^{20\cdot4^\circ}$ 0·92761, $n_{D}^{20\cdot4^\circ}$ 1·46250, and $[\alpha]_D - 10\cdot7^\circ$. A specimen obtained from oil of pennyroyal had b. p. 100—105°/17 mm., $d_{4^\circ}^{18\cdot3^\circ}$ 0·91024, n_D 1·46470, $[R_L]_D$ 46·18, and $[\alpha]_D + 36\cdot7^\circ$. Both formed a semicarbazone crystallising in needles, m. p. 174°.

Methylation. This proceeded exactly as in the case of pulegone; the yield of the fraction, b. p. 104—107°/16 mm., was above 50%. Both natural and synthetic *iso*pulegone gave a strongly lævorotatory product from which the same semicarbazone, m. p. 203—204°, identical with that obtained from pulegone, was prepared. A small specimen of the ketone regenerated from it gave $[\alpha]_D$ in alcohol — 122·6°.

Condensation with ethyl cyanoacetate. The compound, m. p. 78°, obtained was identical with the compound prepared from pulegone; the yield was about the same in the two cases.

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