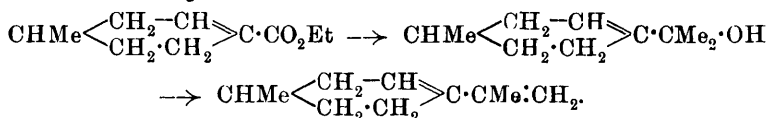


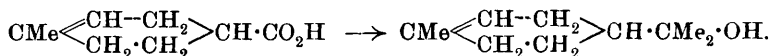
LXII.—*Experiments on the Synthesis of the Terpenes.*
Part XVII. d-Δ³-p-Menthenol(8) and d-Δ^{3:8(9)}-p-Menthadiene.

By TSAN QUO CHOU and WILLIAM HENRY PERKIN, jun.

THE externally compensated modifications of Δ³-*p*-menthenol(8) and Δ^{3:8(9)}-*p*-menthadiene were first prepared in 1905 (Perkin and Pickles, *Trans.*, **87**, 647) from the ester of *dl*-1-methyl-Δ³-cyclohexene-4-carboxylic acid by treatment with magnesium methyl iodide and subsequent elimination of water:



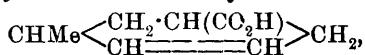
Shortly afterwards, Kay and Perkin (*Trans.*, 1906, **89**, 839) resolved *dl*-1-methyl-Δ³-cyclohexene-4-carboxylic acid by means of the brucine salt into the *d*- and *l*-acids, which were obtained with rotations $[\alpha]_D + 101.1^\circ$ and -100.8° respectively. From these active acids the *d*- and *l*-modifications of Δ³-*p*-menthenol(8) and Δ^{3:8(9)}-*p*-menthadiene were prepared, and the rotations of all these substances are tabulated on p. 529. During the progress of these experiments on the synthesis of the terpenes, other attempts were made to prepare active menthenols and menthadienes by processes similar to that just mentioned. Thus, in 1908, Fisher and Perkin (*Trans.*, **93**, 1871) resolved *dl*-1-methyl-Δ¹-cyclohexene-4-carboxylic acid into the *d*- and *l*-acids of rotations $[\alpha]_D + 50^\circ$ and -52° respectively, and prepared from these the *d*- and *l*-modifications of terpineol which were obtained with the rotations $[\alpha]_D + 44.2^\circ$ and -46.6° :



The attempt to convert these active terpineols into the pure active

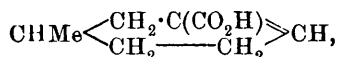
limonenes was not successful, since, even when the elimination of water was carried out at the ordinary temperature with the aid of magnesium methyl iodide, the resulting limonene had a rotation of only 5°

Shortly afterwards (Perkin, *Trans.*, 1910, **97**, 2131), the resolution of *dl*-1-methyl- Δ^5 -cyclohexene-3-carboxylic acid:



was attempted with the aid of *l*-menthylamine as the active base, and the *d*- and *l*-acids were obtained with the rotations $[\alpha]_D + 33.1^\circ$ and -30.9° respectively. These yielded, on treatment with magnesium methyl iodide and subsequent elimination of water, Δ^5 -*m*-menthenol(8) and $\Delta^{5:8(9)}$ -*m*-menthadiene, which, in the *d*-series, had $[\alpha]_D + 36.7^\circ$ and $+29.6^\circ$ respectively.

In the paper directly preceding the present communication (p. 521), experiments on the resolution of *dl*-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid:



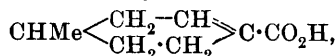
are described, and it is there shown that this acid may be resolved with the aid of *l*-menthylamine into the *d*- and *l*-modifications with the rotations $[\alpha]_D + 40.1^\circ$ and -35.8° respectively, and these were converted, by the usual methods, into the corresponding *d*- and *l*-menthenols and menthadienes, of which the highest rotations observed, in the *d*-series, were $[\alpha]_D + 20.9^\circ$ and $+17.5^\circ$ respectively. In all these cases, separation of the optically active acids from the externally compensated modifications has always been a long and tedious process, and there appears to be no doubt that this is largely, if not wholly, due to the isomeric salts separating from solvents as isomorphous mixtures or mixed crystals, which are only very gradually resolvable by further fractional crystallisation. This difficulty might conceivably be got over if the active base employed for the separation could be varied, but the cyclohexenecarboxylic acids are, unfortunately, so feebly acidic that very few of their salts with active bases are sufficiently stable or well characterised to make them suitable for fractional crystallisation.

When the available data are carefully considered, it is difficult to avoid the conclusion that, in the cases detailed above, separation may have, after all, been incomplete. The salts of the active acids were probably still partly racemic, and in the form of mixed crystals, and, for these reasons, separation by further fractional crystallisation was practically impossible, at all events with the comparatively small amounts of material which were available.

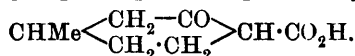
Confirmatory evidence of this is afforded by the experiments of

Fisher and Perkin on the resolution of *dl*-1-methyl- Δ^1 -cyclohexene-3-carboxylic acid (see p. 526). The value observed for the *l*-acid was $[\alpha]_D -52^\circ$, and that this is probably not the maximum value is indicated by the fact that the *l*-terpineol obtained from this acid had only $[\alpha]_D -46.6^\circ$, whereas an *l*-terpineol has been obtained from pinene with $[\alpha]_D -117.5^\circ$ (Ertshikowsky, *Ber.*, 1896, **29**, 887).

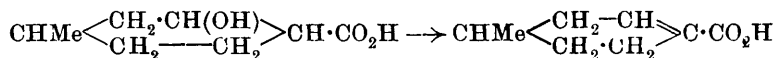
Considerations such as these made it desirable that the actual extent of the resolution effected by the fractional crystallisation of the salts of the cyclohexene acids with active bases should, at least in one instance, be experimentally tested, and we have therefore carried out an interesting series of experiments in connexion with the optical activity of 1-methyl- Δ^3 -cyclohexene-4-carboxylic acid:



which have a direct bearing on this problem. In a communication recently published (Gardner, Perkin, and Watson, *Trans.*, 1910, **97**, 1759, 1767), it was shown that *d*-1-methylcyclohexan-3-one (from pulegone, $[\alpha]_D +8.8^\circ$) is converted, by the action of sodamide and carbon dioxide, into a carboxylic acid, in which it was assumed that the carboxyl group occupied the position (4):



That this acid, which has $[\alpha]_D +97.2^\circ$, is, in fact, *d*-1-methylcyclohexan-3-one-4-carboxylic acid has now been proved in the following way. When this keto-acid is reduced with sodium amalgam, it is converted into *d*-1-methylcyclohexan-3-ol-4-carboxylic acid, which has $[\alpha]_D -31.8^\circ$, and this, on treatment with sulphuric acid at $85-90^\circ$, yields *p*-toluic acid, a proof that the carboxylic group in the hexanol acid occupies the position (4) in relation to the methyl group. The elimination of water from *d*-1-methylcyclohexan-3-ol-4-carboxylic acid takes place with difficulty, but it may be accomplished (p. 533) with the aid of phosphorus trichloride, and the resulting *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid:



was found to have $[\alpha]_D +150.1^\circ$. This acid was converted into the corresponding *d*- Δ^3 -*p*-menthenol(8) and $\Delta^{3:8(9)}$ -*p*-menthadiene by the usual methods, and the $[\alpha]_D$ values observed (I) may be conveniently tabulated in comparison with those previously observed by Kay and Perkin (II) (*loc. cit.*):

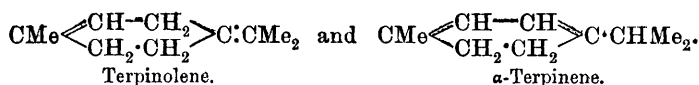
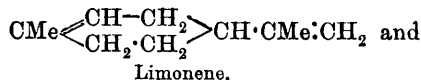
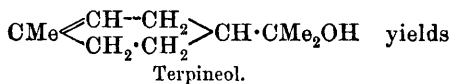
	I.	II.
<i>d</i> -1-Methyl- Δ^3 -cyclohexene-4-carboxylic acid	+150.1°	+101.1°
Ethyl <i>d</i> -1-methylcyclohexenecarboxylate	122.3	86.5
<i>d</i> - Δ^3 - <i>p</i> -Menthenol(8).....	83.2	67.3
<i>d</i> - $\Delta^{3:8(9)}$ - <i>p</i> -Menthadiene.....	100.0	98.2

This table shows quite clearly that the substances obtained by Kay and Perkin had rotations which were only about two-thirds of the maximum value. There is, however, one curious exception to this, and that is the case of the menthadienes, which, although derived from menthenols of the widely different values as $[\alpha]_D + 83.2^\circ$ and $+67.3^\circ$, had, in both cases, practically the same rotations, namely, $+100.0^\circ$ and $+98.2^\circ$. This seems to indicate quite clearly that some racemisation must have taken place in any case during the formation of the menthadiene from the menthenol of rotation $[\alpha]_D + 83.2^\circ$.

That racemisation does undoubtedly take place under certain conditions, to some extent at least, is proved by the following experiment.

Pure *d*- Δ^3 -*p*-menthenol(8) of rotation $[\alpha]_D + 83.2^\circ$ was converted into *d*- $\Delta^{3:8(9)}$ -*p*-menthadiene by two different processes, namely, (i) by digesting with 5 per cent. oxalic acid, and (ii) by the action of magnesium methyl iodide in the cold. The menthadiene obtained in (i) had $[\alpha]_D + 100.0^\circ$, whereas the preparation resulting from (ii) had a rotation of $[\alpha]_D + 90.4^\circ$ only. Racemisation in unsaturated compounds is usually assumed to be due to the reversible migration of the double linking, with consequent loss of optical activity, and seems to have been observed previously only in cases where the double linking is closely associated with the asymmetric carbon atom.

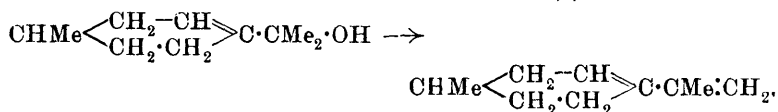
Thus, for example, Wallach has shown that terpineol yields, on treatment with dehydrating agents, not only limonene, but also terpinolene and α -terpinene:



This group of terpenes probably represents an equilibrium mixture, but, however that may be, it is quite clear that, if the terpineol in the first instance is optically active, the reversible change into terpinolene alone must ultimately result in the inactivity of the

whole. This migration of the double linking with consequent loss of optical activity accounts therefore in a satisfactory manner for the fact that Fisher and Perkin (*loc. cit.*) were unable to obtain an active limonene with a rotation of more than 5° (*d*-limonene has $[\alpha]_D +105^\circ$) from active terpineol by the elimination of water.

It is, however, difficult to understand how this explanation of loss of activity can be applied to the case of racemisation during the elimination of water from *d*- Δ^3 -*p*-menthenol(8):

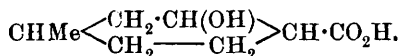
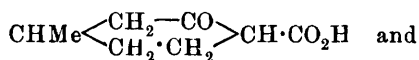


since migration of the double linking could hardly affect the asymmetric grouping $>\text{CHMe}$ to which optical activity is due unless, indeed, some profound change in constitution is assumed to take place.

Moreover, it is clear that a profound change in constitution does not take place, because the menthadiene obtained is found to exhibit all those physical properties which are known to be associated with the presence of the conjugated double linking.

Note by W. H. Perkin.—The paper by Kay and Perkin already referred to (Trans., 1906, **89**, 850; compare *ibid.*, 1905, **87**, 639) contains a description of some of the physical properties of *dl*- $\Delta^{3:8(9)}$ -*p*-menthadiene, which subsequent investigation has shown to be incorrect, and which has resulted in some confusion (compare Perkin and Wallach, Trans., 1910, **97**, 1437). As this terpene was very carefully prepared from crystalline *dl*- Δ^3 -*p*-menthenol(8), and had the correct boiling point (184 — 185°), it was difficult to understand the inaccuracy of the density and refraction values. The reason has now been ascertained to be the following one. The terpene was obtained in rather small quantity, and was washed into the bottle with a little ether and sent to Sudbury for investigation, the intention being that the final distillation should be carried out just before the physical constants were determined. This was, however, not done, and the determinations were made with the specimen in the condition in which it was received. The specimen has now been re-examined, and, after twice distilling over sodium, it gave the following correct values: b. p. 184 — 185° ; $d_{20/20^\circ}$ 0.8598 ; n_D 1.4919 ; M 45.9 . Calc. for $\text{C}_{10}\text{H}_{16}$ F^2 45.24 .

d-1-Methylcyclohexan-3-one-4-carboxylic Acid and *d*-1-Methylcyclohexan-3-ol-4-carboxylic Acid,



d-1-Methylcyclohexan-3-one-4-carboxylic acid had already been prepared in small quantities by Gardner, Perkin, and Watson (Trans., 1910, **97**, 1767) from *d*-1-methylcyclohexan-3-one (from pulegone) by the action of sodamide and carbon dioxide at the ordinary temperature on its solution in light petroleum, but the yield obtained at that time was very unsatisfactory. As it was necessary to obtain a large quantity of this acid for the experiments described in the present communication, we made a number of comparative experiments, and succeeded in working out the following method of preparation, which gives excellent results. *d*-1-Methylcyclohexan-3-one (from Schimmel, $[\alpha]_D + 8.8^\circ$), in quantities of 100 grams, is dissolved in one and a-quarter litres of light petroleum (b. p. $50-60^\circ$) in a three-necked flask fitted with a reflux condenser and mechanical stirrer, and the whole heated to boiling on the steam-bath. The steam is then turned off, the stirrer set in motion, and powdered sodamide (40 grams) added in several portions during twenty minutes, when a rapid evolution of ammonia takes place. A rapid current of carefully dried carbon dioxide is now passed, when reaction readily occurs with sufficient rise of temperature to keep the light petroleum boiling, and, in a short time, a quantity of the sodium salt of the ketonic acid separates. As soon as the liquid ceases to boil, the steam is turned on again, and the passage of the carbon dioxide continued for three and a-half hours; the contents of the flask are allowed to cool, and washed into a separating funnel with sufficient ice water to dissolve all the sodium salt. The aqueous layer is separated, filtered, if necessary, and acidified with ice-cold dilute hydrochloric acid, when the ketonic acid separates as a crystalline mass, which is collected and drained on porous porcelain. The yield of air-dry acid is usually about 70 grams, but on more than one occasion 90 grams have been obtained; in this condition it is pure enough for conversion into the hydroxy-acid (see below). The pure keto-acid is obtained from this product by dissolving in ether, extracting with sodium carbonate, and cautiously adding dilute hydrochloric acid to the alkaline solution until traces of yellow impurity have been precipitated. After filtering, the filtrate deposits, on acidifying, pure *d*-1-methylcyclohexan-3-one-4-carboxylic acid as a colourless, crystalline mass. The petroleum layer,

separated from the sodium salt of the acid in the manner described above, yields, on evaporation, a good deal of unchanged ketone, which is readily purified by distillation in steam.

d-1-Methylcyclohexan-3-ol-4-carboxylic Acid.—In preparing this acid, *d*-1-methylcyclohexan-3-one-4-carboxylic acid (15 grams) is dissolved in sodium carbonate, diluted to one litre with hot water (50°), and reduced in a wide-necked bottle with one kilo. of freshly prepared sodium amalgam (3 per cent.), which is added all at once.

During the operation, which takes about three hours, a rapid current of carbon dioxide is passed, the whole is vigorously stirred by a mechanical stirrer, and the temperature gradually raised to 70° by circulating a stream of hot water round the bottle. After remaining overnight, the aqueous liquor is decanted from the mercury, acidified with hydrochloric acid, and distilled in steam.

By this means, unchanged keto-acid, which is always present, is decomposed, the ketone passes over and is recovered from the distillate. The liquid in the steam distillation flask is evaporated on the steam-bath until a pale yellow oil commences to separate; it is then saturated with salt, and extracted three times with ether.

After drying over anhydrous sodium sulphate, and evaporating, the ethereal solution deposits a viscid syrup, which gradually becomes semi-solid; it distils at 185—190°/22 mm., but with some decomposition, and the distillate has $[\alpha]_D$ about -7.5° (compare p. 528). This doubtless consists of a mixture of the *cis*- and *trans*-modifications of *d*-1-methylcyclohexan-3-ol-4-carboxylic acid.

The best way to purify this hydroxy-acid is with the aid of its ethyl ester, which is readily prepared by digesting on the steam-bath with a large excess of 10 per cent. alcoholic sulphuric acid for two to three hours. The ester is isolated by diluting with water and extracting with ether in the usual manner, the ethereal solution washed with sodium carbonate, dried, evaporated, and the residue fractionated, when almost the whole quantity passes over at 135°/20 mm.:

0.1679 gave 0.3961 CO₂ and 0.1484 H₂O. C=64.4; H=9.8.

C₁₀H₁₈O₃ requires C=64.5; H=9.7 per cent.

d 20/20° 1.026; *n*_D 1.458; *M* 49.25 (calc., 49.51). 1.0221, made up to 20 c.c., with ethyl acetate, gave, in a 2-dcm. tube, $\alpha +0.6^\circ$, whence $[\alpha]_D +5.9^\circ$.

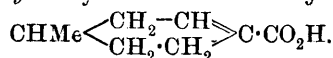
Conversion of d-1-Methylcyclohexan-3-ol-4-carboxylic Acid into *p*-Toluic Acid.—The hydroxy-acid employed in this experiment was the crystalline modification obtained by leaving the semi-solid mixture direct from the reduction of the keto-acid in contact with porous porcelain. This acid dissolves readily in concentrated sulphuric acid, and, when the colourless solution is heated at

85—90°, evolution of sulphur dioxide occurs freely with very little darkening.

After a few minutes, the hot solution is diluted with water, the crystalline precipitate collected, washed well, dissolved in dilute sodium carbonate, and digested with animal charcoal. Finally the acid is again precipitated and crystallised from dilute acetic acid. (Found, C=70·5; H=6·0. Calc., C=70·6; H=5·9 per cent.)

This acid separated from dilute acetic acid in colourless, glistening needles, melted at 177—178°, and had all the properties of *p*-toluic acid. The identity was further proved by mixing it with a specimen of pure *p*-toluic acid, when there was no alteration in the melting point.

d-1-Methyl- Δ^3 -cyclohexene-4-carboxylic Acid,



The conversion of *d*-1-methylcyclohexan-3-ol-4-carboxylic acid into *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid by the elimination of water does not take place very readily, but digesting the hydroxy-acid with acetyl chloride containing phosphorus trichloride, and distilling the product first under diminished pressure and then in steam, yields small quantities of the unsaturated acid. Other dehydrating agents give a similar result, but the best yield is apparently produced under the following conditions. Ethyl *d*-1-methylcyclohexan-3-ol-4-carboxylate, in quantities of 10 grams, is digested on the water-bath with an equal weight of phosphorus trichloride for one hour, and then heated to boiling on the sand-bath for half an hour.

The orange-coloured product is poured into excess of alcohol, and, after two hours, water is added, the ester extracted with ether, the ethereal solution washed with sodium carbonate, dried, evaporated, and the residue distilled, when crude ethyl *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylate passes over at 148—150°/100 mm., the yield being about 60 to 70 per cent. of that theoretically possible. The ester is hydrolysed by digesting with excess of methyl-alcoholic potassium hydroxide, and, after diluting with water, evaporating until free from methyl alcohol and acidifying, the semi-solid precipitate is collected and distilled in a current of steam. The unsaturated acid passes over with some difficulty, but in a pure condition, and is collected and left in contact with porous porcelain until dry. From the aqueous filtrate, a further considerable quantity of acid is recovered by neutralising, evaporating to a small bulk, and acidifying:

0·1101 gave 0·2760 CO₂ and 0·0849 H₂O. H=68·5; H=8·6.

C₈H₁₂O₂ requires C=68·6; H=8·6 per cent.

1·007, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 15\cdot02^\circ$, whence $[\alpha]_D + 150\cdot1^\circ$. *d*-1-Methyl- Δ^3 -cyclohexene-4-carboxylic acid is very sparingly soluble in water, but the hot concentrated solution deposits the acid as a chalky powder, which, under the microscope, is seen to consist of well-defined, elongated, four-sided prisms. It melts at $136\text{--}137^\circ$ (the *dl*-acid melts at 134° : Trans., 1905, **87**, 646), and the solution in sodium carbonate reduces permanganate instantly.

Ethyl d-1-Methyl- Δ^3 -cyclohexene-4-carboxylate.—The ester obtained by the action of phosphorus trichloride on ethyl *d*-1-methylcyclohexan-3-ol-4-carboxylate (see above) is far from pure, and usually has a rotation of $[\alpha]_D + 65^\circ$ only; the pure ester is obtained from the pure acid by means of alcohol and sulphuric acid, but esterification takes place with some difficulty, especially in the cold. The acid (18 grams) was left in contact with alcohol (200 c.c.) and sulphuric acid (15 c.c.) for twenty-four hours, and then heated for three hours on the steam-bath. After adding water, the ester was extracted with ether, the ethereal solution washed with sodium carbonate (which extracted 3 grams of unchanged acid), dried, evaporated, and the ester distilled, when it passed over constantly at $151\text{--}152^\circ/100$ mm.:

0·1094 gave 0·2870 CO_2 and 0·0954 H_2O . $\text{C} = 71\cdot5$; $\text{H} = 9\cdot7$.

$\text{C}_{10}\text{H}_{16}\text{O}_2$ requires $\text{C} = 71\cdot4$; $\text{H} = 9\cdot5$ per cent.

d 20/20° 0·9757; n_D 1·4688; M 47·9 (calc., 47·3). 0·9639, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 11\cdot79^\circ$, whence $[\alpha]_D + 122\cdot3^\circ$.

d-3-Bromo-1-methylcyclohexan-4-carboxylic Acid.*—In order to prepare this acid, *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid was mixed with a large excess of fuming hydrobromic acid (saturated at 0°), in which it gradually dissolved, and, after remaining overnight, the product was heated at 80° for one hour and then mixed with three volumes of water. The bromo-acid, which separated as a voluminous, crystalline mass, was collected, washed, and crystallised from formic acid, from which it was deposited, on slow cooling, as a mass of asbestos-like threads, melting at $133\text{--}134^\circ$:

0·1633 gave 0·1395 AgBr . $\text{Br} = 36\cdot4$.

$\text{C}_8\text{H}_{13}\text{O}_2\text{Br}$ requires $\text{Br} = 36\cdot2$ per cent.

1·1866, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 8\cdot50^\circ$, whence $[\alpha]_D + 71\cdot7^\circ$. This bromo-acid dissolves readily in sodium carbonate, and when the solution was boiled, a small quantity of an oil having the odour of a bromo-

* The corresponding *dl*-bromo-acid has already been described (Trans., 1905, **87**, 646), but the melting point was accidentally omitted. It softens at 135° and melts at $140\text{--}142^\circ$.

hydrocarbon separated, and, after this had been removed, the alkaline solution gave, on acidifying, a colourless precipitate of *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid, which melted at 134–136°, and had approximately the same rotation, $[\alpha]_D + 150^\circ$, as before the conversion into the bromo-acid.

d-3: 4-Dibromo-1-methylcyclohexan-4-carboxylic Acid.—This dibromo-acid is readily obtained when *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid, dissolved in chloroform and cooled to -10° , is mixed with a chloroform solution of the calculated amount of bromine. Addition takes place slowly in the cold, but if the temperature of the solution is allowed to gradually rise to 17° , the colour of the bromine disappears, and the chloroform solution deposits, on evaporation in the air, a solid residue. After remaining in contact with porous porcelain until dry, the substance was crystallised from formic acid, from which it separated as a colourless, glistening mass of flat needles, melting at about 158° :

0.1591 gave 1.1990 AgBr. Br = 53.1.

$C_8H_{12}O_2Br_2$ requires Br = 53.3 per cent.

0.9364, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 9.58^\circ$, whence $[\alpha]_D + 102.2^\circ$. This dibromo-acid dissolves readily in sodium carbonate, but the solution, on boiling, does not deposit a bromo-hydrocarbon, as has so often been observed in analogous cases.

Reduction of d-1-Methyl- Δ^3 -cyclohexene-4-carboxylic Acid. *Formation of the cis- and trans-Modifications of 1-Methylcyclohexan-4-carboxylic Acid.*

The reduction of *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid was carried out with colloidal palladium and hydrogen according to the excellent method described by A. Skita (*Ber.*, 1909, **42**, 1630), with the modification that the process was conducted at the ordinary pressure instead of under a pressure of two atmospheres. Gum arabic (5 c.c. of a solution of 25 grams in 100 c.c. of water) was diluted with warm water (200 c.c.), mixed with a solution of the unsaturated acid (15 grams) in alcohol (200 c.c.), and, after cooling to 25° , a solution of palladous chloride (1 gram) in water was added. The solution was transferred to a long, narrow cylinder, and hydrogen passed in for two days; the product was then distilled in steam, when an oil passed over at first, but towards the end of the distillation this crystallised.

The distillate was neutralised with sodium carbonate, evaporated to about 300 c.c. and mixed with powdered ice and a few c.c. of permanganate solution, and allowed to remain for one hour, but

hardly any decoloration of the permanganate took place, showing that reduction was practically complete. After removing the excess of permanganate with sodium sulphite, the acid was liberated by hydrochloric acid and again distilled in steam. The distillate was extracted with ether, the ethereal solution dried, evaporated, and the residual oil fractionated, when almost the whole passed over at $141^{\circ}/20$ mm. as a colourless oil, which, in the ice chest, deposited a quantity of crystals. The product was transferred to porous porcelain, and, when the oil had been absorbed, the residue (2 grams) was crystallised from a little formic acid; it consisted then of pure *trans*-1-methylcyclohexan-4-carboxylic acid:

0.1154 gave 0.2853 CO_2 and 0.1031 H_2O . $\text{C}=67.4$; $\text{H}=9.9$.

$\text{C}_8\text{H}_{14}\text{O}_2$ requires $\text{C}=67.6$; $\text{H}=9.8$ per cent.

This acid melted at 112° , and is obviously identical with the hexahydro-*p*-toluic acid described by Perkin and Pickles (*Trans.*, 1905, **87**, 644). The *p*-toluidide was prepared by warming the acid (1 gram) with phosphorous trichloride (0.5 gram) on the water-bath, and then mixing with an ethereal solution of *p*-toluidine (5 grams). The ethereal solution was washed with water, dried, and evaporated, during which operation the *p*-toluidide, which is rather sparingly soluble in ether, separated in crystals. It is readily soluble in alcohol, and separates from 80 per cent. alcohol as a glistening mass of flat prisms, which melt at 179 — 180° :

0.1482 gave 8.4 c.c. N_2 at 17° and 735 mm. $\text{N}=6.3$.

$\text{C}_{15}\text{H}_{21}\text{ON}$ requires $\text{N}=6.1$ per cent.

The porous plates used in the purification of the *trans*-acid were extracted with ether in a Soxhlet apparatus, and the oily acid boiled with much water and freshly precipitated calcium carbonate.

When the filtered solution was concentrated on the water-bath, a calcium salt separated in long needles; this was found to be the calcium salt of the *trans*-acid, and, on acidifying, 0.7 gram of this acid separated at once in the crystalline form. On further concentration, the mother-liquors of this calcium salt deposited a second crop, which consisted principally of the salt of the *cis*-acid, and, when this and a further crop had been removed, the filtrate yielded, on acidifying, an oily acid which distilled constantly at $140^{\circ}/20$ mm.

After the purification of the calcium salt had been repeated, the *cis*-1-methylcyclohexan-4-carboxylic acid was analysed:

0.1149 gave 0.2827 CO_2 and 0.1034 H_2O . $\text{C}=67.2$; $\text{H}=10.0$.

$\text{C}_8\text{H}_{14}\text{O}_2$ requires $\text{C}=67.6$; $\text{H}=9.8$ per cent.

The *p*-toluidide of this acid was prepared in the way already described in the case of the *trans*-acid. It is more soluble in ether or alcohol than the *p*-toluidide of the *trans*-acid, and separates

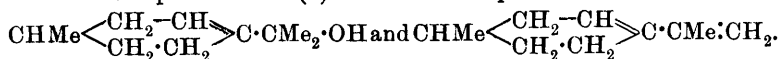
from 70 per cent. alcohol in colourless needles, which soften at 135° and melt at 142—143°:

0.1833 gave 10.3 c.c. N₂ at 15° and 736 mm. N=6.4.

C₁₅H₂₁ON requires N=6.1 per cent.

So far as could be judged, the product of the reduction of *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid, under the conditions described above, consists of about 75 per cent. of the *cis*- and 25 per cent. of the *trans*-acids.

d- Δ^3 -*p*-Menthenol(8) and *d*- $\Delta^{3:8(9)}$ -*p*-Menthadiene,



In order to prepare the former of these substances, pure ethyl *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylate (20 grams) was added to an ethereal solution of magnesium methyl iodide (containing 9 grams of magnesium), and, after remaining for twenty-four hours, water was added and the product distilled in steam. The ethereal extract of the distillate was dried, evaporated, and the residue distilled, when almost the whole quantity passed over at 105°/20 mm.:

0.1414 gave 0.4028 CO₂ and 0.1502 H₂O. C=77.7; H=11.8.

C₁₀H₁₈O requires C=77.9; H=11.7 per cent.

d 20/20° 0.9236; *n*_D 1.4783; M 47.2 (calc., 47.2). 0.9099, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, α +7.57°, whence $[\alpha]_D$ +83.2°. *d*- Δ^3 -*p*-Menthenol(8) is a colourless, rather viscid oil, which, even on long keeping in the ice chest, showed no signs of crystallising; it possesses a pungent odour, recalling that of peppermint and cymene.

d- $\Delta^{3:8(9)}$ -*p*-Menthadiene was first prepared by boiling the pure menthenol (15 grams) with 200 c.c. of 5 per cent. oxalic acid in a reflux apparatus for ten hours with frequent shaking, when elimination of water was practically complete. The product was distilled in steam, the distillate extracted with ether, the ethereal solution dried, evaporated, and the terpene distilled twice alone and then three times over sodium, when it boiled constantly at 184—185°/776 mm.:

0.1296 gave 0.4183 CO₂ and 0.1356 H₂O. C=88.0; H=11.7.

C₁₀H₁₆ requires C=88.2; H=11.8 per cent.

The amount available for the density determination was so small that the value obtained must be accepted as approximate only.

d 16/16° 0.8649; *n*_D 1.4965; M 45.9; calc. for C₁₀H₁₆ F^2 45.24. 0.8544, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, α +8.54°, whence $[\alpha]_D$ +100.0°. For reasons stated in the intro-

duction to this paper (p. 529), it seemed probable that racemisation had taken place to some extent during the formation of this terpene from *d*- Δ^3 -*p*-menthenol(8) under the conditions just described, and that the value $[\alpha]_D + 100^\circ$ does not represent the maximum rotation of the terpene. In order to test this supposition, the following experiment was carried out. Pure ethyl *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylate (12 grams) was added to magnesium methyl iodide (containing 7 grams of magnesium), and, after remaining overnight and then warming on the steam-bath for one hour, the product was mixed with water and dilute hydrochloric acid and distilled in steam (compare footnote, Trans., 1910, **97**, 2154). The ethereal extract of the distillate was dried, evaporated, and the residue, which distilled almost completely below $85^\circ/20$ mm., three times fractionated over sodium.

The *d*- Δ^3 :⁸⁽⁹⁾-*p*-menthadiene thus obtained distilled constantly at $182\text{--}183^\circ/760$ mm., and had an even lower rotation than the preparation made by the first process. 0.8410, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 7.6^\circ$, whence $[\alpha]_D + 90.4^\circ$.

The authors wish to state that much of the heavy expense of this investigation was met by a grant from the Research Fund of the Royal Society.

THE UNIVERSITY,
MANCHESTER.
