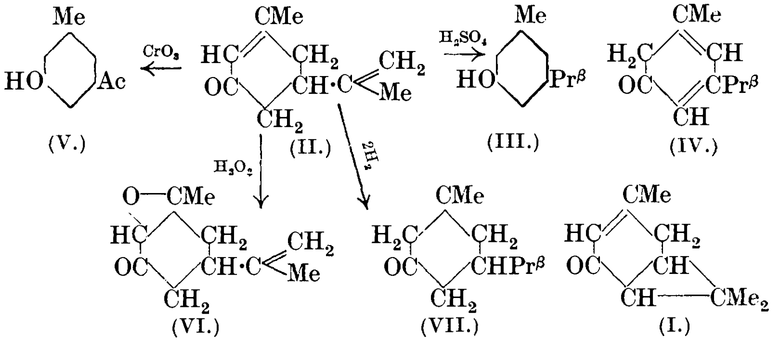
CCCCXVII.—*The Constituents of Indian Turpentine from* Pinus longifolia, *Roxb. Part VI. The Auto-oxidation of* d-Δ^3-*Carene.*

By JOHN OWEN and JOHN LIONEL SIMONSEN.

ALTHOUGH attention was directed in Part I (J., 1920, 574) of this series to the great rapidity with which *d*-Δ^3-carene is attacked by oxygen, and some quantitative experiments on the rate of oxidation of the hydrocarbon, both alone and in the presence of anti-catalysts, were made by Rau (*Ind. For. Rec.*, 1924, **11**, 197), no attempt has been made to study the products formed. During recent years the investigation of auto-oxidations has been much facilitated by the introduction of catalysts, such as cobalt resinate (siccativ), and since it has been found (*inter al.*, Wienhaus and Schumm, *Annalen*, 1924, **439**, 31) that the main products, verbenol and verbenone, of the auto-oxidation of α-pinene are obtained both in the absence and in the presence of resinates, we have confined ourselves to a study of the action of moist oxygen on *d*-Δ^3-carene in the presence of cobalt resinate.

According to Semmler and Schiller (*Ber.*, 1927, **60**, 1603) a dicyclic ketone (I) is obtained by the oxidation of Δ^3-carene by potassium permanganate in acetone solution and we had anticipated, following the analogy of α-pinene, that this ketone, together with the corresponding secondary alcohol, would be formed on auto-oxidation. Although we have obtained evidence of its presence, Δ^3-carene has shown its usual tendency to undergo ring fission with the formation of unsaturated monocyclic alcohols and ketones. Separation of the products of the oxidation by the method described on p. 3007 showed them to consist of these in approximately equal proportions. Comparatively little difficulty was experienced in determining the nature of the chief ketonic constituents, but the alcohols were a complex mixture, which we have only partially identified.

The lævorotatory ketone, $C_{10}H_{14}O$, isolated through the compound which it formed with sodium sulphite, and characterised by the preparation of a *semicarbazone*, m. p. 185—186°, and a 2 : 4-*dinitrophenylhydrazone*, m. p. 173°, was found to be not entirely homogeneous, but it consisted essentially of *l*-1-*methyl*-3-iso*propenyl*-Δ^6-cyclo*hexen*-5-*one* (II). The constitution was established in the following manner. The presence of two ethylenic linkages was shown by the absorption of two molecules of hydrogen on catalytic hydrogenation with the formation of a saturated ketone (see below); it is therefore somewhat remarkable that the ketone (II) was quite unaffected by treatment with benzoylhydroperoxide in chloroform solution (compare, *inter al.*, Wedekind and Teitweiler, *Ber.*, 1931, **64**, 1799). The relative positions of the substituent groups in the ketone were proved by conversion, on digestion with dilute sulphuric acid, into 5-*iso*propyl-*m*-cresol (III). This symmetrical phenol was prepared from 1-methyl-3-*iso*propyl-Δ^6-*cyclo*hexen-5-one by Knoevenagel (*Ber.*, 1894, **27**, 2347), who described it as a solid, m. p. 54°. We were unable to obtain our phenol crystalline and we met with the same difficulty with a specimen of the phenol prepared by Knoevenagel's method. The two phenols were, however, shown to be identical, since, on bromination in aqueous solution, they gave the same *tetrabromide*, m. p. 138—140°. This bromide readily liberated iodine from a potassium iodide solution and it is therefore probably a derivative of 1-methyl-3-*iso*propyl-$\Delta^{1:3}$-*cyclo*hexadien-5-one (IV), but its constitution was not determined.



The presence of an *iso*propenyl group was proved by oxidation of the ketone with chromic acid, a ketonic phenol, $C_9H_{10}O_2$, m. p. 88—90°, being obtained. The constitution of this ketone was not directly established, but there can be no doubt that it is 5-*hydroxy*-3-*methylacetophenone* (V). As was anticipated, the second ethylenic linkage was found to be in the αβ-position to the carbonyl group, since an *oxide* (VI) was obtained when the ketone was treated with hydrogen peroxide in alkaline solution under conditions similar to those suggested by Weitz and Scheffer (*Ber.*, 1921, **54**, 2327). Further, the ketone reacted with hydrogen sulphide to give a crystalline, but extremely unstable, derivative and some evidence was obtained of the formation of a hydroxylamino-oxime and semicarbazido-semicarbazone, although these derivatives could not be obtained pure.

The ketone reacted with piperonal in the presence of sodium ethoxide to yield a microcrystalline yellow *derivative* having the composition $C_{36}H_{36}O_7$ or $C_{36}H_{38}O_7$. This is formed apparently by the interaction of two molecules of the ketone with two of piperonal with the loss of one molecule of water, but its constitution was not determined.

Although the auto-oxidation ketone was thus conclusively shown to consist essentially of the *m*-menthadienone (II), it was not homogeneous. When it was oxidised with potassium permanganate (see p. 3009), the only crystalline acid which could be isolated was *as*-dimethylsuccinic acid. Further, the saturated ketone, prepared by catalytic hydrogenation of (II), gave a semicarbazone, which consisted mainly of the optically active *m*-menthanone (VII), but contained a small quantity of an isomeric, optically inactive semicarbazone. Although it is possible that the substituted succinic acid is a final degradation product of the dicyclic ketone (I), we regard it as more probably derived from the presence of a small amount of eucarvone. Support is lent to this view by the observation (p. 3007) that the sodium sulphite compound of the ketone, when decomposed by alkali, yields a deep cobalt-blue solution, a reaction referred to by Baeyer (*Ber.*, 1894, **27**, 812) as characteristic of eucarvone.

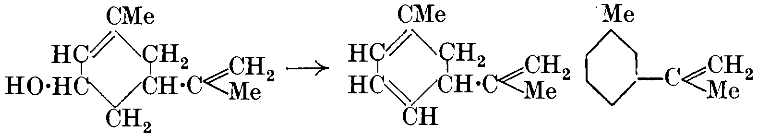
The purification of the ketone obtained by the catalytic hydrogenation of (II) was most conveniently carried out by the fractional crystallisation of the semicarbazone, since the progress of the fractionation could be controlled by polarimetric observations. The semicarbazone was comparatively readily separated into two fractions, the main fraction consisting of *l*-1-*methyl*-3-iso*propyl*-cyclo*hexan*-5-*one semicarbazone*, decomp. 203°, from which the lævorotatory *ketone* was regenerated by hydrolysis with oxalic acid. *dl*-1-Methyl-3-*iso*propyl*cyclo*hexan-5-one was prepared by Knoevenagel (*Annalen*, 1897, **297**, 172) by oxidation of the corresponding alcohol and later by Wallach and Schlubach (*ibid.*, 1913, **397**, 210) by hydrogenation of Δ^6-*m*-menthen-5-one. As will be seen from the table given below, there is a considerable difference in the physical constants of the ketones, for which we cannot at present offer a satisfactory explanation.

dl-Ketone.		*l*-Ketone.	
K.	W. & S.		
B. p. 222°	B. p. 221—223°	B. p. 217°/754 mm.	
$d_{4°}^{18°}$ 0·9040	$d^{20°}$ 0·8965	$d_{25°}^{25°}$ 0·9168	
$n_D^{18°}$ 1·45359	n_D 1·4541	$n_D^{25°}$ 1·4591	
$[R_L]_D$ 46·03	$[R_L]_D$ 46·53	$[R_L]_D$ 45·92	Calc., 46·19

As mentioned above, the *l-m*-menthanone was mixed with an optically inactive isomeride, the *semicarbazone* of which decomposes at 197—198°. The quantity (4 g.) of this semicarbazone precluded any possibility of determining its constitution, but since it yields a *nitroso*-derivative it cannot be the isomeric *m*-menthan-2-one.

The product from the auto-oxidation which did not react with sodium sulphite was readily separable by distillation into two fractions, the more volatile of which consisted of unchanged hydrocarbon and the less volatile of a mixture of alcohols. The lævorotatory alcohol fraction distilled over a narrow range and gave analytical figures corresponding to an unsaturated alcohol, $C_{10}H_{16}O$, with two ethylenic linkages. The physical constants ($[R_L]_D = 46{\cdot}49$; calc. for $C_{10}H_{16}O$, $2|^{=}$ 46·77) were also in accord with this assumption, which was confirmed by a quantitative oxidation with benzoylhydroperoxide. Attempts to prepare crystalline derivatives were unsuccessful : it was found that the alcohol was a mixture and we can only offer indirect evidence of its composition. It contained a small quantity of a ketone, $C_{10}H_{14}O$, which was isolated as its very sparingly soluble 2 : 4-*dinitrophenylhydrazone*, m. p. 212—213°. It seems to us not improbable that this is derived from the unsaturated dicyclic ketone (I).

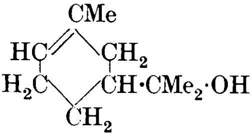
On oxidation with either potassium permanganate in acetone solution or with Beckmann's reagent the alcohol underwent extensive degradation, but in each case a small quantity of a substance was separated which was found to be a mixture of 3- and 4-methylacetophenones. Whilst the formation of these ketones proves the presence of two alcohols containing an *iso*propenyl group in the 3- and 4-positions in the auto-oxidation alcohol, the mechanism of their formation seems somewhat obscure. The most simple assumption is that the oxidation is preceded by dehydration, which, in the case of an alcohol having formula (VIII), would lead to the dihydrobenzene derivative (IX) and thence to *m*-*iso*propenyltoluene (X).

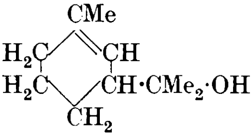

(VIII.) (IX.) (X.)

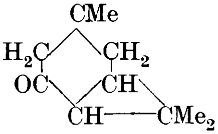
Evidence of the facility with which the auto-oxidation alcohols undergo dehydration was furnished by other experiments.

It occurred to us that the simplest method of determining the constituents of the alcohol would be to reduce it catalytically and oxidise the resulting saturated alcohols to the corresponding ketones, which could be more readily separated. The alcohol, however, only absorbed hydrogen (approximately one-third of a molecule) very slowly even in the presence of a large amount of catalyst and the product was found to consist mainly of a hydrocarbon which, apart from its somewhat low boiling point, had physical constants agreeing closely with those of the cymenes. Oxidation of the hydrocarbon, which was not attacked by cold Beckmann's reagent, with potassium permanganate furnished a mixture of acids. We were unable to effect a separation with the material available, but consider the hydrocarbon to be a mixture of *m*- and *p*-cymenes.

Since it appeared possible that this result was due, at least in part, to the presence of a catalyst poison in the alcohol, it was decided to effect a partial reduction by chemical methods and then to complete the reduction catalytically. The alcohol was not attacked by sodium in moist ethereal solution, but partial reduction was effected with sodium and alcohol. The alcohol so obtained was either oxidised with chromic acid and then reduced catalytically or reduced prior to oxidation. In both cases the reduction was very incomplete and the products obtained were identical. After removal of the ketonic constituents of the oil with sodium bisulphite and semicarbazide acetate, an *alcohol*, $C_{10}H_{18}O$, was obtained. This alcohol, which, since it was stable to chromic acid, must contain a tertiary alcohol group, had constants, apart from the fact that it was dextrorotatory, agreeing very closely with those of the dihydro*iso*carvestrenol (XI) prepared by Fisher and Perkin (J., 1908, **93**, 1889; compare Haworth, Perkin, and Wallach, J., 1913, **103**, 1228; Haworth and Perkin, *ibid.*, p. 2225) and it gave the same colour reactions with sulphuric acid in acetic acid solution. If we accept the view of Aschan ("Naphthenverbindungen, Terpene und Campherarten," p. 121) regarding this colour reaction, it is probable that the alcohol is a mixture of (XI) and (XII). Attempts to confirm the presence of this alcohol by the preparation of a crystalline dihydrochloride or nitrosochloride were not successful, but, since it is not improbable, although we have no direct evidence to offer, that the alcohol contained also α-terpineol, this is not surprising.

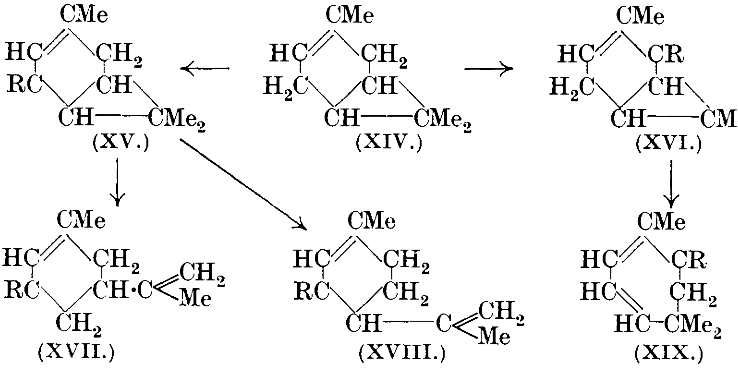

(XI.)


(XII.)


(XIII.)

The ketone regenerated from the bisulphite compound was converted into the semicarbazone and this was found to consist mainly of the *l*-*m*-menthanone semicarbazone described above. A second more readily soluble and lower-melting semicarbazone was present also, but this could not be obtained pure. A third *semicarbazone*, m. p. 228—229°, derived from a ketone, $C_{10}H_{16}O$, was slowly formed when the oil, which did not react with sodium bisulphite, was treated with semicarbazide acetate. This semicarbazone we consider to be identical with that, m. p. 223—224°, obtained by Semmler and Schiller (*loc. cit.*) from the saturated ketone (XIII).

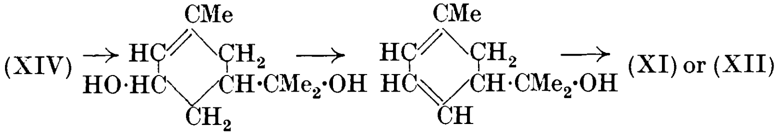
The results outlined above appear to us to show that the autoxidation of *d*-Δ^3-carene (XIV) proceeds in an exactly analogous manner to that of α-pinene, but that subsequently secondary reactions of two kinds occur. The main reaction proceeds in accordance with the scheme



[R = HOH or O.]

the chief product of the reaction being the alcohol (or corresponding ketone) (XV). This is comparatively unstable and isomerises mainly to the monocyclic alcohol (XVII) and probably also to (XVIII). Oxidation to the alcohol (XVI) occurs to a much more limited extent, since the presence of the ketone, eucarvone (XIX), to which the dicyclic ketone would immediately isomerise (compare Wallach, *Annalen*, 1905, **339**, 94; Clarke and Lapworth, J., 1910, **97**, 13), has only been indicated by a colour reaction and by the formation of *as*-dimethylsuccinic acid on oxidation. The dicyclic alcohol or ketone (XV) is undoubtedly more stable, since we were able to isolate in small amount the semicarbazone of the corresponding saturated ketone, but here also the stability is obviously of a low order.

The isolation of a tertiary alcohol giving the sylvestrene colour reactions indicates that ring fission occurs also by hydration. Since this colour reaction is not shown by the original oxidation ketone, this probably contains an alcohol having the structure (XXI), formed by dehydration of the glycol (XX). Partial hydrogenation of this might yield (XI) or (XII).



(XX.) (XXI.)

EXPERIMENTAL.

Moist oxygen was passed through the hydrocarbon (500 g.), in which cobalt resinate (50 g.) was suspended, for 160 hours, the temperature being kept at 35—40°. In order to expose as large a surface as possible the hydrocarbon was contained in a series of long tubes. On completion of the reaction the oil was distilled in steam, the aqueous distillate saturated with ammonium sulphate and extracted with ether, and the ether dried and evaporated. The residual oil (290 g.) was distilled under diminished pressure (100 mm.) until the temperature rose to 100° in order to remove the unchanged hydrocarbon (A) (70 g.). The remaining oil, which consisted essentially of a mixture of alcohols and ketones,* was shaken mechanically at 60—80° with an excess of sodium sulphite solution, the alkali formed being neutralised by the addition of acetic acid. When absorption was complete the insoluble oil (B) was removed with ether and reserved for subsequent investigation (see p. 3012).

1-1-*Methyl*-3-iso*propenyl*-Δ^6-cyclo*hexen*-5-*one*.—The sodium sulphite solution was made alkaline by the addition of sodium hydroxide; a deep brown solution was obtained, which became green and then deep cobalt-blue, whilst at the same time an oil separated. This was removed by extraction with ether, and the alkaline solution was warmed on the water-bath; a further quantity of oil was then liberated and the colour of the solution changed to a dirty brown. The aqueous solution was extracted with ether, the combined ethereal extracts dried over potassium carbonate, the solvent evaporated, and the residual oil distilled under diminished pressure (13 mm.). The main fraction, b. p. 100—102°, was redistilled for analysis; b. p. 101°/14 mm., $d_{25^\circ}^{25^\circ}$ 0·9283, $n_D^{25^\circ}$ 1·504, $[\alpha]_{5461}$ − 35·14° (Found: C, 79·5, 79·6; H, 9·5, 9·2. $C_{10}H_{14}O$ requires C, 80·0; H, 9·3%). The ketone was a pale yellow, somewhat viscid oil, with an odour resembling that of both camphor and menthone. Since, as mentioned above, the ketone was not homogeneous, diffi-

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* A quantitative estimation by absorption with sodium sulphite solution showed a ketonic content of approximately 48%.

culty was encountered in the preparation of crystalline derivatives. When dissolved in ammonia-alcohol solution, the ketone reacted with hydrogen sulphide below — 10° to give an additive compound which crystallised in leaflets, m. p. below 0°. This compound was extremely unstable and decomposed rapidly in the absence of an excess of hydrogen sulphide, even when maintained well below its melting point. In chloroform solution bromine was readily absorbed with the formation of a brown oil which decomposed with evolution of hydrogen bromide. When the ketone was treated with an excess of a chloroform solution of benzoylhydroperoxide at 0°, no oxidation took place and after being kept at this temperature for 3 days and at room temperature until the peroxide had decomposed, the ketone was recovered unchanged and was identified by the preparation of the 2 : 4-dinitrophenylhydrazone (see below). With hydroxylamine, the ketone yielded a mixture of an oxime and a hydroxylamino-oxime, the latter being isolated by the precipitation of its hygroscopic oxalate from an ethereal solution. The hydroxylamino-oxime, regenerated from the salt by sodium carbonate, was a viscid oil which gave a readily soluble picrate and reduced Fehling's solution. It could not be obtained crystalline and neither it nor the liquid oxime was further examined. The *semicarbazone*, which was only slowly formed, crystallised from methyl alcohol in prisms, m. p. 185—186°, decomposing slightly above this temperature (Found : C, 63·9 ; H, 8·0. $C_{11}H_{17}ON_3$ requires C, 63·8 ; H, 8·2%). During the preparation of the semicarbazone the formation of an amorphous solid was observed, which was readily soluble in alcohol and separated from much hot water in white flocks. It could not be obtained pure for analysis, but was probably a semicarbazido-semicarbazone. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate, in which it was sparingly soluble, in garnet-coloured prisms, m. p. 173° (Found : N, 17·3. $C_{16}H_{18}O_4N_4$ requires N, 17·0%). Owing to its sparing solubility and ease of preparation this derivative is most suitable for the characterisation of the ketone.

For the preparation of the piperonal derivative, sodium ethoxide (Na, 0·2 g. ; alcohol, 3 c.c.) was added to a mixture of the ketone (3 g.) and piperonal (3 g.) in alcohol (20 c.c.) cooled in salt-ice. After remaining for 4 days, the deep brown alcohol was decanted from the viscid oil which had separated. The oil, which became pasty when ground with water, was dissolved in ether, the ether dried and evaporated, and the residue dissolved in hot *cyclo*hexanol, from which it separated on cooling as a yellow powder. This was recrystallised twice from methyl alcohol, a small quantity of a sparingly soluble substance being removed by filtration. The *compound* so obtained was a yellow microcrystalline powder, which sintered at 130°, m. p. 141—143°. Two distinct preparations were analysed (Found : C, 74·5, 74·6; H, 5·9, 6·0. $C_{36}H_{38}O_7$ requires C, 74·2; H, 6·5%. $C_{36}H_{36}O_7$ requires C, 74·5; H, 6·2%).

Oxidation of 1-1-*Methyl*-3-iso*propenyl*-Δ^6-cyclo*hexen*-5-*one*.—(1) *With hydrogen peroxide.* 1-1-*Methyl*-3-iso*propenyl*-1 : 6-*oxido*cyclo*hexan*-5-*one*. To a solution of the menthadienone (20 g.) in methyl alcohol (200 c.c.), cooled in ice and salt, a mixture of hydrogen peroxide (15%; 64 c.c.) and sodium hydroxide solution (4*N*; 34 c.c.) was added gradually, the temperature being kept below 5°. After 1 hour, the reaction mixture was kept at room temperature overnight, and addition of water then precipitated an oil. This was dissolved in ether, and the ether dried and evaporated. The *oxide* had b. p. 113—115°/18 mm., $d_{25^\circ}^{25^\circ}$ 1·0329, $n_D^{25^\circ}$ 1·4808, $[\alpha]_{5461}$ — 11·2°, $[R_L]_D$ 45·73 (Found : C, 72·6; H, 8·6. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%). The *semicarbazone* crystallised from alcohol, in which it was very sparingly soluble, in needles, decomp. 209—210° after sintering at 197° (Found : N, 18·7. $C_{11}H_{17}O_2N_3$ requires N, 18·8%).

(2) *With potassium permanganate.* To a mechanically stirred suspension of the ketone (5 g.) in dilute sodium carbonate solution, potassium permanganate (2·5% solution) was gradually added, the temperature being kept at 5°. When the oxidation was complete, the excess of permanganate was destroyed with sulphur dioxide, the solution filtered, the manganese dioxide sludge well washed with water, and the combined filtrate and washings concentrated to a small bulk in a current of carbon dioxide. The solution was acidified and extracted with ether (10 times), and the ether dried and evaporated; a viscid oil (4 g.) remained. This was dissolved in aqueous ammonia, and the faintly alkaline solution filtered from tar and mixed with an excess of calcium chloride solution, which precipitated a resinous salt. The filtered solution was boiled, and the crystalline calcium salt that separated was collected, decomposed with hydrochloric acid, and the liberated acid dissolved in ether. On removal of the solvent a crystalline cake (1 g.) remained, which, after crystallisation from hydrochloric acid, had m. p. 137—138°. It was identified as *as*-dimethylsuccinic acid by the method of mixed m. p. and analysis (Found : C, 49·5; H, 6·7. Calc. : C, 49·3; H, 6·9%). The filtrate from the sparingly soluble calcium salt gave, after acidification and extraction with ether, a liquid acid (2·7 g.). This could not be crystallised and since it gave no precipitate with aqueous copper acetate the absence of caronic acid may be inferred.

(3) *With chromic acid.* 5-*Hydroxy*-3-*methylacetophenone*. To a suspension of the ketone (5 g.) in dilute sulphuric acid (water, 100 c.c.; H_2SO_4, 10 c.c.), chromic acid (14 g.) in water (25 c.c.) was gradually added, the oxidation being completed by warming on the

water-bath. During the process a heavy oil separated; this was dissolved in ether, and the ethereal solution, after being washed with sodium carbonate solution, and with very dilute aqueous sodium hydroxide, which removed a little resinous material, was dried and evaporated; an oil remained which rapidly crystallised. After being drained on porous porcelain, the phenol was recrystallised from light petroleum (b. p. 60—80°) (charcoal), from which it separated in hard prisms having a faint yellow colour, m. p. 88—90° (Found : C, 72·3; H, 7·2. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%). 5-*Hydroxy*-3-*methylacetophenone* gave no colour with ferric chloride, was readily soluble in methyl alcohol and benzene, somewhat readily so in hot water and light petroleum, and dissolved in aqueous sodium hydroxide, yielding a yellow solution, which rapidly darkened on exposure to the air. The *semicarbazone* crystallised from methyl alcohol in small prismatic needles, decomp. 218—220° (Found : N, 20·5. $C_{10}H_{13}O_2N_3$ requires N, 20·3%). The *oxime* separated from either water or benzene–light petroleum in minute prisms, m. p. 138—140° (Found : N, 8·2. $C_9H_{11}O_2N$ requires N, 8·5%).

Action of Sulphuric Acid on 1-1-*Methyl*-3-iso*propenyl*-Δ^6-cyclo*hexen*-5-*one*. 5-iso*Propyl*-m-*cresol*.—A mixture of the ketone (10 g.) and sulphuric acid (100 c.c.; 10%) was boiled for 3 hours and the cooled solution, after saturation with ammonium sulphate, was extracted with light petroleum (b. p. 40—60°). The petroleum extract was washed with sodium hydroxide solution (10%), dried, and evaporated and the residual oil was again digested for 3 hours with dilute sulphuric acid, the product being worked up as before. The oil (3 g.) which was insoluble in alkali distilled at 95—105°/18 mm. and consisted of unchanged ketone, identified as the semicarbazone, m. p. 185—186° (Found : C, 63·6; H, 8·2%). The combined sodium hydroxide washings deposited on acidification a viscid oil, which, after isolation in the usual manner, distilled at 121°/10 mm., but it was not analytically pure (Found : C, 78·4; H, 9·3. $C_{10}H_{14}O$ requires C, 80·0; H, 9·3%). The oil did not crystallise even when cooled in liquid air, but it was readily characterised by the preparation of a crystalline tetrabromide, which separated when the phenol was treated with an excess of bromine water. *Tetrabromo*-1-*methyl*-3-iso*propyl*cyclo*hexan*-5-*one* crystallised from acetic acid, in which it was somewhat sparingly soluble, in faintly yellow prisms with sharp edges, m. p. 138—140° (Found : C, 25·9; H, 2·1; Br, 68·3. $C_{10}H_{10}OBr_4$ requires C, 25·7: H, 2·1; Br, 68·5%). When dissolved in ether or chloroform, the tetrabromide immediately liberated iodine from potassium iodide solution, but the resulting debrominated product could not be crystallised.

A specimen of the phenol prepared by Knoevenagel's method (*loc. cit.*) had b. p. 120°/10 mm. and on bromination yielded a tetrabromide identical with that described above, m. p. both alone and in admixture 138—140° (Found : Br, 68·8%).

Catalytic Hydrogenation of 1-1-*Methyl*-3-iso*propenyl*-Δ^6-cyclo*hexen*-5-*one*. 1-1-*Methyl*-3-iso*propyl*cyclo*hexan*-5-*one*.—A mixture of the ketone (10 g.), acetic acid (60 c.c.), and palladium-norite (2 g.; Pd, 10%) was shaken in an atmosphere of hydrogen until absorption was complete (H_2 absorbed, 2·68 l.; calc. for $2H_2$, 3·17 l.). The filtered solution was neutralised with sodium carbonate, the ketone extracted with ether, and the oil remaining after removal of the solvent mixed with an excess of semicarbazide acetate. The semicarbazone obtained (12 g.) was dried on porous porcelain, and then had $[\alpha]_{5461}$ + 18·23° in acetic acid. It was purified by systematic crystallisation from ethyl acetate, the fractionation being controlled by polarimetric observations; ultimately, two pure fractions (A) and (B) were obtained, the latter being only small. The final mother-liquors contained a small quantity of an amorphous solid, consisting probably of the semicarbazido-semicarbazone of the parent ketone which had escaped reduction.

Fraction (A), 1-1-*methyl*-3-iso*propyl*cyclo*hexan*-3-*one semicarbazone*, crystallised from ethyl acetate, in which it was sparingly soluble, in needles, decomp. 203°; in acetic acid, $[\alpha]_{5461}$ + 28·75° (c = 0·9044; l = 1) (Found : C, 62·6; H, 9·6. $C_{11}H_{21}ON_3$ requires C, 62·6; H, 9·9%). For the preparation of the ketone, a mixture of the semicarbazone (10 g.), oxalic acid (10 g.), and water (50 c.c.) was distilled in steam; the ketone, which was somewhat readily soluble in water, then rapidly passed over. The aqueous distillate, after saturation with ammonium sulphate, was extracted with ether, and the ether dried and evaporated; the residual oil had b. p. 141°/100 mm., 217°/754 mm., $d_{25^\circ}^{25^\circ}$ 0·9168, $n_D^{25^\circ}$ 1·4591, $[\alpha]_{5461}$ − 21·68° (Found : C, 78·3; H, 11·5. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). 1-1-*Methyl*-3-iso*propyl*cyclo*hexan*-5-*one* is a colourless mobile oil with a strong odour of peppermint. In acetic acid it readily absorbs bromine with the evolution of hydrogen bromide, but the product is an oil. The piperonylidene derivative is a yellow oil. The *oxime* crystallised from dilute methyl alcohol in prisms, m. p. 74—75° (Found : C, 71·0; H, 11·1; N, 8·5. $C_{10}H_{19}ON$ requires C, 71·0; H, 11·2; N, 8·4%). The p-*nitrophenylhydrazone* separated from alcohol in pale yellow needles, m. p. 183—185° (Found : N, 14·1. $C_{16}H_{23}O_2N_3$ requires N, 14·5%). The 2 : 4-*dinitrophenylhydrazone* was deposited from methyl alcohol in soft terra-cotta needles, which, when kept in the solution, changed gradually into leaflets, and which, examined under the microscope, were seen to consist of small prisms, m. p. 110—111° (Found : N, 16·8. $C_{16}H_{22}O_4N_4$ requires N, 16·8%).

The *nitroso*-derivative, prepared by the treatment of a well-cooled mixture of the ketone and amyl nitrite with hydrochloric acid, crystallised from chloroform–methyl alcohol in prismatic needles, decomp. 141—142° (Found : N, 7·6. $C_{10}H_{17}O_2N$ requires N, 7·6%); it was insoluble in alkali and gave no colour with ferric chloride in alcoholic solution.

Fraction (B) of the *semicarbazone* (4 g.) obtained from the hydrogenated ketone (see above) crystallised from methyl alcohol in needles, m. p. 197—198°. It was optically inactive in acetic acid solution (Found : C, 63·0; H, 9·6. $C_{11}H_{21}ON_3$ requires C, 62·6; H, 9·9%). The *ketone*, regenerated from the semicarbazone by oxalic acid, was a colourless mobile oil, b. p. 138—139°/100 mm., with a strong camphoraceous smell (Found : C, 77·5; H, 11·4. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). The *nitroso*-derivative crystallised from alcohol–chloroform in prisms, decomp. 138° (Found : N, 7·6. $C_{10}H_{17}O_2N$ requires N, 7·6%). As mentioned on p. 3004, the constitution of this ketone was not determined, but its nitroso-derivative does not depress the decomp. point of the nitroso-derivative of the *m*-menthanone described above.

Examination of the Alcohol Fraction.—The alcohol fraction (B) (p. 3007) remaining after the removal of the ketone with sodium sulphite was distilled under diminished pressure (19 mm.), a large fraction, b. p. 100—110°, being obtained, which on redistillation passed over mainly at 100°/16 mm. and then had $d_{25^\circ}^{25^\circ}$ 0·9574, $n_D^{25^\circ}$ 1·4975; a second preparation had the constants $d_{25^\circ}^{25^\circ}$ 0·9579, n_D^{25} 1·4988, $[\alpha]_{5461}$ − 15·31° (Found : C, 79·2, 79·0; H, 10·3, 10·6. $C_{10}H_{16}O$ requires C, 79·0; H, 10·5%). The *alcohol* was a colourless mobile oil with an odour reminiscent of that of menthol. It gave no colour with sulphuric acid in acetic anhydride solution. When it was treated with 2 : 4-dinitrophenylhydrazine sulphate, a 2 : 4-*dinitrophenylhydrazone* separated (0·2 g. from 1 g.). This crystallised from acetic acid, in which it was very sparingly soluble, as a bright red powder, seen under the microscope to consist of truncated prisms, m. p. 212—213° (Found : N, 17·4. $C_{16}H_{18}O_4N_4$ requires N, 17·0%). The presence of two ethylenic linkages was proved by oxidation with benzoylhydroperoxide in chloroform solution; the oxygen used was 0·2967 g. (calc. for O_2, 0·280 g.).

Oxidation of the Alcohol.—Since on oxidation with potassium permanganate in acetone solution or with Beckmann's reagent the alcohol did not yield any acidic products which could be identified and since the neutral products were identical, only the former oxidation is described. To a solution of the alcohol (5 g.) in acetone (100 c.c.), potassium permanganate (11·5 g.) was gradually added, the mixture being cooled in ice. After 48 hours the excess of permanganate was removed with sulphur dioxide, the solution filtered (the manganese dioxide sludge was extracted with hot water and examined for acids in the usual manner, but no crystalline acids could be isolated), and the acetone removed. The residual oil was mixed with an excess of semicarbazide acetate, sufficient alcohol being added to give a clear solution. After remaining over-night, the crystalline *semicarbazone* which had separated, decomp. 200—201°, was recrystallised from methyl alcohol and obtained in clusters of irregular prisms, decomp. 201° (Found: C, 62·8; H, 6·8. $C_{10}H_{13}ON_3$ requires C, 62·8; H, 6·8%); it did not depress the m. p. of authentic 4-methylacetophenone semicarbazone (decomp. 205—206°). The original filtrate, from which the semicarbazone had separated, gave after standing for some days and dilution with water a further quantity of a semicarbazone which only slowly crystallised. This was collected, washed free from oil with light petroleum, and without further purification hydrolysed with sulphuric acid (10%). When the resulting oil, which resembled acetophenone in smell, was shaken with an excess of potassium hypobromite solution, bromoform and carbon tetrabromide immediately separated. After 1 hour the insoluble products were removed with ether, the excess of hypobromite was destroyed with sulphur dioxide, and the solution acidified. The precipitated acid was dissolved in ether, the solution dried, and the solvent removed, leaving a solid, m. p. 110—155°. After crystallising once from dilute alcohol and three times from hot water, the more sparingly soluble acid was obtained in needles, m. p. 177—178°, both alone and in admixture with authentic *p*-toluic acid. The aqueous-alcoholic mother-liquor from the first crystallisation was made alkaline, the alcohol evaporated, and the acid, which separated on acidification of the concentrated solution, recrystallised twice from hot water; it then had m. p. 105—107°, both alone and in admixture with *m*-toluic acid.

Reduction of the Alcohol.—(i) *Catalytic hydrogenation.* The alcohol (20 g.) in acetic acid (25 c.c.) was, after the addition of palladium-norite (0·5 g.; Pd, 10%), shaken in an atmosphere of hydrogen. The reduction proceeded extremely slowly and it was necessary to add a further quantity of the catalyst (1·5 g.). The addition of hydrogen ceased after the absorption of 2·41 l. (calc. for $2H_2$, 6·236 l.). The hydrogenated product, isolated in the usual manner, had b. p. 82—95°/17 mm. and evidently contained a considerable quantity of a hydrocarbon. The oil was dissolved in acetic acid and oxidised with a slight excess of chromic acid, the reaction being completed by warming on the water-bath. Steam was passed into the mixture after basification and the volatile oil was separated and distilled under diminished pressure, two fractions being obtained: (i) b. p.

75—80°/16 mm., $d_{25^\circ}^{25^\circ}$ 0·8604, $n_D^{25^\circ}$ 1·4710, and (ii) b. p. 80—105°/16 mm., $d_{25^\circ}^{25^\circ}$ 0·9046, $n_D^{25^\circ}$ 1·4710. Analysis (Found : C, 86·8 ; H, 11·8%) showed fraction (i) to consist essentially of a hydrocarbon, which was present also in (ii) (Found : C, 81·0 ; H, 11·4%). After distillation over sodium fraction (i) had b. p. 165—168°/766 mm., $d_{25^\circ}^{25^\circ}$ 0·8516, $n_D^{25^\circ}$1·4732. The hydrocarbon was oxidised with hot potassium permanganate solution under the conditions used by Wallach (*Annalen*, 1891, **264**, 10) for the identification of *p*-cymene. The acid so obtained was a mixture, from which a few milligrams were obtained of an acid, m. p. 120—126°. This was possibly 3-α-hydroxy*iso*propylbenzoic acid (m. p. 123—124°), but further crystallisation did not improve the m. p.

Fraction (ii), which contained some ketone, was combined with similar fractions (see below).

(ii) *With sodium and alcohol.* The alcohol (40 g.) in hot ethyl alcohol (400 c.c.) was treated with sodium (100 g.), and the product isolated by steam distillation. The oil (34 g.) had b. p. 110—111°/21 mm., $d_{25^\circ}^{25^\circ}$ 0·9253, $n_D^{25^\circ}$ 1·4870, $[\alpha]_{5461}$ − 1·67° (Found : C, 78·4 ; H, 11·0%). The alcohol (34 g.) in acetic acid (100 c.c.) was treated gradually with chromic acid (14·5 g.) in acetic acid, added so that the temperature was maintained at 50—60°. The mixture was heated for 15 minutes on the water-bath, cooled, diluted with water, and extracted with ether. The ethereal extract was washed with sodium carbonate solution, which removed the acetic acid and a small quantity of a resinous acid (not further examined), and then with sodium hydroxide solution (see below), and dried, and the ether evaporated ; an oil (23 g.) was then obtained, b. p. 108—112°/22 mm., $d_{25^\circ}^{25^\circ}$ 0·9436, $n_D^{25^\circ}$1·4870, $[\alpha]_{5461}$ − 11·6° (Found : C, 79·0 ; H, 9·7%). The sodium hydroxide extract (see above) gave on acidification a viscid brown oil. This was dissolved in ether and, after removal of the solvent, mixed with semicarbazide acetate ; the gummy solid that had separated after 12 hours was washed with ether and recrystallised twice from methyl alcohol (charcoal), giving a semicarbazone as a faintly brown, crystalline powder, decomp. 217—220°, identical with that prepared from 5-hydroxy-3-methylacetophenone.

The oil (21·5 g.) from the oxidation with chromic acid was dissolved in acetic acid (20 c.c.) and, after the addition of palladium-norite (1·5 g.), shaken with hydrogen until the absorption of gas (1·505 l. in 24·5 hours) ceased. After basification the oil was dissolved in ether, the solution shaken mechanically for 4 hours with an excess of freshly prepared sodium bisulphite solution, and the ether separated, dried, and removed. The residual oil, b. p. 110—112°/25 mm., $d_{25^\circ}^{25^\circ}$ 0·9234, $n_D^{25^\circ}$ 1·4798, $[\alpha]_{5461}$ + 3·79° (Found : C, 77·8 ; H, 11·5. $C_{10}H_{18}O$ requires C, 77·9 ; H, 11·7%), had a strong smell of peppermint and gave with concentrated sulphuric acid in acetic anhydride solution a purple coloration, which changed to blue and finally violet. The oil, the constitution of which was discussed on p. 3005, did not react with semicarbazide acetate even on long standing. A small quantity of a higher-boiling fraction, 112—117°/25 mm., reacted with semicarbazide acetate to yield a semicarbazone, decomp. 228—229° after crystallisation from ethyl acetate (see below).

From the sodium bisulphite solution an oil (3·5 g.) was separated which was converted into the semicarbazone. This was a mixture, m. p. 150—190°, from which by fractional crystallisation from methyl alcohol and ethyl acetate a sparingly soluble fraction was obtained, decomp. 200—201°. This was identified as *l*-1-methyl-3-*iso*propyl*cyclo*hexan-5-one semicarbazone.

A quantity of semicarbazone (7 g.) which had been obtained in another experiment by direct treatment of the oil after catalytic hydrogenation with semicarbazide acetate was systematically fractionated from ethyl acetate and methyl alcohol and finally resolved into two fractions. The more sparingly soluble of these (0·3 g.) crystallised from much ethyl acetate in fine needles, decomp. 228—229°; $[\alpha]_{5461}$ $-$ 109·5° in acetic acid ($c = 1{\cdot}232$, $l = 1$) (Found: C, 63·2; H, 9·1. $C_{11}H_{19}ON_3$ requires C, 63·1; H, 9·1%). The constitution of this semicarbazone is discussed on p. 3006. The second, somewhat more readily soluble semicarbazone, decomp. 200—201° (Found: C, 62·3; H, 9·5. Calc.: C, 62·6; H, 9·9%), was identified as that of the *l*-*m*-menthanone. A lower-melting and more soluble semicarbazone was present but could not be obtained pure.

Hydrocarbon Fraction.—The hydrocarbon fraction (A) (p. 3007), which distilled below 100°/100 mm., was fractionated at the ordinary pressure; in addition to *d*-Δ^3-carene, a small fraction was then obtained which after distillation over sodium had b. p. 153·5—154·5°/755 mm., $d_{25^\circ}^{25^\circ}$ 0·8590, $n_D^{25^\circ}$ 1·4687, $[\alpha]_{5461}$ $-$ 35·33° (Found: C, 88·3; H, 11·8. Calc.: C, 88·2; H, 11·8%). This was identified as *l*-α-pinene by the preparation of the nitrosochloride, decomp. 103°, and by oxidation to pinonic acid (semicarbazone, m. p. 202—203°).

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