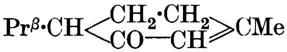
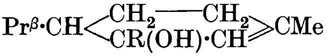
CCLXXVIII.—*Piperitone. Part X. The Synthesis of Certain Menthadienes, Menthenes, and Menthanols.*

By John Read and Andrew James Watters.

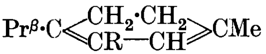
Previous investigations on piperitone have been concerned chiefly with the diagnosis and characterisation of the ketone and the study of its reduction and oxidation (this vol., p. 2068, etc.), the only published reference to any synthetical application being contained in the work of Jupp, Kon, and Lockton (J., 1928, 1638) on the condensation of piperitone with ethyl acetoacetate. In entering upon a consideration of the possibilities of piperitone (I) as a synthetic agent, we show below that it reacts readily with Grignard reagents to yield 3-substituted homologues (III) of α-terpinene directly, no intermediate Δ^1-menthenols (II) being isolable :

(I.) 

$$\mathrm{Pr^{\beta}\cdot CH}\!<\!\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CO-CH}\end{matrix}\!\!>\!\mathrm{CMe}$$

 (II.)

$$\mathrm{Pr^{\beta}\cdot CH}\!<\!\begin{matrix}\mathrm{CH_2 \text{——} CH_2}\\ \mathrm{CR(OH)\cdot CH}\end{matrix}\!\!>\!\mathrm{CMe}$$

 (III.)

$$\mathrm{Pr^{\beta}\cdot C}\!\lessgtr\!\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CR-CH}\end{matrix}\!\!\geqslant\!\mathrm{CMe}$$

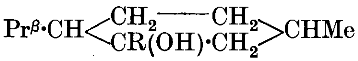
Simonsen (*Indian Forest Records*, 1924, **10**, viii) has shown that *d*-piperitol is converted to α-terpinene when heated with magnesium methyl iodide, and the dehydration would appear to occur still more readily with the above homologues (II) of piperitol, owing to the influence of the radical attached to the carbon atom carrying the hydroxyl group. In all these instances, the elimination of hydroxyl is probably facilitated by the presence of a double bond in the αβ-position. In accordance with the general conclusions of Kohler (*Amer. Chem. J.*, 1905, **33**, 153, 333; 1906, **34**, 132), the double bond in the molecule of piperitone is unaffected by Grignard reagents.

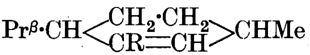
The constitution of the hydrocarbons synthesised from piperitone in this way is indicated by their physical properties and confirmed by the formation of ω-dimethylacetonylacetone,

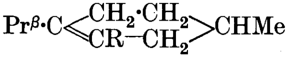
$$\mathrm{COMe\cdot[CH_2]_2\cdot CO\cdot CHMe_2},$$

as a result of their oxidation with permanganate. These substituted terpinenes (III) are symmetric, and thus the faint dextrorotation shown by specimens of the four members of the series which have been synthesised from *dl*-piperitone indicates that reaction occurs also between Grignard reagents and the lævorotatory impurity which is usually present in small amount in *Eucalyptus* piperitone (J., 1922, **121**, 1865); when *l*-piperitone is used in the reactions, the faint dextrorotation is masked by the presence of *l*-α-phellandrene or other lævorotatory impurities. These observations strengthen the conjecture that *Eucalyptus* piperitone may contain a small admixture of another ketone (or possibly aldehyde) which is not easily racemised.

The action upon *l*-menthone of magnesium methyl iodide has been examined by Wanin (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 353; 1912, **44**, 1068) and also by Zelinski (*Ber.*, 1901, **34**, 2882); further, Murat (*J. Pharm. Chim.*, 1911, [viii], **4**, 294) applied magnesium phenyl bromide to the same ketone. We now show that both *l*-menthone and *d*-*iso*menthone react in general with Grignard reagents to form 3-substituted methan-3-ols (IV), and that these tertiary alcohols readily undergo dehydration when heated with anhydrous oxalic acid, yielding 3-substituted Δ^2- or Δ^3-menthenes, (V) or (VI):

(IV.)

$\mathrm{Pr^{\beta}\cdot CH}<\begin{matrix}\mathrm{CH_2{-\!-\!-}CH_2}\\ \mathrm{CR(OH)\cdot CH_2}\end{matrix}>\mathrm{CHMe}$


$\mathrm{Pr^{\beta}\cdot CH}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CR{=}CH}\end{matrix}>\mathrm{CHMe}$
(V.)


$\mathrm{Pr^{\beta}\cdot C}<\!\!\!\!\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \!\!\!=\mathrm{CR{-}CH_2}\end{matrix}>\mathrm{CHMe}$
(VI.)

The results now recorded are not altogether in keeping with previous observations: according to Wanin (*loc. cit.*), for example, *l*-menthone passes directly to 3-ethylmenthene when treated with magnesium ethyl iodide. There is no doubt, however, that upon saturating the αβ-ethylenic linking of piperitone the difficulty of isolating the intermediate tertiary alcohols disappears.

The alcohols (IV) are probably stereochemically heterogeneous, because they are formed by partial asymmetric synthesis from equilibrium mixtures of *l*-menthone and *d*-*iso*menthone. The products from the latter, in particular, may well consist of mixtures of the four possible stereoisomerides. It is seen from the appended table that the sense of rotation of the parent ketone tends to be preserved in the derived alcohols. The molecular exaltation of the alcohols is greater in the *iso*-series, and is much more pronounced in the 3-phenyl-menthanols, -menthene, and -menthadiene than in the corresponding alkyl derivatives.

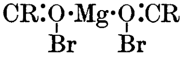
In any particular instance, all four stereoisomeric menthanols should yield the same 3-substituted menthene only if dehydration occurs exclusively in the Δ^3-position, thereby eliminating the asymmetry of carbon atoms (3) and (4): in such circumstances, therefore, *l*-menthone and *d*-*iso*menthone should give rise to identical hydrocarbons. In all the instances examined, the physical constants of corresponding menthenes from the two sources are in close agreement, except that the preparations from *l*-menthone exhibit considerably higher optical rotations than the others :

	$[\alpha]_D$ of substituted menthanol :		$[\alpha]_D$ of substituted menthene :	
Substituent.	Ex *l*-menthone.	Ex *d*-*iso*-menthone.	Ex *l*-menthone.	Ex *d*-*iso*-menthone.
Me	− 6·5°	+27·0°	+62·8°	+17·9°
Et	+ 1·5	+22·0	+39·2	+ 6·8
n-Pr	− 0·7	—	+35·9	—
Ph	−22·9	+ 0·4	+43·5	+16·3

It was sought to avoid partial racemisation, such as occurs when *l*-menthol is dehydrated directly, by applying Tschugaev's xanthic ester method (compare J., 1926, 2217) ; unfortunately, however, the 3-homologues of menthol reacted so sluggishly with sodium that the method could not be used, and it is thus in doubt whether the observed differences in the rotatory powers of the hydrocarbons may be attributed wholly to different degrees of racemisation of Δ^3-derivatives.

In no case was any action observed to occur between magnesium *iso*propyl iodide and piperitone or menthones, possibly owing to steric hindrance. Piperitone failed also to react with bromoacetic ester and zinc, thus rendering nugatory a proposed alternative synthesis of 3-methyl-α-terpinene from the anticipated piperitol-acetic ester. Since *l*-menthone responds readily to this reagent (*Annalen*, 1902, **323**, 151), it is apparent that the reactivity of the keto-group may be impaired or inhibited by an αβ-ethylenic linking.

It has recently been shown by Tschelinzev and Nasarov (*Bull. Soc. chim.*, 1927, **41**, 806) that certain ketones form crystalline additive products with specially prepared anhydrous magnesium bromide. The products yielded by *l*-piperitone and *d*-*iso*menthone were gummy, but *l*-menthone gave a crystalline derivative, $2C_{10}H_{18}O,MgBr_2$, similar in composition to the camphor derivative described by the above authors. Upon recovering the ketones by the addition of water, *d*-*iso*menthone was found to be partly " inverted," whilst piperitone had undergone complete racemisation. This striking result indicates that the symmetric enol-form of piperitone is concerned in the formation of the derivative, and that Tschelinzev and Nasarov's " oxonium " formula (VII) should be replaced by an " enol " formula, such as (VIII) :

(VII.) 

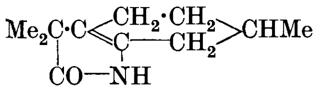
$$\mathrm{CR{:}\underset{\underset{Br}{|}}{O}\cdot Mg\cdot \underset{\underset{Br}{|}}{O}{:}CR}$$

 (VIII.)

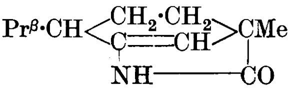
$$\mathrm{CR'\cdot \underset{\underset{H}{|}}{O}\cdots\cdots(MgBr_2)\cdots\cdots \underset{\underset{H}{|}}{O}\cdot CR'}$$

The results of the study of the additive reactions of piperitone with Grignard reagents and magnesium bromide rendered it of interest to investigate the action upon the ketone of alcoholic potassium cyanide. With pulegone, as shown by Lapworth (J., 1906, **89**, 1869), this reagent yields a product, $C_{11}H_{17}ON$, which is not the simple additive compound, cyanodihydropulegone, but a bicyclic anhydramide (IX). With piperitone, the reaction appears to follow a precisely similar course, yielding an exceedingly stable compound (X), from which it has not been found possible to eliminate the nitrogen by any simple means :

(IX.)



$$\mathrm{Me_2\underset{\displaystyle CO{-}NH}{C}{\cdot}C{<}\genfrac{}{}{0pt}{}{CH_2{\cdot}CH_2}{C{-}CH_2}{>}CHMe}$$



$$\mathrm{Pr^{\beta}{\cdot}CH{<}\genfrac{}{}{0pt}{}{CH_2{\cdot}CH_2}{C{=}CH}{>}CMe \quad NH{-}CO}$$

(X.)

In conclusion, it is of interest to note that the unsaturated hydrocarbons described in this paper would pass by hydrogenation into 3-substituted menthanes. Evidence is forthcoming also which indicates that isomeric series of menthanols, menthenes, and menthadienes may be prepared by applying the methods reviewed above to tetrahydrocarvone, pulegone, and other alicyclic ketones, and the investigation is being continued in these directions.

EXPERIMENTAL.

The Application of Grignard Reagents to Piperitone.—The *dl*-piperitone used in these experiments was extracted from the essential oil of *Eucalyptus dives* with normal sodium sulphite (*J. Soc. Chem. Ind.*, 1923, **42**, 339T), racemisation being brought about by maintaining the product at 200° for 3 hours (J., 1923, **123**, 2267). *dl*-Piperitone isolated in this way contains small amounts of a lævorotatory impurity (J., 1922, **121**, 1865). *l*-Piperitone was extracted from the same oil by fractional distillation under diminished pressure; it had $[\alpha]_D^{14°}$ $-49{\cdot}1°$, and probably contained *l*-α-phellandrene.

1. To an ice-cooled solution of a Grignard reagent, prepared from magnesium (3 g.), methyl iodide (19 g.), and ether (120 c.c.), was added gradually *dl*-piperitone (19 g., 1 mol.) dissolved in an equal volume of dry ether. The mixture was kept over-night at the ordinary temperature and then worked up in the usual way. After three successive fractional distillations under diminished pressure, the mixed product from several experiments yielded a main fraction distilling at 81—82°/15 mm. The colourless liquid obtained in this way gave the following physical and analytical data charac-

teristic of 3-*methyl*-$\Delta^{1:3}$-*menthadiene*: b. p. 184—186°/737 mm.; $d_{4°}^{25°}$ 0·8585; $n_D^{25°}$ 1·4845; $[R_L]_D$ 49·97 (Calc. for $C_{11}H_{18},2|^{=}$, 49·54). (Found: C, 86·7; H, 12·1. $C_{11}H_{18}$ requires C, 88·0; H, 12·0%). It displayed a faint optical activity, the observed value of $\alpha_D^{16°}$ in a 1-dcm. tube * being + 0·04°.

It was not found possible to prepare a crystalline nitrosite or nitrosochloride from the substance. In the initial experiments the yield was low, but by using 2 mols. of the Grignard reagent about 60% of the calculated amount of the hydrocarbon was isolated; heating appeared to be unnecessary in applying the reagent. In certain experiments the procedure was reversed by adding the Grignard reagent to the ketone, but in no instance could the formation of an alcohol be established.

The hydrocarbon (7 g.) was oxidised by shaking it for an hour with a mixture of water (400 c.c.), ice (400 g.), potassium hydroxide (14 g.), and potassium permanganate (33 g.). Unchanged hydrocarbon was removed by steam-distillation, and the filtrate and washings from the manganese dioxide were evaporated to dryness on the water-bath with passage of a current of carbon dioxide. When extracted with boiling alcohol, the powdered residue yielded a dark red syrup, the aqueous solution of which was (i) extracted with ethyl acetate, (ii) acidified with dilute sulphuric acid, and (iii) extracted with ether. The viscid acid extract had an equivalent value of 187. It was dissolved in water (3·75 g. in 100 c.c.) and treated gradually at 60—70° with a solution of potassium permanganate (2·25 g.) in water (60 c.c.) containing sulphuric acid (2·25 g.). The steam distillate from the product, when saturated with salt and extracted with ether, gave an oil (0·45 g.) having $n_D^{18°}$ 1·4290. The oil yielded an oxime, m. p. 127—128°, and reacted with semicarbazide to form a derivative, m. p. 202—203° (Found: C, 59·0; H, 8·1; N, 22·7. Calc. for $C_9H_{15}ON_3$: C, 59·6; H, 8·3; N, 23·2%). The oxime became gummy when kept, and was not analysed. ω-Dimethylacetonylacetone has $n_D^{18°}$ 1·4305, and yields a semicarbazone (pyrrole derivative), m. p. 201—202° (Wallach, *Annalen*, 1908, **362**, 263).

The hydrocarbon obtained by the interaction of *l*-piperitone and magnesium methyl iodide had b. p. 73·5—74·5°/9 mm., $n_D^{14°}$ 1·4865, $\alpha_D^{15°}$ − 5·39°.

2. 3-*Ethyl*-$\Delta^{1:3}$-*menthadiene*. The method outlined above was applied, the following amounts of reactants being used: 38 g. (0·5 mol.) of *dl*-piperitone, 12 g. of magnesium, and 80 g. of ethyl iodide. After repeated fractional distillation under diminished pressure, a product (20·3 g.) was isolated having b. p. 83—85°/15 mm., 199—

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* All the values of α_D quoted in this paper refer to a 1-dcm. tube.

202°/737 mm.; $d_{4^\circ}^{25^\circ}$ 0·8631; $n_{\mathrm{D}}^{25^\circ}$ 1·4854; $[R_L]_{\mathrm{D}}$ 54·47 (Calc. for $C_{12}H_{20},2|^{=}$, 54·10). A slight optical activity was again manifest, $\alpha_{\mathrm{D}}^{16^\circ}$ + 0·07°. *l*-Piperitone yielded a practically identical product, except that it possessed a decided lævorotation, $\alpha_{\mathrm{D}}^{16^\circ}$ − 3·31°.

3. 3-n-*Propyl*-$\Delta^{1:3}$-*menthadiene*. From 34 g. (0·5 mol.) of *dl*-piperitone, 14·8 g. of magnesium and 96 g. of *n*-propyl iodide, 18·7 g. of the hydrocarbon were obtained, with b. p. 104—106°/14 mm.; $d_{4^\circ}^{25^\circ}$ 0·8872; $n_{\mathrm{D}}^{25^\circ}$ 1·4865; $[R_L]_{\mathrm{D}}$ 57·70; $\alpha_{\mathrm{D}}^{16^\circ}$ + 0·12° (Calc. for $C_{13}H_{22},2|^{=}$, 58·66).

4. 3-*Phenyl*-$\Delta^{1:3}$-*menthadiene*. The following quantities were used: 38 g. of *dl*-piperitone (0·5 mol.), 12 g. of magnesium, and 80 g. of bromobenzene. The *hydrocarbon* isolated in the usual way had b. p. 145—148°/15 mm.; $d_{4^\circ}^{25^\circ}$ 0·9552; $n_{\mathrm{D}}^{25^\circ}$ 1·5525; $[R_L]_{\mathrm{D}}$ 70·96 (Calc. for $C_{16}H_{20},5|^{=}$, 69·07) (Found: C, 89·6; H, 9·2. $C_{16}H_{20}$ requires C, 90·6; H, 9·4%).

The Application of Grignard Reagents to l-*Menthone*.—The *l*-menthone used in the following syntheses was prepared by oxidising *l*-menthol with chromic acid (*Annalen*, 1889, **250**, 335) and had b. p. 92—94°/15 mm., $\alpha_{\mathrm{D}}^{16^\circ}$ − 25·65°.

1. 3-*Methylmenthan*-3-*ol*. The following quantities were used: 30 g. of *l*-menthone, 7 g. of magnesium, 41·4 g. of methyl iodide. The magnesium methyl iodide was applied to the ketone as described above. On distilling the product under diminished pressure, a clear oil (24·3 g.) with a mint-like odour was obtained, having b. p. 101—102°/17 mm.; $\alpha_{\mathrm{D}}^{16^\circ}$ − 6·47°; $d_{4^\circ}^{25^\circ}$ 0·8964; $n_{\mathrm{D}}^{25^\circ}$ 1·4605; $[R_L]_{\mathrm{D}}$ 51·98 (Calc. for $C_{11}H_{21}\cdot OH$, 51·78). The 3-methylmenthan-3-ol obtained by Wanin (*loc. cit.*) had b. p. 102—103°/16 mm., $d_{0^\circ}^{0^\circ}$ 0·9143, $d_{0^\circ}^{20^\circ}$ 0·8980; Zelinski (*loc. cit.*) used menthone having α_{D} + 0° 40′ in a 0·25-dcm. tube, and obtained an alcohol with b. p. 100°/20 mm., $d_{4^\circ}^{25^\circ}$ 0·8952, $[\alpha]_{\mathrm{D}}$ + 12° 22′.

When heated with twice its weight of anhydrous oxalic acid at 140° for 5 hours, 3-methylmenthan-3-ol yielded a 3-methylmenthene, b. p. 180—182°/763 mm., $\alpha_{\mathrm{D}}^{17^\circ}$ +62·80°, $n_{\mathrm{D}}^{25^\circ}$ 1·4585. When the dehydration was accomplished by heating the alcohol at 130° for 3 hours with twice its weight of potassium bisulphate, the product had b. p. 184—186°/767 mm., $\alpha_{\mathrm{D}}^{16^\circ}$ + 41·06°, $n_{\mathrm{D}}^{25^\circ}$ 1·4600. Very similar values were recorded by Wanin and Zelinski (*loc. cit.*) for specimens of 3-methyl-Δ^2- or -Δ^3-menthene.

2. 3-*Ethylmenthan*-3-*ol*. By using 30 g. of *l*-menthone, 7 g. of magnesium and 46·5 g. of ethyl iodide, 24·2 g. of the alcohol were obtained; it had a heavy, mint-like odour, and the following physical constants were determined: b. p. 112—113°/16 mm., 217—219°/759 mm.; $\alpha_{\mathrm{D}}^{16^\circ}$ + 1·54°; $d_{4^\circ}^{25^\circ}$ 0·8992; $n_{\mathrm{D}}^{25^\circ}$ 1·4650; $[R_L]_{\mathrm{D}}$

56·58 (Calc. for $C_{12}H_{23}\cdot OH$, 56·36). (Found: C, 78·0; H, 13·3. $C_{12}H_{24}O$ requires C, 78·3; H, 13·0%). 3-Ethylmenthene, prepared by heating the alcohol at 160° for 4 hours with twice its weight of anhydrous oxalic acid, had b. p. 90—92°/21 mm.; $\alpha_D^{16°}$ + 39·18°; $d_{4°}^{25°}$ 0·8302; $n_D^{25°}$ 1·4614; $[R_L]_D$ 54·91 (Calc. for $C_{12}H_{22},1|^{=}$, 54·46).

3. 3-n-*Propylmenthan*-3-*ol*. The following quantities were used: 30 g. of *l*-menthone, 7 g. of magnesium, 50·8 g. of *n*-propyl iodide; the resulting alcohol (12·8 g.) distilled at 123—125°/16 mm., and had $\alpha_D^{17°}$ −0·68°; $d_{4°}^{25°}$ 0·8957; $n_D^{25°}$ 1·4664; $[R_L]_D$ 61·32 (Calc. for $C_{13}H_{25}\cdot OH$, 60·91). 3-n-Propylmenthene, prepared by heating the alcohol with twice its weight of anhydrous oxalic acid at 150° for 4 hours, had b. p. 100—103°/18 mm.; $\alpha_D^{18°}$ + 35·90°; $d_{4°}^{25°}$ 0·8348; $n_D^{25°}$ 1·4605; $[R_L]_D$ 59·10 (Calc. for $C_{13}H_{24},1|^{=}$, 59·03).

4. 3-*Phenylmenthan*-3-*ol*. From 30 g. of *l*-menthone, 7 g. of magnesium and 47 g. of bromobenzene, 18 g. of the alcohol were obtained; it had b. p. 170—172°/18 mm.; $\alpha_D^{17°}$ − 22·87°; $d_{4°}^{25°}$ 0·9872; $n_D^{25°}$ 1·5265; $[R_L]_D$ 72·14 (Calc. for $C_{16}H_{23}\cdot OH,3|^{=}$, 71·33). 3-Phenylmenthene, prepared by heating the alcohol with twice its weight of anhydrous oxalic acid at 150° for 4 hours, had b. p. 149—151°/18 mm.; $\alpha_D^{17°}$ + 43·48°; $d_{4°}^{25°}$ 0·9365; $n_D^{25°}$ 1·5275; $[R_L]_D$ 70·26 (Calc. for $C_{16}H_{22},4|^{=}$, 69·45) (Found: C, 89·2; H, 10·1. Calc. for $C_{16}H_{22}$: C, 89·7; H, 10·3%). The optical rotatory powers of these two products are substantially higher than the values given by Murat (*loc. cit.*).

The Application of Grignard Reagents to d-iso*Menthone*.—*d-iso*-Menthone was prepared by the catalytic hydrogenation of *l*-piperitone by means of colloidal palladium (J., 1923, **123**, 2921). It had b. p. 97—99°/18 mm., $[\alpha]_D^{17°}$ + 69·90°, $n_D^{17°}$ 1·4566. The proportions of the reactants were the same as those used in the corresponding syntheses starting from *l*-menthone, and the analogous operations were conducted as indicated in the preceding section.

3-Methyl*iso*menthan-3-ol had b. p. 105—106°/20 mm.; α_D^{16} +26·95°; $d_{4°}^{25°}$ 0·8959; $n_D^{16°}$ 1·4658, $n_D^{25°}$ 1·4640; $[R_L]_D$ 52·33 (Calc. for $C_{11}H_{21}\cdot OH$, 51·78). The derived 3-methylmenthene had b. p. 68—74°/10 mm.; $\alpha_D^{17°}$ +17·86; $d_{4°}^{25°}$ 0·8550; $n_D^{17°}$ 1·4578.

3-Ethyl*iso*menthan-3-ol had b. p. 105—106°/10 mm.; $\alpha_D^{17°}$ + 22·04°; $d_{4°}^{25°}$ 0·8985; $n_D^{25°}$ 1·4648; $[R_L]_D$ 56·58 (Calc. for $C_{12}H_{23}\cdot OH$, 56·36). The derived 3-ethylmenthene had b. p. 73—75°/10 mm.; $\alpha_D^{16°}$ + 6·79°; $n_D^{25°}$ 1·4610.

3-Phenyl*iso*menthan-3-ol had b. p. 150—152°/9 mm.; $\alpha_D^{16°}$ + 0·44°; $d_{4°}^{25°}$ 0·9812; $n_D^{25°}$ 1·5265; $[R_L]_D$ 72·57 (Calc. for $C_{16}H_{23}\cdot OH,3|^{=}$, 71·33). The derived 3-phenylmenthene had b. p. 127—130°/8 mm.; $\alpha_D^{17°}$ + 16·28°; $n_D^{25°}$ 1·5270.

The Action of Magnesium Bromide on Piperitone and Menthones.—The magnesium bromide used in these experiments was prepared by the gradual addition of dry bromine (63 g.) to dry magnesium powder (10 g.) in dry ether (100 c.c.); the thick oily product obtained by warming the mixture on the water-bath contained 55—58% of ether, *i.e.*, about 3 mols. of ether per mol. of magnesium bromide.

When the specially prepared magnesium bromide was added in excess to *l*-piperitone ($[\alpha]_D^{16^\circ}$ − 49·20°) dissolved in light petroleum, a thick gummy product was formed; this could not be induced to crystallise, and when decomposed with water it yielded *dl*-piperitone ($[\alpha]_D^{16^\circ}$ − 0·06°).

The similar gummy product furnished by *d*-*iso*menthone ($[\alpha]_D^{16^\circ}$ + 69·90°) gave a partly "inverted" *d*-*iso*menthone ($[\alpha]_D^{16^\circ}$ + 35·11°) when decomposed with water.

l-Menthone ($[\alpha]_D^{17^\circ}$ −25·65°) gave a crystalline *compound* when treated similarly; this was recrystallised from dry ethyl acetate (Found, by titration: Br, 46·5. $2C_{10}H_{18}O,MgBr_2$ requires Br, 47·1%).

The Action of Alcoholic Potassium Cyanide on l-*Piperitone.*—*l*-Piperitone (15 g.) in 96% alcohol (25 c.c.) was mixed with a solution of potassium cyanide (8·3 g.) in water (10 c.c.) and heated under reflux on the water-bath. After 30 minutes, ethyl acetate (9 g.) was introduced beneath the surface of the liquid, and the boiling was continued for 2 hours. The oil (14 g.) obtained upon pouring the product into water distilled at 151—153°/13 mm., and had $d_4^{25^\circ}$ 0·9720, $n_D^{25^\circ}$ 1·4680, $[R_L]_D$ 51·24 (Calc. for $C_{11}H_{17}ON,1|^{=}$, 52·24) (Found: C, 74·2; H, 9·7; N, 7·4. $C_{11}H_{17}ON$ requires C, 73·8; H, 9·5; N, 7·8%). This *substance* (X) was optically inactive; it was stable towards hot acid and alkali, and gave no oxime or semicarbazone.

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