action of cyanacetic ester on β-iodopropionic ester) is hydrolysed to pentane-aye-tricarboxylic acid (2), which when boiled, with acetic anhydride and distilled gives δ-kctohexahydrobcnzoic acid (3). The ester of this acid, when treated with the Grignard reagent, yields δ-oxyhexahydrotoluic acid (4), which is converted into the corresponding brom-compound by fuming hydrobromic acid. This latter compound on treatment with dilute alkali or pyridine yields Δ∙3-tetrahydr0-para-t0luic acid (5), the, ester of which with mag­nesium and methyl iodide furnishes terpineol (6) :—

zCH2∙C‰

(RO2C∙CH2∙CH2)2C(CN)CO2R -> aiOsC·CHa·CHîJaCH·COîH÷COÇ^,^^ ^^CH·COíH

(1) (s) ∕ħ (3)

**rn∙** ch2. *.ch-* ch2, c‰ zch2∙c‰ w

CHrC<f }CH(CH>)sOH <- CHι∙C< >CH∙CO2H <r >CΠ∙CO2Π

×CH2∙CU2z xCH2-CH2z H0z xCH2∙CH2z

(6) (5) (4)

This synthesis determines the constitution of terpin (7) and of dipentene (8), since the former is produced by the action of 5, per cent, sulphuric acid on terpineol, and the latter by heating terpineol with acid sodium sulphate.

CHιx zCH2∙CHκ *.CH* ∙CHjs, *,CHi*

>C< >CH∙C(CHs)2OH, *chs∙c<7* >CH∙C<

HOz ×CH2∙CH2z ×CH2∙CH2z 'CHj

(7) Terpin (8) Dipenlene.

Terpineol adds on nitrosyl chloride to form a nitrosochloride, which on elimination of hydrochloric acid yields the oxime of an unsaturated oxyketone; this on boiling with acids is converted into inactive carvone. When reduced by the method of Sabatier and Senderens it forms hexahydrocymene (A. Haller, *Comptes rendus,* 1905, 140, p. 1303); when oxidized with Caro’s reagent it yields trioxyhexahydrocymene (A. v. Baeyer and V. Villiger, *Ber.,* 1899, 32, ρ. 3625). For an isomeric terpineol (Δ-8(9) terpenol-l) see A. v. Baeyer, *Ber.,* 1894, 27, pp. 443, 815.

*Menthone* (terpan-0ne-3), CwHt8O, occurs with menthol in oil of peppermint. It was first obtained by Μ. Moriya *(Jour. Chem. Soc.,* 1881, 39, p. 77) by oxidizing menthol with chromic acid mixture at 120° C., and was described as an inactive compound; but R. W. Atkinson (ibid., 1882, 41, p. 50) showed that when menthol was oxidized at 1350 C. a strongly dextro-rotatory menthone was pro­duced. For the preparation of Z-menthone and <Z-isomenthone (Beckmann’s «/-menthone) see E. Beckmann, *Ann.,* 1889, 250, p. 325; 1891, 262, pp. 21 seq. The menthone obtained by Beckmann by the reduction of pulegone hydrobromide was shown by C. Martine *(Ann. chim. phys.,* 1904 (8), 3, p. 49) to be not com­pletely identical with /-menthone; it is consequently designated P-mcnthone. An inactive menthone has been synthesized as follows. £-Methyl pimelic ester is converted by sodium ethylate into methyl-ι-cycZ0hexanon-3-carboxylic ester-4, into which the iso­propyl group, is introduced (also in position 4) by the action of isopropyl iodide and sodium ethylate. The ester is then hydrolysed, and carbon dioxide eliminated from the carboxyl group, when inactive menthone is obtained (A. Einhorn and L. Klages, *Ber.,* 1901, 34, p. 3793). It boils at 204-206° C., whereas Beckmann’s menthones boil at 208° C. A. Haller and C. Martine *(Comptes rendus,* 1905, 140, p. 130) synthesized natural menthone from isopropyl iodide and the sodium derivative of methyl-*ι-cyclo-* hexan0ne-3. It has also been prepared by condensing methyl­hexanone with ethyl acetate, the resulting methyl-ι-acetyl-4-cycZ0- hexan0ne-3 being converted into the isopropyl derivative, yielding acetyl ment hone, which is then hydrolysed to menthone (G. Leser, *Comptes rendus,* 1902, 134, p. 1115). A. Koltz and L. Hesse *(Ann.,* 1905, 342> P∙ 3°6) convert methylhexanone (1) by means of ethyl oxalate and subsequent hydrolysis into methylhexanone oxalic acid (2), the isopropyl ester of which on treatment with a methyl alcohol solution of caustic potash yields «/-menthone (3).

zCH2∙CO ·. zCH2∙CO x zCH2∙CO v

CH1∙CH< >CH2 -> CHa∙CH< >CH∙C0∙C0ιR -> CHs∙CH< >CH∙CaH7.

xCH2∙CH2z xCH2∙CΠ2z xch2∙ch2z

(1) (a) (3)

O. Wallach *(Ann.,* 1900, 312, p. 171) showed that the oximes of cyclic ketones are converted by phosphorus pentoxide into iso­oximes, which are readily decomposed by concentrated hydro­chloric acid to yield aliphatic amino-acids; in this way menthone may be converted into e-amido-decylic acid,

(CH3)2CH∙CH(NH2)∙(CH2)2∙CH(CH3)∙CH2∙CO2H.

*Diosphenol,* CιoHιβ02, which occurs in the essential oil of bucco leaves *(Borosma betulina)* may be synthesized by oxidizing oxy­methylene menthone. Sodium in alcoholic solution reduces it to para-terpane-di-ol (2-3).

*Pulegone (is* 4(8)-terpenone-3), Cu>HιβO, is an unsaturated ketone found in-pennyroyal oil, from which it may be obtained by dis­tillation *in vacuo.* It is a dextro-rotatory liquid which boils at 221-2220 C. F. Tiemann *(Ber.,* 1897, 30, p. 22) synthesized it

is an unsaturated optically active ketone which is found very widely distributed in nature. The, dextro-form is the chief constituent of oil of caraway, and is also found in oil of dill;,, the laevo-form is found in oil of spearmint and kuromoji oil.. The dextro-form is obtained practically pure by the fractional distillation of caraway oil; the laevo-form from the, oils containing it, by first forming its addition com­pound with sulphuretted hydrogen, decomposing this by alcoholic potash, and distilling the product in a current of steam. It may be synthetically prepared from limonene nitrosochloride, alcoholic potash converting this compound into ∕-carvoxime, which on boiling with dilute sulphuric acid yields Z-carvone; similarly terpineol nitrosochloride by the action of sodium ethylate yields oxydihydro- carvoxime, which on hydrolysis yields /-carvone. On heating with phosphoric acid carvone is converted into carvacrol (ι-methyl-2- 0xy-4-is0pr0pylbenzene). Carvone is closely related to phellandrene, for C. Harries and Μ. Johnson *(Ber.,* 1905, 38, p. 1832), by reduction of carvone hydrobromide, obtained Δ 6-terpenone-2, which with phosphorus pentachloride gives chlor-2-a-phellandrene.

Βι-Cyclic Terpene Group

A nomenclature for the bicyclic hydrocarbons was devised by A. v. Baeyer *(Ber.,* 1900, 33, p. 3771). According to this system each hydrocarbon contains two tertiary carbon atoms, which are combined with, each other three times, either directly or by means of other intervening carbon atoms, the combination forming a series of “ bridges.” These bridges are distinguished bý numbers; denoting the number of carbon atoms contained in them, the direct union of the two tertiary carbon atoms being designated as o; if one carbon atom intervenes, then the number 1 is used, and so on. Thus three numbers serve as the “ characteristic ’·’ for the compound. Hydrocarbons of this class with five atoms of carbon are termed “ o/cyc/opentanes,” with six atoms of carbon “ Wcyc/ohexanes,” &c. Thus, for example, the compound (1) would be called “ *bicyclo· (1* · 1 · 3)- h2C-CH k H2C-CH2 '.,

¾⅛Λ¾JX⅛ ω'⅛>- ∙⅛⅛%

*Thujene* (tanacetene), H2C-CHz H2C-CHZ

C10H1β, is a derivative of *bicyclo-(o* · 1 · 3)-hexane. The name was first given to the hydrocarbon obtained by F. W. Semmler *(Ber.,* 1892, 25, p. 3345) on the dry distillation of thujylamine hydrochloride. It is a liquid which boils at 60-63° (14 mm.)', and has been shown by L. Tschugaeff to be a monocyclic hydrocarbon, for which he proposes the name “ isothujene.” The true thujene was prepared by L. Tschugaeff *(Ber.,* 1900, 33, p. 3118) by heating the methyl xanthogenic ester obtained from thujyl alcohol. It is exceedingly unstable. The isomeric ß-thujene was also obtained by the same investigator by the dry distillation of trimethylthujyl ammonium hydroxide. It boils at 150-151° C., and possesses a different rotatory power.

*Sabinene,* C10Hlβ, also a *bicyclo-(o ·* 1 · 3)-hexane derivative, is found in oil of savine, from which it was first obtained by F; W. Semmler *(Ber.,* 1900, 33, p. 1455). On shaking with dilute sulphuric

acid it yields terpinenol (Δι-terpcn-0l-4) (O. Wallach, *Ber.,* 1907, 40, p. 592). ■ . , .■:·.·

*Pinene,* C10H1β, derived from *bicyclo-(t ■* I · 3)-heptane, is found in many essential oils, and is the chief constituent of oil of tur­pentine; the /-variety is found in French oil of turpentine, the «/-variety in Russian, American and Swedish oil of turpentine. Pinene is also a constituent of the oils of sage, lemon, eucalyptus, olibanum, bay, fennel, sassafras, rosemary and of valerian. The active varieties are obtained by the fractional <listillation of the various oils of turpentine. The inactive variety is obtained by heating pinene nitrosochloride with án excess of aniline (O. Wallach, *Ann.,* 1889, 252, p. 132; 1890, 258, p. 243), or better with methyl­aniline (W. A. Tilden). The three varieties boil at 155-156° \_C. Pinene readily absorbs oxygen from the air, resinous products being formed, together with small quantities of formic and acetic acids.

from citronellal by converting this· compound into isopulegol acetate by acetic anhydride; this ester is hydrolysed, and the isopulegol oxidized to isopulcgone, which on treatment with baryta yields pulegone. Pulegone reduces ammoniacal silver nitrate on long boiling. It is reduced by hydrogen to /-menthol. When heated with water to 250° C. it yields methyl-l-cyc∕0hexan0ne-3 and acetone. When methylcyc/ohexanone and acetone, are condensed together in the presence of sodium methylate, an isomer of pulegone boiling at 215-216° C. is obtained. Pulegone combines with hydrobromic acid to form a hydrobromide,, which on heating in methyl alcohol solution with basic lead] nitrate is converted into isopulegone (Δ 8(9)-terρcnone-3) (C. Harries and G. Röder, *Ber.,* 1899, 32, p. 3361). It is a laevo-rotatory liquid. Adextror form (a mixture) is also obtained by the oxida­tion of isopulegol with chromic acid. On reduction it yields isopulegol and no menthol (cf. pulegone).

*Carvone* (Δ 6 : 8(9)-terpadiene-0ne-2), Cu>Hu,O,