XXVIII.—*On Terpin and Terpinol.* (*Preliminary.*)

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TERPINOL is the name given by List to the liquid obtained by the action of dilute acids upon terpin hydrate, but the statements of Wiggers (*Ann. Chem. Pharm.*, 1846, i, 251), List (*ibid.*, 1848, 362), and Oppenheim (*ibid.*, 1864, 149), regarding the composition and properties of this substance are at variance with one another.

Terpinol is described by List as a liquid of specific gravity ·852, boiling constantly at 168°. On the other hand, Oppenheim states that when terpinol is distilled it begins to boil at 165°, and that the temperature gradually rises to 208°. Moreover, Oppenheim asserts that distillation causes a decomposition in terpinol in such a manner that the first portions of the distillate contain more carbon and less hydrogen and oxygen than the last. The analyses of Wiggers and List indicate the formula $C_{20}H_{34}O$ or $(C_{10}H_{16})_2OH_2$.

My experiments lead me to conclusions differing materially from those of the chemists to whom I have referred, and although the subject is by no means complete, I beg leave to bring before the Society such results as I have obtained.

Crystallised Terpin, $C_{10}H_{20}O_2.OH_2$.

This beautiful compound was prepared by a process essentially the same as that given many years ago by Wiggers. I find that it is advantageous to use a rather large proportion of nitric acid. A mixture of 1 measure of nitric acid (sp. gr. 1·4), 1 measure of methylated spirit, and 2½ measures of rectified turpentine oil becomes very warm, and in about two days loses the smell of turpentine. If such a mixture is then poured out into an open dish, a small quantity of methylated alcohol being added every few days, it deposits crystals which in about a fortnight amount to one-third of the weight of the turpentine employed. More crystals are obtained by prolonged exposure.

I have ascertained that no crystalline compound is formed under similar circumstances from the terpenes of the orange group; also that the same compound is obtained whether American or French turpentine oil be employed.

The crystals from both sources agree in melting point, in crystalline form, and in giving an alcoholic solution which does not act upon a ray of polarised light.

Action of Dilute Hydrochloric Acid upon Terpin.

Separate experiments were made upon the terpins obtained from the two kinds of turpentine oil. The product is, however, always the same, and it will be necessary therefore to quote only one experiment.

To 53½ grams of crystallised terpin, boiled up with 700—800 c.c. of water, 12 drops of hydrochloric acid were added. In a few minutes the crystals had disappeared, and the liquid, now turbid from the presence of oily matter, was distilled. A distillate of peculiar and fragrant odour was obtained. When about half the liquid had passed over, a little water containing 12 more drops of hydrochloric acid was added to the residue in the flask, and the distillation continued until all the oil had distilled over. I retain the name terpinol for the oily product.

When this terpinol was submitted to distillation, the temperature went up immediately to above 200°, and all but a few drops came over between 205° and 215°. When redistilled it came over again between the same limits of temperature, but no product of more definite boiling point was obtained.

It undergoes no change of properties by distillation; neither is it changed appreciably in composition. Two analyses were made, the one of the crude product dried by chloride of calcium, but not redistilled (1); the other of the liquid redistilled, and collected between 205° and 215°.

1. ·18925 gram gave ·5445 of CO_2 and ·2080 of OH_2.
2. ·2803 gram gave ·8110 of CO_2 and ·3010 of OH_2.

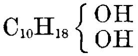
These results give percentages of carbon and hydrogen, which closely approximate to the numbers calculated from the formula $C_{10}H_{18}O$ or $C_{10}H_{16}.H_2O$.

	1.	2.	Calculated.
C....	78·3	78·9	77·9
H....	12·2	11·9	11·7

The formula $C_{20}H_{34}O$ or $(C_{10}H_{16})_2OH_2$ requires C 82·75, H 11·72 per cent.

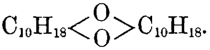
Whether the formula $C_{10}H_{18}O$ correctly represents the molecular weight of this compound is a question which cannot be finally determined till the vapour-density has been taken and further experiments made. For the present I am much disposed to consider that this formula should be doubled, and that terpinol should be regarded as the anhydride or ether of terpin, bearing in fact a relation to that compound similar to the relation of common ether to ethylic alcohol.

Terpin being—



$$C_{10}H_{18}\left\{\begin{matrix}OH\\OH\end{matrix}\right.$$

terpinol must be written



$$C_{10}H_{18}<\begin{matrix}O\\O\end{matrix}>C_{10}H_{18}.$$

Almost conclusive evidence of this is supplied by the action of hydrochloric acid, which does not give a monochloride, as might be expected if terpinol had the constitution expressed by $C_{10}H_{17}(OH)$.

Terpinol is a colourless, somewhat viscid liquid, inactive upon the polarised ray, and having at 16° a specific gravity ·9274. When dry hydrochloric acid gas is passed into it, the liquid becomes very hot, and assumes an intense purple colour. It ultimately sets into a mass of crystals, which after strong pressure become perfectly white. These crystals were analysed, and found to contain 33·94 per cent. of chlorine. They melt at 50°. The compound is therefore identical with the dihydrochloride, $C_{10}H_{18}\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$, obtained by saturating terpin with hydrochloric acid gas; also by saturating with hydrochloric acid a solution of turpentine in ether or alcohol.

This compound is entirely converted into terpinol by boiling for an hour or two with water.

When this dichloride is boiled for a few minutes with a solution of sodium in absolute alcohol, a precipitate of common salt is thrown down; and on adding water to the liquid an oil separates, which becomes slightly yellow on exposure to air. In contact with ordinary strong hydrochloric acid, it is instantly converted into a crystalline mass of dichloride. It was found to contain 24·9 per cent. of chlorine. The formula $C_{10}H_{18}\left\{\begin{matrix}OC_2H_5\\Cl\end{matrix}\right.$ requires 16·24 per cent. of chlorine. I am therefore in doubt whether this compound was formed, or whether the liquid examined was a solution of the dichloride in the compound $C_{10}H_{18}\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.$.

Terpinol is miscible with alcohol in all proportions. If the alcoholic solution is acidified with nitric acid and placed in a dish, it deposits in a few hours abundant crystals of terpin. This fact, and the peculiar odour of the liquid left in the preparation of terpin by the ordinary process, lead me to the belief that terpinol is formed at a certain stage of the reaction between turpentine oil, alcohol, and nitric acid.

$$C_{10}H_{16} + C_2H_5OH + HONO_2 = \underset{\text{Terpinol.}}{C_{10}H_{18}O} + C_2H_5ONO_2.$$

The liquid which has begun to deposit crystals, when separated, washed free from nitric acid, and heated, evolves nitric oxide and then distils chiefly between 200° and 230°. I look upon the production of terpin as probably accomplished through the intermediate formation of a compound of terpinol with the elements of ethyl nitrate,

$$C_{10}H_{18}O\left\{\begin{matrix}OC_2H_5\\NO_2\end{matrix}\right.,$$

which is subsequently decomposed by water.

$$C_{10}H_{18}O\left\{\begin{matrix}C_2H_5\\NO_2\end{matrix}\right. + 2H_2O = \underset{\text{Terpin.}}{C_{10}H_{18}\left\{\begin{matrix}OH\\OH\end{matrix}\right.} + C_2H_5OH + NO_2OH.$$

The same succession of changes may be supposed to be repeated indefinitely.

Action of Sulphuric Acid on Terpin.

76 grams of terpin crystals were placed in a large flask, together with about 50 grams of sulphuric acid diluted with seven or eight times its bulk of water. Steam was passed through the mixture, till all the oily matter had distilled over. After separating from the water the product was found to distil entirely between 177° and 187°. After redistillation a portion was collected between 176° and 177°, and analysed. It gave 84·7 per cent. of carbon and 11·8 per cent. of hydrogen. The formulæ $(C_{10}H_{16})_2OH_2$ and $C_{10}H_{16}$ require respectively 82·75 and 88·2 per cent. of carbon.

The product was therefore presumed to be a mixture of terpinol with a hydrocarbon. It was boiled for two to three hours with about two volumes of water and one volume of oil of vitriol. The product fractioned and finally distilled from sodium gave about one-third of its bulk at 176—178°, and this portion when burnt gave numbers corresponding with 87·33 per cent. of carbon and 11·8 of hydrogen in one experiment, and 87·43 per cent. of carbon and 11·79 of hydrogen in a second. Its vapour-density was taken by Hofmann's method in aniline vapour, and was found to be 68·8.

This, then, is evidently a hydrocarbon, having the formula $C_{10}H_{16}$.

	Theory.		
C	88·2	Density ..	68
H	11·8		

It seems to stand in the same relation to terpin as ethylene to common alcohol, and it is probably formed by a similar reaction. It is, however, exceedingly difficult to get rid of the last traces of terpinol which accompany it. After very careful purification, another specimen boiling at the same temperature, namely, at 176—178°, had a specific gravity of ·8526 at 15°. This compound is optically inactive. Treated with hydrochloric acid it gave no crystalline deposit, but after exposure in a dish for several days, the liquid left a few crystals of the dichloride $C_{10}H_{18}Cl_2$. These were attributed to the presence of a small quantity of terpinol in the specimen operated upon. No crystalline nitroso-compound could be obtained by the action of nitrosyl chloride. When diluted with chloroform, cooled, and mixed with two equivalents of bromine, it gave a dibromide which on heating splits up into hydrobromic acid and cymene, yielding a quantity of the latter compound equal to half the weight of the hydrocarbon operated upon.

In many respects this hydrocarbon agrees with the terpene characteristic of Russian turpentine oil, and described in a recent paper of mine (*J. Chem. Soc.*, February, 1878). It differs, however, from that compound in having no action on polarised light, and to the extent of about 4° or 5° in the observed boiling points.

The oxidation products are of course very important, and I have ascertained that both terpinol and terpinylene, as this hydrocarbon may be called, yield, besides other acids, an appreciable quantity of toluic acid melting at 176°. I do not regard this as a serious obstacle to the acceptance of the formulæ for the terpenes I have lately proposed. Assuming these hydrocarbons to consist of an open chain, which is liable to be closed by the removal of hydrogen from the terminal carbon atoms, it is not improbable that this closing of the chain may be effected during processes of oxidation. But that this occurs in a fortuitous and irregular manner is shown by the very small amount of the toluic or terephthalic acid ever obtained from any of the $C_{10}H_{16}$ group. Cymene, $C_{10}H_{14}$, in which we must admit the closed benzene ring, yields under the same circumstances something like a third of its weight.
