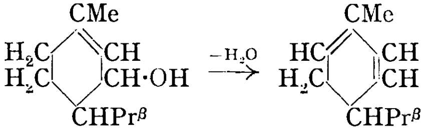
75. *Piperitone.* Part XII. The Two Varieties of Piperitol.*

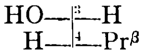
By John Read and James Walker.

Read and Storey (J., 1930, 2770) found that dextrorotatory piperitol was formed, together with *d*-α-phellandrene, by the action of moist silver oxide on *l*-piperityltrimethylammonium iodide. In distilling the product, two fractions containing piperitol were obtained; these had somewhat different physical constants, and the values † of $\alpha_D^{16°}$ were + 21·22° and + 40·22°, respectively. Although a complete separation was not claimed, it thus appeared that two dextrorotatory piperitols, both of which yielded *d*-piperitone when oxidised, were formed in this reaction.

New work has now shown that the isolation of stereochemically pure piperitols is attended by unexpected difficulties. Careful repetition, on a larger scale, of the experiments of Read and Storey yielded piperitol fractions which were slightly lævorotatory, a result which was traced to contamination with the powerfully lævorotatory *N*-methyl-*l*-piperitylamine, having $[\alpha]_D^{13\cdot7°}$ − 355° (chloroform). When this impurity was removed, the residual piperitol had values of $[\alpha]_D^{15°}$ as high as + 50·8° (alcohol). Further, all piperitol (I) specimens made and purified in this way had one very remarkable property in common : when kept at the ordinary temperature for several days, they lost water spontaneously, with the production of *d*-α-phellandrene (II), and a consequent rise in optical rotatory power. Thus, one of the two possible varieties of piperitol undergoes spontaneously the striking 1 : 4-dehydration which forms a feature of the breakdown of the corresponding quaternary ammonium hydroxide (*loc. cit.*, p. 2773). In conformity with the usage adopted in the menthone and carvone series, it is convenient to indicate the more readily dehydrated variety of the alcohol by the prefix *neo*; and on the same grounds this variety may be provisionally assigned the *trans*-H configuration (III) :



(I.) (II.)



d(or *l*)-*neo*Piperitol, or *trans*-Piperitol.

(III.)

It is not certain that the preparation having $[\alpha]_D^{15°}$ + 50·8° consisted of pure *d*-*neo*-piperitol (*d*-*trans*-piperitol) with or without some *d*-α-phellandrene. It seems likely, indeed, that the same reaction would give rise to some of the corresponding ordinary piperitol (*cis*-piperitol). *neo*Piperitol appears to be stabilised (see below) by traces of the basic impurity which probably occurred in the first specimens prepared by this method; it is possible, therefore, that such specimens may be successfully submitted to fractional distillation as recorded by Read and Storey (*loc. cit.*), although this process cannot be applied satisfactorily to purified *neo*piperitol. It is certainly remarkable that the two optical rotations observed for Read and Storey's fractions are in good general agreement, both in sign and numerically, with the values now indicated for the two varieties of piperitol related to *d*-piperitone and obtained by a combination of two methods.

A second variety of piperitol (*cis*-piperitol) has, in fact, been prepared by reducing *l*-piperitone with aluminium *iso*propoxide in dry *iso*propyl alcohol, by the method of Ponndorf. The purified piperitol, which was obtained with difficulty and in poor yield

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* Some early references of historical interest in the chemistry of piperitone, which have escaped due recognition, may conveniently be noted here. The first recorded mention of the oil of *Eucalyptus piperita* (J., 1921, **119**, 780) appears to have been made by Dr. John White's assistant, First-Assistant Surgeon D. Considen, in a letter to Sir Joseph Banks, dated from Port Jackson, November 18th, 1788 : " We have a large peppermint-tree which is equal, if not superior, to our English peppermint. I have sent you a specimen of it. If there is any merit in applying these and many other simples to the benefit of the poor wretches here, I certainly claim it, being the first who discovered and recommended it." For the first references to the ketone now known as piperitone, see Callenbach, *Ber.*, 1897, **30**, 639, and Baer, Dissertation, Leipzig, 1898 (cf. Schimmel's *Semi-Annual Report*, Leipzig, October, 1898, p. 49).

† All values of α recorded in this paper are for a 1-dcm. tube.

(cf. Gibson and Simonsen, *Chem. and Ind.*, 1930, **49**, 540), had $[\alpha]_D^{16°}$ − 24·5° (alcohol). It showed no tendency to eliminate water spontaneously, and differed also in other respects from *neo*piperitol. From it was prepared, although only in small yield, a crystalline *l*-piperityl 3 : 5-dinitrobenzoate, m. p. 84—85°, $[\alpha]_D$ − 30°. It seems likely that the corresponding *l*-*neo*piperitol was also produced in the reaction, particularly as *l*-α-phellandrene was present in the crude product; moreover, partial racemisation of the *l*-piperitone may have attended its reduction (J., 1923, **123**, 2267). It cannot be laid down at this stage, therefore, that the specimen having $[\alpha]_D^{16°}$ − 24·5° was a stereochemically homogeneous piperitol, although possibly *l*-*neo*piperitol would not have survived the processes of purification.

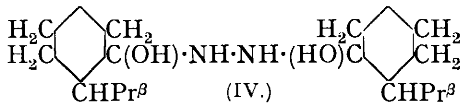
The present position is, then, that two varieties of piperitol have been prepared, although possibly not in the pure state. One of these (*neo*piperitol) eliminates water spontaneously, yielding thereby α-phellandrene of the same sign of optical rotation; the other (piperitol) is stable, and its 3 : 5-dinitrobenzoate has been prepared. The most precise optical rotations (in alcohol) which can be advanced at present for the two varieties corresponding to *l*-piperitone are $[\alpha]_D^{15°}$ − 50·8° (*l*-*neo*piperitol) and $[\alpha]_D^{16°}$ − 24·5° (*l*-piperitol).

H. G. Smith (Baker and Smith, " A Research on the Eucalypts," 2nd edn., Sydney, 1920, p. 373) observed the value α_D − 34·1° for a specimen (homogeneous) of *l*-piperitol from the leaf-oil of *E. radiata*, and Simonsen (*Indian Forest Records*, 1924, **10**, part viii) gave $\alpha_D^{30°}$ + 41·9° (homogeneous) for *d*-piperitol from an unnamed species of *Andropogon* growing in the United Provinces. The piperitols obtained from these oils showed no tendency to eliminate water spontaneously when kept for long periods (private communications); despite their higher rotatory powers, they must therefore be identified with stable *l*- and *d*-piperitol, obtainable by applying Ponndorf's method to *l*- and *d*-piperitone, respectively. It now appears that *l*-piperitone gives rise to *l*-α-phellandrene in *Eucalyptus* oils through a preliminary reduction to the unstable *l*-*neo*piperitol, which then yields the terpene as a result of spontaneous dehydration (cf. *Chem. Reviews*, 1930, **7**, 44). The occurrence of the stable variety of piperitol in such oils is capricious (Smith, unpublished observations), and is perhaps occasioned by relative acidity of plant sap and other seasonal factors. The phenomenal ease with which *neo*piperitol changes into α-phellandrene renders it unlikely that this alcohol could function as the precursor of Δ^4-carene; so that, if this terpene arises from a piperitol at all, it must be apparently from the stable variety (cf. Simonsen, *loc. cit.*; Read, *Chem. Reviews*, 1930, **7**, 46).

Verbenol, the bridged-ring analogue of piperitol, also readily undergoes the 1 : 4-dehydration which *neo*piperitol affords voluntarily, the product being verbenene (*Ber.*, 1913, **46**, 1178; *Annalen*, 1927, **453**, 48; *Helv. Chim. Acta*, 1924, **7**, 489).

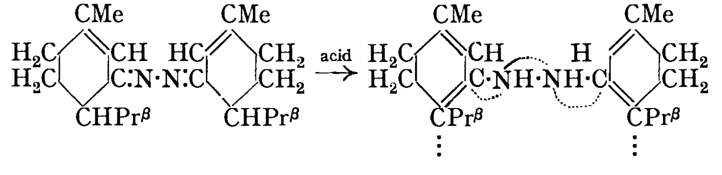
If *d*-*neo*piperitol conforms to the postulated configurational relationships, it should yield a mixture of *d*-*neo*- and *l*-*neoiso*-menthol upon hydrogenation; and *l*-piperitol should similarly yield *d*-*iso*- and *d*-menthol (cf. *Chem. Reviews*, 1930, **7**, 37). These hydrogenations have not yet been attempted, but it has been shown that *l*-piperitylamine furnishes a mixture of *l*-*iso*- and *l*-menthylamine when hydrogenated, so that presumably it has the *cis*-H configuration (cf. J., 1930, 2761).

During the present research, preparations of piperitylamine have been shown to contain a stable and unreactive substance having the formula $C_{10}H_{21}ON$, corresponding to a menthylhydroxylamine or 3-aminomenthol and possibly originating from the reduction product (IV) of the fully hydrated azine of piperitone (cf. J., 1930, 2771; see also Meyer


(IV.)

and Jacobson, " Lehrbuch der Organischen Chemie," 1907, I, i, 763). Since the substance $C_{10}H_{21}ON$ may be responsible for diminishing the yield of *dl*-piperitylamine and also for impeding its optical resolution (see below), it appears to be important to dehydrate the azine fully before reducing it (*loc. cit.*, p. 2775). Indeed, according to the following scheme, it is only the fully dehydrated azine which is convertible into piperitylamine. In the reduction, the true azine (V) probably dissolves in the acetic acid as the lactam form (VI), at which stage asymmetry is completely annulled. The addition of two atoms of hydrogen at the ends of the conjugated system, followed by reversal of the lactam form to the lactim form, gives an azo-compound, which is further reduced to *dl*-piperitylamine. This scheme accounts satisfactorily for two very remarkable facts which would otherwise be difficult to explain, namely, the loss of optical activity and the preservation of the Δ^1-double bond of piperitylamine during the reduction.

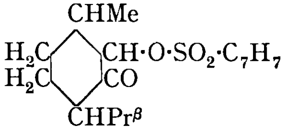
(V.)



(VI.)

In view of the possible formation of Δ^2-menthen-1-ol in the decomposition of piperityltrimethylammonium hydroxide and of the further possibility that it might yield piperitone on oxidation, through preliminary anionotropic conversion into piperitol (cf. Ingold, *Chem. and Ind.*, 1930, **49**, 1008), this alcohol (cf. Wallach, *Annalen*, 1908, **359**, 285) was synthesised from *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one; when treated with Beckmann's oxidation mixture, however, it did not yield piperitone.

Of a number of schemes directed towards the synthesis of piperitols, two may be mentioned here. Reduction of the keto-group of *p*-toluenesulphonyldihydrodiosphenol (VII) (this vol., p. 240) was expected to lead to the corresponding secondary alcohol, which, by successive acetylation and pyrolysis, should yield piperityl acetate; unfortunately, however, it has so far proved impracticable to reduce the keto-group without removing the sulphonyl radical.



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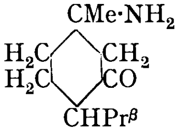

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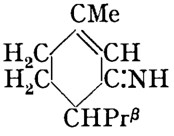
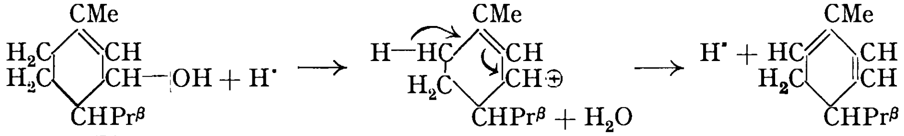


(IX.)

The possibility was also examined that piperitone might share the capacity of mesityl oxide to add ammonia at the double bond (*Ber.*, 1874, **7**, 1384), with the production of the analogue of diacetoneamine, *i.e.*, 1-aminomenthone (VIII) : this might then be converted, eventually through a Hofmann degradation, into piperityl esters. The product of the reaction was, however, the unstable *piperitone-imine* (IX), which on reduction passed into a mixture of menthylamines. Similar reactions occurred with methylamine and ethylamine, leading in a very convenient way to *N*-monoalkyl derivatives of menthylamines. Diethylamine failed to react with piperitone (cf. *Monatsh.*, 1932, **61**, 299).

In conclusion, reference may be made to the apparent stabilisation of *neo*piperitol by traces of a basic impurity. Since negative catalysis of a reaction is usually conditioned by inhibition of the positive catalyst, the hydrogen ion may be regarded as the active promoter of the dehydration of *neo*piperitol. The basic impurity depresses the hydrogen-ion concentration, $R_3N + H^{\cdot} \longrightarrow [R_3NH]^{\cdot}$; on the other hand, the dehydration of piperitol takes the following route :



(X.) (XI.) (XII.)

EXPERIMENTAL.

Piperitylamines.

l-*Piperitylamine.*—*dl*-Piperitylamine was prepared by reducing the hydrated azine of *l*-piperitone according to the method of Read and Storey (J., 1930, 2775). *l*-Piperitylamine (*loc. cit.*, p. 2776) had $\alpha_D^{18\cdot5^\circ}$ — 75·94° (homogeneous). In a normal resolution, pure *l*-piperitylamine hydrogen *d*-tartrate was readily obtained, with $[\alpha]_D$ — 43·0° (*c* 1·4, water). In certain abnormal experiments, however, the value of $[\alpha]_D$ remained at — 37·3° to — 38° after repeated recrystallisation, and the resulting base had α_D — 61·5° to — 64°; this base was essentially *l*-piperitylamine, because it readily yielded pure phenylacetyl-*l*-piperitylamine, m. p. 89—90°.

A small crystalline deposit which had formed after several months in some residual piperitylamine (*ca.* 400 g.) was collected and washed with light petroleum. The small colourless prisms obtained were stable in air and had m. p. 89—90·5°, b. p. 136°/18 mm., $[\alpha]_D^{17\cdot5^\circ}$ — 7·24° (*c* 0·9, chloroform). This new *substance* was odourless, and was sufficiently soluble in water to render the solution alkaline to litmus; it dissolved readily in dilute hydrochloric acid but not in sodium hydroxide solution. It affected acid potassium permanganate solution only slightly, and gave no appreciable reaction with Fehling's solution, ammoniacal silver nitrate, nitrous acid, or benzoyl chloride in pyridine (Found: C, 69·9, 70·1; H, 11·8, 12·3; N, 8·3; *M*, by Rast, 178, 180. $C_{10}H_{21}ON$ requires C, 70·1; H, 12·4; N, 8·2%; *M*, 171).

Experiments with Crude d-*Piperitylamine.*—The residual base from the above optical resolution was examined with the aim of isolating *d*-piperitylamine, and also any stereoisomerides which might be present. The application of *l*-tartaric acid (Kellett, *J. Soc. Chem. Ind.*, 1932, **51**, 204T) to the base (α_D about + 30°) gave, after four recrystallisations, the antimeric form of the salt mentioned above. The phenomenon already noticed occurred again, repeated recrystallisation failing to raise the specific rotation of the salt from + 36·9° to the required value of + 43·0°. *d*-Piperitylamine prepared from this salt resembled the pure *l*-base, except that its optical rotation was lower: it had $n_D^{17^\circ}$ 1·4795 and $\alpha_D^{16^\circ}$ + 56·5° (homogeneous). Although the base was optically impure, it readily yielded pure derivatives of *d*-piperitylamine. *Acetyl*-d-*piperitylamine* crystallised from aqueous alcohol in magnificent flat prisms, m. p. 101—102°, $[\alpha]_D^{17^\circ}$ + 159° (*c* 1·2, chloroform) (Found: C, 73·6; H, 11·0. $C_{12}H_{21}ON$ requires C, 73·8; H, 10·8%). *Benzoyl*-d-*piperitylamine* formed handsome prismatic needles, m. p. 102—103°, $[\alpha]_D^{17^\circ}$ + 175° (Found: C, 79·0; H, 8·9. $C_{17}H_{23}ON$ requires C, 79·3; H, 9·0%) (cf. J., 1930, 2777).

The salicylidene derivative (cf. J., 1927, 2172) of crude *d*-piperitylamine was a syrup. Somewhat similar results were obtained with benzaldehyde, *p*-nitrobenzaldehyde, and anisaldehyde. *p*-Dimethylaminobenzaldehyde gave a definite *derivative*, which after repeated recrystallisation from ethyl acetate had m. p. 127—128·5°, $[\alpha]_D$ + 1° (*c* 2, alcohol) (Found: C, 80·1; H, 9·7. $C_{19}H_{28}N_2$ requires C, 80·3; H, 9·9%). Since it was found that pure *p*-dimethylaminobenzylidene-*l*-piperitylamine had $[\alpha]_D$ — 350°, the attempted purification was abandoned. Similarly, *l*-piperitylamino-*l*-methylenecamphor was found to have m. p. 134—135°, $[\alpha]_D$ — 471° (*c* 1·4, alcohol), while the impure *d*-piperitylamino-*d*-methylenecamphor prepared from the residual base was a very soluble microcrystalline powder, m. p. 132—133°, $[\alpha]_D$ + 361°.

Salts of the crude *d*-base with a large variety of optically active and inactive acids (including racemic acid) were examined without success.

When the phosphate of a specimen of crude *d*-piperitylamine (α_D + 23°) was dry distilled, it yielded *l*-α-phellandrene (α_D — 22°).

Methylation of l-*Piperitylamine.*—The use of methyl sulphate and caustic alkali (*Ber.*, 1931, **64**, 2866) failed to give complete methylation to the quaternary ammonium salt, and the method of Read and Storey (J., 1930, 2778) was followed, with the use, however, of larger quantities of materials. Even so, methylation was incomplete, as the following observation shows. The piperitol fractions from the decomposition of *l*-piperityltrimethylammonium iodide with silver iodide (J., 1930, 2779) were dissolved in ether and washed with dilute hydrochloric acid. A base (10·2 g.) was recovered from the acid washings, which distilled at 95—99°/16 mm. as a colourless mobile oil (8·6 g.) with an unpleasant odour; it had $n_D^{13\cdot5^\circ}$ 1·4771, $[\alpha]_D^{13\cdot5^\circ}$ — 355° (*c* 2·0, chloroform). It did not absorb carbon dioxide from the air, like the unmethylated base, and appeared to be N-*methyl*-l-*piperitylamine* (Found: C, 79·1; H, 12·5; N, 8·2. $C_{11}H_{21}N$ requires C, 79·1; H, 12·6; N, 8·4%).

Hydrogenation of l-*Piperitylamine.*—When an ethereal solution of *l*-piperitylamine (4 g.) was hydrogenated with a palladium catalyst in presence of gum arabic (J., 1923, **123**, 2921), it absorbed the calculated amount of hydrogen in 3 hours. The crude benzoyl derivative of the product had $[\alpha]_D^{16^\circ}$ — 32·3° (*c* 1·3, chloroform). Upon recrystallisation from absolute alcohol this yielded a less soluble fraction of benzoyl-*l*-menthylamine. The mother-liquors appeared to contain benzoyl-*l*-*iso*menthylamine, and the crude product thus probably consisted of about 31% of benzoyl-*l*-menthylamine and 69% of benzoyl-*l*-*iso*menthylamine (J., 1930, 2766).

When hydrogenated in a similar way, acetyl-*l*-piperitylamine ($[\alpha]_D$ — 153°) readily absorbed the calculated quantity of hydrogen, yielding a pale brown, viscid syrup with $[\alpha]_D$ — 37·5° (*c* 1·9, chloroform). The values of $[\alpha]_D$ for the acetyl derivatives of *l*-, *l*-*iso*-, *d*-*neo*-, and *l*-*neoiso*-menthylamine are — 81·7°, — 30·7°, + 53·0°, and + 2·6°, respectively (J., 1930, 2766); hence, in the absence of unchanged material, the above product probably consisted of about 13% of acetyl-*l*-menthylamine and 87% of acetyl-*l*-*iso*menthylamine.

Piperitols.

d-neo*Piperitol*.—*l*-Piperityltrimethylammonium iodide was decomposed with silver oxide in the manner described by Read and Storey (J., 1930, 2780), except that larger quantities of materials were used. The terpene fractions were similar to those described (*loc. cit.*); but the piperitol fractions, instead of being dextrorotatory, were slightly lævorotatory, having values of $[\alpha]_D^{15^\circ}$ from — 9° to — 10° in absolute alcohol (*c* 1·5). In spite of the low optical rotation, a portion (3 c.c.) of one of these fractions, when oxidised with Beckmann's chromic acid mixture (20 c.c.), yielded *d*-piperitone with b. p. 105°/10 mm., $n_D^{16^\circ}$ 1·4848, $[\alpha]_D^{16\cdot5^\circ}$ + 63·3° (*c* 3·0, benzene). The piperitol fractions were dissolved in ether and washed with dilute hydrochloric acid (see above). The base-free piperitol was then fractionally distilled under diminished pressure, the operation being conducted as speedily as possible after removal of the basic impurity. The dried distillate, which was the purest specimen of *d*-*neo*piperitol prepared, had $[\alpha]_D^{15^\circ}$ + 50·8° (*c* 1·4, absolute alcohol), $n_D^{15^\circ}$ 1·4775. When this product was kept in a closed vessel at the ordinary temperature, globules of water were deposited in a few days; these grew in size, and after 19 days the dried material had $[\alpha]_D^{14^\circ}$ + 60·0°, $n_D^{14^\circ}$ 1·4848. The enhanced dextrorotation was shown to be due to the presence of *d*-α-phellandrene. Owing to the instability of such specimens of *neo*piperitol, it has not yet been convenient to determine accurate physical constants, or to prepare derivatives, apart from the related *d*-piperitone.

Similarly, purified specimens of *l*-*neo*piperitol, made from *d*-piperitylamine, eliminated water and developed an enhanced lævorotation when heated, or when kept for a few days at room temperature.

A specimen of optically inactive piperitol, prepared in a similar way from *dl*-piperitylamine (Read and Storey, J., 1930, 2779), was found to be perfectly homogeneous 18 months after it had been made, no water having been eliminated. It was shown to contain a basic impurity; after this had been washed out, the residual dried oil when kept for a week in a sealed vessel showed a separation of globules of water. As a result of a fire (November, 1931), none of the original specimens of optically active piperitols (*loc. cit.*, p. 2780) were available for examination.

l-*Piperitol*.—Dry redistilled *l*-piperitone (100 c.c.) was mixed with dry *iso*propyl alcohol (150 c.c.) and aluminium *iso*propoxide (37 g.), and submitted to a slow constant-volume distillation through a 30-cm. Vigreux column for 7 hours (Ponndorf, *Z. angew. Chem.*, 1926, **39**, 141); acetone was not found in the last third of the distillate (total, 430 c.c.) by the sodium nitroprusside test. Most of the *iso*propyl alcohol was distilled from the product, and the residue was steam-distilled. The oily distillate (88 g.), after being shaken for 7 hours at 100° with a solution of sodium bisulphite (70 g.) in water (105 c.c.), gave a colourless mobile oil (31 g.), from which two fractions were obtained: (i) b. p. to 81°/16 mm., $n_D^{15^\circ}$ 1·4790 (10·4 g.); (ii) b. p. 81—108·5°/16 mm., $n_D^{15^\circ}$ 1·4798 (16·4 g.). Fraction (i) consisted essentially of *l*-α-phellandrene (nitrosite, m. p. 102° unrecrystd.); so that this reaction affords a new way of passing from *l*-piperitone to *l*-α-phellandrene. Fraction (ii), when redistilled, yielded two further fractions: (iii) b. p. to 88°/14 mm., $n_D^{19^\circ}$ 1·4794 (5·0 g.) (Found: C, 84·3; H, 11·5%); (iv) b. p. 98·5—100·5°/13 mm., $n_D^{19^\circ}$ 1·4776, $[\alpha]_D^{16^\circ}$ — 24·5° (*c* 1·4, absolute alcohol) (5·7 g.). Fraction (iv) was the purest specimen of *l*-piperitol obtained (Found: C, 77·7; H, 11·4%): it was a colourless mobile oil, having an odour distinct from that of *neo*piperitol obtained from piperitylamine; it showed no tendency to eliminate water when kept for 8 months. When treated in dry pyridine for 5 days with a slight excess of 3 : 5-dinitrobenzoyl chloride, it yielded a pale brown, mobile oil, which upon steam distillation to remove terpene left an amber glass. This gradually crystallised. Recrystallisation from absolute alcohol gave needles, m. p. 79—81°, and a second recrystallisation yielded small needles with a faint yellow tinge, which softened at 78° and melted at 84—85°; $[\alpha]_D^{14^\circ}$ — 30° (*c* 0·1, chloroform). This substance, possibly pure l-*piperityl*

3 : 5-*dinitrobenzoate*, was readily soluble in most of the common organic solvents (Found : C, 58·4; H, 5·9. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·8%). The yield of crude ester was only 13%, owing to the formation of terpene. The crystalline material from the mother-liquors had $[\alpha]_D^{14°}$ — 17° (*c* 0·4, chloroform).

The Action of Ammonia and Aliphatic Amines on Piperitone.

Action of Ammonia.—*l*-Piperitone (75 c.c.) was dissolved in a solution of ammonia (42 g.) in rectified spirit (500 c.c.) and kept in a stoppered vessel for 6 weeks at room temperature. Most of the alcohol and ammonia were distilled away in a vacuum, and the ethereal solution of the residue was extracted with dilute sulphuric acid. The ether contained piperitone; and a brownish-red oil (14 g.) was obtained upon basifying the acid solution. The base distilled with some decomposition at 99—105°/10 mm., yielding a colourless oil, with a repugnant basic odour, $n_D^{25°}$ 1·4898, $d_{4°}^{25°}$ 0·925; this appeared to be impure *piperitone-imine* (Found : C, 77·8; H, 10·9; N, 5·3. $C_{10}H_{17}N$ requires C, 79·4; H, 11·3; N, 9·3%). It yielded piperitone when boiled with dilute mineral acids, and decomposed slowly when kept.

The crude undistilled base when reduced with sodium (1·5 g. per gram) in absolute alcohol, yielded a colourless mobile oil with a strong basic odour, b. p. 90—92°/14 mm., $n_D^{18°}$ 1·4642. This appeared to consist of a mixture of menthylamines (Found : C, 77·5; H, 13·1; N, 8·8. Calc. for $C_{10}H_{21}N$: C, 77·4; H, 13·5; N, 9·0%). When benzoylated, it yielded a viscous syrup, which on treatment with light petroleum gave four-sided leaflets, m. p. 105·7—107° (Found : C, 78·8; H, 9·4. $C_{17}H_{25}ON$ requires C, 78·8; H, 9·7%). The hydrochloride of the base was a microcrystalline powder, with a feeble lævorotation, $[\alpha]_D$ — 0·4° (*c* 1·2, water). When treated with nitrous acid (J., 1927, 1280), it yielded a terpene–menthol mixture, in which *dl*-menthol was recognised (J., 1933, 170).

Action of Monomethylamine, etc.—By treating *l*-piperitone (89 g.) in a similar way with 33% alcoholic methylamine (85 g.), a basic material was obtained which distilled at 103·5—105°/13 mm. as a faintly yellow, mobile oil with an offensive odour. The substance had $n_D^{14·5°}$ 1·5032, and appeared to consist of slightly impure *piperitonemethylimine* (Found : C, 79·5; H, 11·4; N, 7·5. $C_{11}H_{19}N$ requires C, 80·0; H, 11·5; N, 8·5%). When reduced with sodium and alcohol, the crude undistilled material (153 g.) yielded N-*methylmenthylamine*, a colourless mobile oil, with a strong basic odour, b. p. 96·5—98°/16·5 mm., $n_D^{17°}$ 1·4654 (98 g. crude; 68 g. redistilled). Although chemically pure, this base was stereochemically heterogeneous (Found : C, 77·8; H, 13·9. $C_{11}H_{23}N$ requires C, 78·0; H, 13·7%).

In a similar way, monoethylamine yielded piperitone-ethylimine and *N*-ethylmenthylamine, b. p. 95—99·5°/11·5 mm., $n_D^{19°}$ 1·4610. Diethylamine did not react with piperitone under these conditions. Owing to the racemising effect of alkaline reagents on *l*-piperitone (J., **1923**, **123**, 2267), the substances described in this section showed at the most a faint optical activity.

We thank Prof. J. L. Simonsen, F.R.S., for the *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one used in this research, and the Carnegie Trust for the Universities of Scotland for a Carnegie Scholarship awarded to one of us (J. W.).

THE UNIVERSITY, ST. ANDREWS.

[*Received, January 8th*, 1934.]