XX.—*On the Hydrocarbons derived from Dipentene Dihydrochloride.*

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It was shown by one of us in 1879 (*Ber.*, **12**, 1131) that the dihydrochloride, $C_{10}H_{16}.2HCl$, whether prepared from dextrorotatory or lævorotatory turpentine, or from the terpene of the citrene (limonene) group, is always the same compound, and when deprived of the elements of hydrogen chloride, yields the same hydrocarbon or mixture of hydrocarbons—then called terpilene or terpinylene.

Four years ago (*Trans.*, **53**, 1888, 879) a further examination of the hydrocarbon thus formed from the dihydrochloride showed that by oxidation with nitric acid it gave a considerable amount of toluic acid, whereas the other terpenes gave only minute quantities or none at all. This terpilene was at that time supposed to be homogeneous, and to be identical with the optically inactive hydrocarbon to which the name dipentene has since been given. The latter, as is well known, is formed by heating isoprene to about 300° , also as a chief product of the action of dilute sulphuric and other acids on pinene (turpentine) and limonene (from lemon or orange oil, &c.) and from other sources.

Limonene exists in two varieties, which are respectively dextrorotatory and lævorotatory. A mixture of equivalent quantities of these two liquids produces an optically inactive mixture which has been shown by Wallach (*Annalen*, **246**, 225; **252**, 123) to have the same properties as dipentene. Tilden having already shown that dextrorotatory limonene (citrene obtained from orange oil) when oxidised by nitric acid gave neither toluic nor terephthalic acid (*Trans.*, 1888, **53**, 880), while the supposed dipentene made from the dihydrochloride gave 27.6 per cent. of its weight of toluic acid, it became obvious either that lævolimonene gave products of oxidation different from those of dextrolimonene or that the hydrocarbon obtained from the dihydrochloride was very far from being pure dipentene. Some further experiments described below were, therefore, undertaken, the results of which show that the latter hypothesis is correct. The hydrocarbon obtained from the dihydrochloride

and formerly called terpinele or terpinylene, and represented by Wallach as consisting chiefly of dipentene (*Annalen*, **239**, 12), is a mixture in which dipentene is associated with cymene, terpinene, terpinolene, and a saturated paraffinoid hydrocarbon probably identical with the liquid referred to by Armstrong and Tilden (*Trans.*, 1879, **35**, 745). This might almost have been anticipated from the much lower bromine-absorptive power exhibited by the supposed dipentene.

Oxidation of Lævolimonene.

The usual sources of lævolimonene, "*oleum pini sylvestris*" and "*fir wool oil*," prepared for use in medicine were found to be no longer available for this purpose. When the oils which now occur in commerce under these names were submitted to fractional distillation they yielded little beside ordinary pinene. Through the intervention of Messrs. Wright, Layman, and Umney, we obtained a supply of the desired material from Messrs. Schimmel and Company, of Leipzig, who very liberally presented us with 500 grams of a product boiling between 175° and 180°, fractionated from the oil of *Pinus picea*. This liquid was shaken with sodium to free it from water and was then fractionally distilled. A large fraction was obtained boiling between 175° and 176°, and having a lævorotatory power of about 94° per 100 mm., when tested by Wild's polaristrobometer and using the sodium flame. The relative density of the liquid at 12.5° was 0.886. Its specific rotatory power, $[\alpha]_D$ is 106°. This hydrocarbon when dissolved in a mixture of alcohol and ether and treated with bromine gave the characteristic tetrabromide (melting at 103°) described by Wallach (*Annalen*, **227**, 301).

It was tested in the usual manner for cymene by shaking up with 4:1 sulphuric acid.* The limonene was thus polymerised and the resulting mixture steam-distilled. The cymene was estimated in this case by measure as the quantity was so small, amounting to about 1 per cent. of the lævolimonene.

10 grams of this lævolimonene were oxidised by boiling with a mixture of 42 grams concentrated HNO_3 and 170 grams of water in a flask attached to a reflux condenser, and at intervals as the oxidation proceeded a few drops of nitric acid were added to maintain the strength of the mixture. The process of complete oxidation occupied about 30 hours. Only a *minute trace* of toluic acid was obtained, showing that lævolimonene does *not* yield toluic acid on oxidation.

* Four vols. of oil of vitriol mixed with 1 vol. of water is referred to as 4:1-acid.

Dipentene.

Owing to the fact that neither dextro- nor lævo-limonene gave any toluic acid on oxidation, dipentene itself was then examined. It was prepared by heating 207 grams of pinene dihydrochloride with 186 grams of aniline first upon a water-bath for half an hour, and then for a short time at the boiling point of the mixture. The product was distilled in a current of steam and washed with a little very dilute sulphuric acid to remove any traces of aniline, dried with calcium chloride and finally over sodium. It was then repeatedly fractionated and finally separated into three large fractions boiling as follows: 175—176°, 176—178°, 178—180°, with small fractions above and below. These three fractions were tested by boiling with concentrated nitric acid and a crystal of silver nitrate: the first two fractions were free from chlorine; the last contained a trace.

10 grams of fraction 175—175° were oxidised with the same proportion of nitric acid and water as in the experiment with limonene. It yielded 2.7 grams of pure toluic acid. 10 grams of fraction 178—180° gave the same amount. As this must be due to the presence of impurity, an attempt was made to determine its nature.

On testing fraction 175—176° for cymene, the barium sulphonate obtained was found to correspond to 12.5 per cent. of that hydrocarbon.

It was also shown to contain terpinene by the formation of terpinene nitroso-nitrite on the addition of potassium nitrite and acetic acid to the hydrocarbon dissolved in light petroleum (Wallach, *Annalen*, **239**, 36).

By treatment first with 4 : 1-sulphuric acid and steam distillation, and subsequently warming the distillate with oil of vitriol, the terpenes and cymene were removed, and a paraffinoid hydrocarbon left, which amounted to about 3 per cent. of the dipentene used. This liquid is not attacked by nitric or sulphuric acid, and boils at 155—156°.

Dipentene was then prepared from india-rubber by distillation. After repeated fractionation, a product was obtained boiling at 175—176°, which, on treatment with bromine, gave the crystalline tetrabromide melting at 120—124° (Wallach, *Annalen*, **227**, 301). 10 grams of this fraction were oxidised with the usual proportions of nitric acid, and gave *no trace* of toluic acid. *Pure* dipentene, therefore, does *not* yield toluic acid on oxidation with nitric acid.

Oxidation of Terpinene.

Terpinene was prepared by shaking up rectified oil of turpentine with 1 : 1-sulphuric acid in the proportion of 1 litre of turpentine to

100 c.c. of acid. Much heat was developed, but the temperature was not allowed to rise above 50°. The product was distilled in a current of steam and again treated in a similar manner until the hydrocarbon was inactive towards polarised light.

It was then dried over sodium and repeatedly fractionated; the larger part distilled below 175°, but a fraction boiling between 178° and 181° was obtained consisting chiefly of terpinene; this readily yielded terpinene nitroso-nitrite on treatment with nitrous acid, but on testing in the usual manner for cymene, it was found to contain 15 per cent. of this hydrocarbon. 10 grams, on oxidation, yielded 4.3 grams of toluic acid.

Terpinene was then prepared by the following method (*Annalen*, **230**, 260):—500 grams of terpin hydrate were boiled with an equal weight of 1 : 7-sulphuric acid. The product, after drying, was repeatedly fractionated, and a fraction boiling constantly at 178—180° under a pressure of 753 mm. was obtained. The higher fraction, 184—190° (terpinolene), was used for a subsequent experiment. This terpinene gave a good yield of terpinene nitroso-nitrite, but treatment with 4 : 1-sulphuric acid indicated the presence of about 15 per cent. of cymene. 10 grams, on oxidation, gave 2.5 grams of toluic acid, but as cymene had been found to give only about three-fourths of its weight of toluic acid, the amount of cymene present in this fraction would account for only about half the toluic acid actually obtained by oxidation. A second preparation of terpinene gave a similar result.

Hence terpinene yields, by oxidation with nitric acid, about 15 per cent. of toluic acid. This terpinene takes up only 2 atoms of bromine, forming an oily dibromide, 136 parts of hydrocarbon requiring 157 parts of bromine as a mean of two experiments. On heating the dibromide with aniline, half its weight of cymene was obtained, thus confirming previous observations (Tilden, *Trans.*, 1878, **33**, 251).

Oxidation of Terpinolene.

The higher fractions from the preparation of terpinene were several times refractionated, and a portion boiling at 184—190° was separated; this, according to Wallach (*Annalen*, **230**, 262), should be nearly pure terpinolene; it seemed to be a definite fraction, and yielded the tetrabromide melting at 112° (*loc. cit.*). 10 grams, on oxidation, gave 2.5 grams of toluic acid. Hence terpinolene seems in this respect to agree with terpinene. It must, however, be admitted that the difficulty of separating terpinolene and terpinene renders it probable that the terpinolene employed may have contained terpinene. Therefore, the question whether terpinolene yields toluic acid on oxidation remains to be settled by more decisive experiments.