Acid oxidizing agents convert it into terephthalic and terebic acids, whilst alkaline potassium permanganate in dilute solution oxidizes it to pinene glycol, Cιt∣Hιi(OH)i, pinonic acid, Cκ∣HιβO>, pinic acid, C>HhO<, &c·, the products of the reaction varying according to the temperature (G. Wagner, *Ber.,* 1894, 27, p. 2270; F. Tiemann and F. W. Semmler, *Ber.,* 1895, 28, pp. 1344, 1778). Concentrated sulphuric acid converts it into camphene; and an alcoholic solution of sulphuric acid gives terpinene and terpinolene. When heated to 250-270° C. it yields dipentene; the moist halogen acids at ordinary temperature convert it into the dihalogen halides of dipentene. Dry hydrochloric acid gives pinene hydrochloride (artificial camphor), CιoH∏Cl, a white crystalline solid identical with bornyl chloride which melts at 131° C. Elimination of halogen hydride by means of a weak alkali *(e.g.* soap, silver acetate, &c.) converts it into camphene. Thus the conversion of pinene into its hydrochloride is probably accompanied by an intramolecular rearrangement—

H·C·C·CH ! (HiC)Cl∙C∙CH 1 H·C · C(CHt)-CHC1

H⅛ i(CIb)l CHι→ H1([ é(CHi)« CH, → I è(CH,), I

1 ILc!∙CH 1 H,C∙⅛II CH,

Pinene. . Bornyl chloride.

Nitric acid in aqueous alcoholic solution converts it into terpin hydrate. Pinene nitrosochloride, CloHιβNOCl, was first obtained in 1874 by W. A. Tilden *(Jahresb.,* 1874 P∙ 214) from nitrosyl chloride and a mixture of pinene and chloroform. O. Wallach *(Ann.,* 1889, 253, p. 251) prepared it by the action of acetic acid and ethyl nitrite on oil of turpentine in presence of fuming hydro­chloric acid. W. A. Tilden *(Jour. Chem. Soc.,* 1904, 85, p. 759) showed that strongly active pinene gives bad yields of the nitroso­chloride, since, being bimolecular, its formation is retarded by the inversion of half of the terpene. The nitrosochloride melts at 1150 C. *(circa)* and is a white pleasant-smelling powder. Alcoholic potash converts it into nitrosopinene, C10HnNO.

*Bornylene,* C10Hn, derived from *bicyclo-(ι ·* 2 · 2)-heptane, is pre­pared by heating bornyl iodide to 1700 C. for several hours with a concentrated solution of alcoholic potash (G. Wagner, *Ber.,* 1900, 33, p. 2121), or by decomposition of the methyl esters of the *I-* and d-bornyl xanthates, the former yielding d-bornylene and the latter /-bornylene (L. Tschugaeff, *Chem. Centralblatt,* 1905, i., p. 94).

*Camphene,* C10Hn, also a *bicyclo-(ι ■ 2 ·* 2)-heptane derivative, is a constituent of the oils of citronella, camphor, ginger and of rosemary, and also of French and American oil of turpentine. It may be obtained by the action of sulphuric acid on pinene; by heating pinene hydrobromide or hydrochloride with sodium acetate or glacial acetic acid to 2000 C. ; or by heating bornyl chloride with aniline (O. Wallach, *Ber.,* 1892, 25, p. 916). According to Konowalow it is best prepared by heating borneol with a diluted sulphuric acid (1 · 2) for about 6-8 hours, between 60-100o C., with continual shaking, a yield of about 90 per cent, being obtained. The melting- and boiling-points of camphene vary slightly according to the sources from which it is obtained, the former being about 50° C. and the latter about 159-161° C. It is known in *d-, I-* and í- forms. It combines with hydrochloric acid to form a hydro­chloride, which on reduction with sodium and alcohol yields cam­phene. Many different oxidation products may be obtained from camphene by varying the conditions of experiment (J. Bredt and W. Jagelki, *Ann.,* 1900, 310, p. 114; G. Wagner, *Ber.,* 1890, 23, p. 2311; S. Moycho and F. Zienkowski, *Ann.,* 1905, 340, p. 17; J. E. Marsh and J. A. Gardner, *Jour. Chem. Soc.,* 1891, 59, p. 648; 1896, 69, p. 74).

*Fenchene,* C10Hu, a *bicyclo-(ι · 2 ·* 2)-heptane derivative, is not found in any naturally occurring products. The. hydrocarbon may be obtained by the reduction of fenchone and elimination of water from the resulting fenchyl alcohol, or by the elimination of halogen hydride from the fenchyl halogen compounds (O. Wallach, *Ann.,* 1892, 263, p. 145; 1898, 3021 pp. 371 seq.).

The above ⅛ιcycZo-terpene hydrocarbons are most probably best represented by the following formulae (pinene is given above) :—

zCH-C(CH,) zCH∙CH(CH>) zCH∙C>CH,

aC<é·CH,>CH ≡Q.ch>CH lhc¾.CH,>∞

C1II7 C>H, C>Ii!

α-Thujene β-Thujeπe Sahinene

CH, ■ C(CH,) ■ CH CΠ,∙CH∙C1CH, CH,∙CH C:CH,

fc(CH,h I I ÓH, I I 0(CHs⅛l

CH,∙⅛ —CH CH, ∙⅛-C(CH,), CH,∙⅛—-CH,

Bornyleπe Camphene Fencheue

Alcohol and Ketone Derivatives

*Borneol* (Borneo camphor), CιoH∏OH occurs in the pith cavities of *Dryobalanops camphora,* and in the oils of spike and rosemary; esters are found in many fir and pine oils. It may be prepared by heating camphor with alcoholic potash (Μ. Berthelot, *Ann.,* 1859, 12, p. 363); or by reducing camphor in alcoholic solution with sodium (O. Wallach, *Ann., 1885,* 230, p. 225; J. Bertram and H. Walbaum, *Jour, prak. Chem.* 1894 (2), 49, p. 12). L. Tschu­gaeff *(Chem. Centralblatt.* 1905 i., ρ. 94) obtains pure «/-borneol as follows;—Impure «/-borneol (containing isoborneoí) obtained in the reduction of camphor is dissolved in xylene and converted into the sodium salt by metallic sodium. This salt is then turned into the xanthate, CιoH∏OC⅛Na, which with methyl sulphate yields the corresponding.methyl ester. The unchanged isoborneoí is removed by steam distillation, which also decomposes any methyl xanthate of isoborneol that may have been formed. The residue is crystal­lized and hydrolysed,, when pure borneol is obtained. It behaves as a secondary alcohol. Nitric acid oxidizes it to camphor and when heated with potassium bisulphate, it gives camphene. ∖∖ ith phosphorus pentachloride it forms a bornyl chloride, identical with pinene hydrochloride..

*Isoborneol* is a tertiary alcohol which may be obtained by dis­solving camphene in glacial acetic acid, adding dilute sulphuric acid and heating to 50-60“ C. fcr a few minutes, the isotornyl acetate so formed being then hydrolysed (J. Bertram and H. Wal­baum, *loc. cit.).* It crystallizes in leaflets, which readily sublime. Chromic acid oxidizes it to camphor.

*Thujone* (tanacetone), C10H1βO, is found in many essential oils. Oil of thuja contains chiefly α-thujone, and oil of tansy chiefly 0-thujone. Oil of artemisia and oil of sage contain a nixture of the two, whilst oil of absinthe contains principally the ß-variety. The two forms may be obtained by fractional distillation of the oils, followed by a fractional crystallization of their semicarbazones from methyl alcohol. α-Thuione is laevo-rotatory and when warmed with alcoholic potash it is partially converted into 3-thujone. Sodium in the presence of alcohol reduces it to thujyl alcohol, which on re-oxidation is converted into ß-thujone. The ß-form is dextro-rotatory and is partially converted into the α-variety by alcoholic potash. When heated to 280° thujone is transformed into the isomeric carvotanacetone (Δ6-terpenone-2). On boiling with ferric chloride it yields carvacrol. Hot dilute sulphuric acid converts it into isothuιone (dimethyl-ι · 2-isopropyl- 3-cyc∕opentene-I-one-5). Thujone behaves as a saturated compound and forms a characteristic tribromide. When heated with zinc chloride it yields hydropseudocumene. According to F. W. Semmler *(Ber.,* 1900, 331 ρ. 275; 1903, 36, p. 4367) it is to be considered as a methyl-2-isopropyl-5-⅛⅛yc∕0-(0 · 1 · 3)-hexanone-3.

*Carone,* C10H1iO, is a trimethyl-3 · 7 · *γ-bicyclo-(o* · 1 · 4)-hepta- n0ne-2, obtained by acting with alcoholic potash on dihydrocarvone hydιobromide (A. v. Baeyer, *Ber.,* 1896, 29, pp. 5, 2796; 1898,

31, pp. 1401, 2067). It is a colourless oil, having the odour of camphor and peppermint, and boiling at 210° C. It is known in *d-, I-,* and «-forms. It does not combine with sodium bisulphite. When heated it is transformed into carvenone. It is stable to cold potassium permanganate solution, but on heating gives a dibasic acid, caronic acid, C,Hs(COaII)j, which Baeyer suggested was a grm-dimethyltrimethylene-1 · 2-dicarboxylic acid. This was confirmed by W. H. Perkin, junr. *(Jour. Chem. Soc.,* 1899, 75. p. 48) who synthesized the acid from dimethylacylic ethyl ester. This ester, with ethyl malonate yields etnyldιmethylproρane- tricarboxylic ester, which on hydrolysis and subsequent heating is converted into ßß-dimethyl glutaπc acid. The α-bromdiπ ethyl ester of this acid when heated with alcoholic potash yields *cis-,* and ∕rαns-caronic acids. Eucarvone, Cn>HnO, is a trimethyl- 3∙7∙7-⅛icycZσ-(0∙ι∙4)-heptene-3-0ne-2. O. Wallach *(Ann.,* 1905, 339> P∙ 94) suggests that the ketone possesses the structure of a trimethyl-l - 4 ■ 4-cycI0heptadiene-5 ■ 7-0ne-2. Phosphorus penta­chloride converts it into 2-chlorcymene (A. Klages, *Ber.,* 1899,

32, p. 2558).

*Camphor,* Cκ>HlnO, is a.trimethyl-l · 7 · *∙j-bicyclo-(l ■* 2 · 2)-hepta- n0ne-2. The «/-variety is found in the camphor tree *(Laurus camphora),* from which it. may be obtained by distillation in steam. The Z-variety is found in the oil of *Matricaria parlhenium.* It crystallizes in transparent prisms which possess a characteristic odour, sublimes readily and is easily soluble in the usual organic solvents. It boils at 209° C. and melts at 176° C. *(circa).* The «/-form may also be obtained by the distillation of calcium homo­camphorate (A. Haller, *Bull. Soc. Chim.,* 1896 (3), 15, p. 324). When, heated with phosphorus pentoxide it yields cyrrene, and with iodine, carvacrol. Nitric, acid oxidizes it to camphoric acid, CβHu(C0aH)a, camphoronic acid, C9HuO6, and other products. It forms.an oxime with hydroxylamine which on dehydration yields a nitrile, from which by hydrolysis campholenic acid, CβHιtCO2H, is obtained, ft combines with aldehydes to form alkylidene com­pounds, and yields oxymethylene compounds when subjected to the “ Claisen ” reaction. It does not combine with the alkaline bisulphites. It is readily substituted by chlorine and bromine; and with fuming sulphuric acid forms a camphor sulphonic acid. S<>dium reduces it, in alcoholic solution, to borneol. When heated with sodium formate to 1200 C. it is converted into bornylamine. Caro's acid converts it into campholid, and a compound CιoHltO< (A. v. Baeyer and V. Villiger, *Ber.,* 1899, 32, p. 3630). When heated with concentrated sulphuric acid to 105-110° C. it yields carvenone and 4-acet0-ι · 2-xylol (J. Bredt, *Ann.,* 1901, 314, p∙ 371)∙