LXXVI.—*The Action of Nitrosyl Chloride on Pinene.*

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Preparation of Pinene Nitrosochloride.

IN the paper (J. Chem. Soc., N. S., 1877, 15, 554) in which, in conjunction with Mr. Shenstone, I first described the application of nitrosyl chloride to the purpose of classifying the terpenes, attention was drawn to the apparent connection between the optical activity of the hydrocarbon operated on and the yield of nitrosochloride. It was found that terpenes of high rotatory power gave a much smaller product than others apparently identical in other respects, but having less action on the polarised ray. Von Baeyer having shown (*Ber.*, 1895, 28, 648) that pinene nitrosochloride is a bimolecular compound with the formula $(C_{10}H_{16} \cdot NOCl)_2$, it occurred to me that the inferior yield of nitrosochloride by the more strongly rotating varieties of the hydrocarbon was due to the destructive effect of heat generated in the process of inversion of one-half of the compound as soon as formed, and that by using a mixture of *d*- and *l*-pinenes in due proportions the bimolecular compound would at once be produced by simple combination of the two semi-molecules without further change in either of them, and a larger product would result. This turns out to be the case.

When to pinene from American turpentine, diluted with half its volume of chloroform and cooled to about 0° , is added very gradually a solution of nitrosyl chloride in chloroform, an intense blue coloration is observed on the addition of each drop of the reagent. The colour quickly fades and a white, crystalline precipitate soon begins to form. A similar, though less intense, blue colour is produced when ethyl or amyl nitrite together with hydrochloric acid is employed, as in the process introduced by Wallach (*Annalen*, 1888, 245, 251). When the blue colour is no longer produced, the liquid diluted with about three times its volume of 84 per cent. alcohol yields a precipitate which, after being washed with alcohol and dried at about 50° , amounted in a series of experiments pretty uniformly to 31—32 per cent. of the pinene. The specimen used had a rotation of about $+7^\circ$ in a 200 mm. tube.

When the *d*-pinene was replaced by *l*-pinene of greater rotatory power ($-57^\circ 48'$ in 200 mm.), the yield was much less and never exceeded 20 per cent. of the pinene employed.

A specimen of pinene from the turpentine of *Pinus Khasyana*, which has a specially high rotatory power ($+80^\circ 41'$ in 200 mm.), and probably

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consists of nearly pure *d*-pinene, was then tried. The amount of nitrosochloride it could be made to yield was only 5.5 per cent. These results confirm the impressions derived from the experiments made in 1877.

An experiment was then made on an optically inactive mixture of the two last-named varieties of pinene, and it was found by the same process to yield 55.6 per cent. of its weight of nitrosochloride. When, in the process described, light petroleum is substituted for chloroform, no blue colour is at first produced on the addition of the nitrosyl chloride, and the yield of nitrosochloride is much smaller, but, with a view to economy, petroleum may be used in place of a portion of the chloroform. The process preferred is therefore as follows :

The pinene from ordinary American turpentine has usually a rotatory power about one-third of that of the corresponding hydrocarbon from French turpentine, but in consequence of the variation in different samples of these liquids it is necessary to distil from the commercial oils of turpentine the fraction boiling at 156—160°, to determine its rotatory power, and to mix the two liquids in exactly corresponding proportions. This inactive mixture of pinenes is then diluted with about two-thirds of its volume of petroleum (boiling at about 90—100°) and cooled to a few degrees below 0°. A solution of nitrosyl chloride in a mixture of equal volumes of chloroform and petroleum, saturated at 0° (which contains about 8 per cent. of its weight of NOCl), is then allowed to drop slowly from a tap-funnel into the liquid, which is kept in motion by a mechanical stirrer. The temperature should not be allowed to rise much above 0°. A green colour is at first developed, but this becomes bluer in shade as the chloroform accumulates in the mixture, and a white precipitate is soon copiously produced. The nitrosyl chloride is ultimately added in decided excess, and a quantity of alcohol is then added, equal to about $1\frac{1}{2}$ times the total volume of the mixed liquids, and the whole left in the ice for half an hour. The precipitate is then collected at the pump, washed with alcohol, and dried, first by exposure to the air, then at about 50°.

The process in which amyl nitrite is mixed with the pinene diluted with glacial acetic acid and hydrochloric acid is allowed to drop into the cooled mixture is very convenient, but less productive. In my hands, using the same mixture of pinenes, it yielded only about 33 per cent. of the pinene employed. This appears to be explained by the fact that the theoretical amount of hydrochloric acid cannot be added without causing decomposition. The temperature can be kept below 0° without difficulty until about half the amount of acid has been introduced ; effervescence then sets in, attended by a rapid rise of temperature.

In the course of trying variations of my process, one experiment led to a result which helps to explain this effect. Pinene was diluted with

three volumes of petroleum, and, with the object of avoiding the separate preparation of a solution of nitrosyl chloride, the gas was passed into a small quantity of ordinary strong hydrochloric acid, upon which the hydrocarbon floated as a separate layer. The whole was cooled below 0° and a white precipitate soon made its appearance. Ultimately a quantity of nitrosochloride corresponding with 14 per cent. of the pinene was collected. The aqueous acid became syrupy, and when diluted with a mixture of alcohol and water it gave a copious crystalline precipitate which, when collected, represented about one-third of the weight of the pinene, while a further quantity remained in the mother liquors. After recrystallisation from methyl alcohol, this compound was recognised as *i*-carvoxime hydrochloride (m. p. $127-128^{\circ}$). Von Baeyer has observed that pinene nitrosochloride is changed into this compound by contact for three days with an ethereal solution of hydrogen chloride. In the circumstances described, however, the conversion is immediate.

In the process for the production of pinene nitrosochloride, the employment of aqueous hydrochloric acid appears to give rise to the same change. The effervescence which occurs can be accounted for by the hydrolysis of the carvoxime, whereby hydroxylamine is formed, which is immediately destroyed by the nitrosyl chloride with evolution of nitrous oxide.

Properties of Pinene Nitrosochloride.

The original statement (Tilden and Shenstone, *J. Chem. Soc., N. S.*, 1877, 15, 556, and Wallach, *Annalen*, 1888, 245, 252) that the melting point of the nitrosochloride is 103° is incorrect. The fusion is accompanied by decomposition, and the temperature at which it occurs varies a little according to circumstances. The melting point of this compound when well washed with alcohol and thoroughly dried, but not recrystallised, is usually $109-111^{\circ}$. After recrystallisation from chloroform, it reaches 115° . The same compound is produced by the employment of inactive pinene regenerated from the nitrosochloride, as described later.

From whatever hydrocarbon prepared, the solution of the nitrosochloride in chloroform is optically inactive. It may be recrystallised from chloroform either by allowing the solution to evaporate at the temperature of the air, or by the addition of alcohol. It is advisable not to operate on more than a few grams at a time, and to avoid the application of heat. Fifty grams mixed with 250 c.c. of chloroform very gently warmed developed so much heat as to cause the liquid to boil, and, although cooled as quickly as possible, the whole was decomposed. The solution yielded on evaporation a red resin, together with a considerable quantity of nitrosopinene (m. p. 129°).

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If pure pinene nitrosochloride dissolved in chloroform is diluted with alcohol, the solution in a few hours assumes the orange-red colour developed in the mother liquors obtained in the ordinary process of preparation. This solution reduces Fehling's solution freely, and evidently contains hydroxylamine.

Nitrosopinene and Pinyllamine.

As the nitrosochloride is undoubtedly formed by the union of a dextro- and a lævo-compound, it seemed probable that nitrosopinene, which is produced from it by removal of 2HCl and is monomolecular, might exist in two forms. Attention was long ago (J. Chem. Soc., N. S., 1877, 15, 557) drawn to the peculiarity of habit exhibited by the nitroso-compound prepared from certain specimens of *l*-pinene. Recent experiments, however, prove that when this variety is mixed with the same compound prepared from *d*-pinene, the melting point is not depressed, and that when the two varieties are dissolved in aqueous caustic soda, reprecipitated by acetic acid, and recrystallised from alcohol, both yield crystals of the same form as described by Maske-lyne (J. Chem. Soc., N. S., 1875, 13, 518). The nitrosopinene derived from *l*-pinene therefore probably owes the peculiarity originally observed to the presence of a trace of some unknown impurity.

Whether obtained from *d*- or from *l*-pinene, however, the crystals of nitrosopinene consist of a mixture of prisms which exhibit hemihedrism. I am indebted to Miss M. A. Whiteley, D.Sc., for kindly undertaking the task of separating a quantity of the *r*- and *l*-forms. The solution of one of them in alcohol was, however, optically inactive. Pinene benzylnitrolamine shows a similar phenomenon (Hintze, *Annalen*, 1889, 252, 131. See also Pope, *Trans.*, 1896, 69, 971, and Clare de Brereton Evans, *Trans.*, 1897, 71, 525 and 1001).

As it seemed hopeless to attempt the resolution of nitrosopinene into optically active isomerides by any process of crystallisation, it was reduced to pinyllamine and the base converted into its salts with optically active strong acids.

Reychler's *d*-camphorsulphonic acid and the *l*-oxime of the same and *d*-bromocamphorsulphonic acid, for which I am indebted to Professor Pope, were used. The camphorsulphonate was crystallised repeatedly from ethyl acetate. In another experiment, about $2\frac{1}{2}$ molecules of pinyllamine nitrate were dissolved in water together with one molecule of ammonium camphorsulphonate, and advantage was taken of the slight solubility of pinyllamine nitrate to precipitate the base from the mixture in successive portions, leaving the elements of pinyllamine camphorsulphonate in solution.

The pinylamine *d*-bromocamphorsulphonate was recrystallised fractionally many times, first from ethyl acetate, and in another series of experiments from acetone. The base was in each case recovered from the most soluble and least soluble portions respectively, converted into hydrochloride and examined in the polarimeter, but no optical activity could be detected. As no formula has yet been proposed which will account for the disappearance of asymmetry from the molecule, ordinary pinylamine must still be regarded as probably consisting of a mixture of optical isomerides, notwithstanding that these attempts to resolve it have been unsuccessful.

Action of Bases on Pinene Nitrosochloride.

Wallach has already shown that primary fatty bases and benzylamine yield nitrolamines, but that aniline acting on the nitrosochloride regenerates pinene and forms aminoazobenzene. I have several times repeated this experiment, and find that the interaction with aniline proceeds slowly but completely in the cold, yielding the same products. The yield of pinene is, however, always small. I have found that methylaniline is a more advantageous reagent. Pinene nitrosochloride, heated gently together with two molecular proportions of methylaniline, diluted with about three times its volume of alcohol, dissolves quietly without any sign of the violent action which occurs when aniline is used. A slight excess of acetic acid may then be added and the liquid distilled in steam. The pinene separated from the first portions of the distillate, dried with caustic potash and distilled, amounts to about 63 per cent. of the theoretical quantity. The latter stage of the steam distillation gives phenylmethylnitrosoamine as the chief secondary product, a small quantity of a purple base remaining in the residue.

Dimethylaniline tried in similar proportions gave about the same yield of pinene. There was no spontaneous heating or evolution of gas, but the liquid assumed an intense green colour. This is due to the formation of the green hydrochloride of a purple base which gives Liebermann's reaction freely, and is not *p*-nitrosodimethylaniline.

Dimethyl-*p*-toluidine gave a similar result; the base formed gave Liebermann's reaction, but in this case no green colour was produced, the liquid assuming a deep yellow tint.

Pyridine behaves in a different way. In alcoholic solution, it produces no pinene, but only viscid products; in chloroform, it fixes hydrogen chloride and produces nitrosopinene.

The inactive pinene recovered by either of these operations from the nitrosochloride is very readily reconverted into that compound by the process I have described. It yields uniformly 55 per cent. of its

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weight of nitrosochloride, an amount which is practically identical with the product obtained, as already stated, from an inactive mixture of *d*- and *l*-pinenes.

Theoretical.

The course of the action of nitrosyl chloride on pinene consists in the formation first of a simple nitrosochloride which, in solution, in common with nitroso-compounds in general, exhibits a blue colour. The union of two such molecules (*d* and *l*) gives rise to the colourless bimolecular or racemic compound $(C_{10}H_{16} \cdot NOCl)_2$, which, from its reactions with aromatic bases, evidently contains the elements of the chloride corresponding with nitrous acid.

The two semi-molecules are supposed by von Baeyer to be linked together by the two NO groups, which must be united by pentadic nitrogen, $\begin{array}{c} \text{N} \cdot \text{N} \\ \text{O} \quad \text{O} \end{array}$. This probably accounts for the disappearance of the blue colour when the compound is formed. Certain of the nitrolamines formed from the nitrosochloride by substitution of the basic residue for the chlorine are also stated by von Baeyer to be bimolecular.

Pinene benzylnitrolamine gave in my laboratory by the cryoscopic method the value 371 for the molecular weight, whilst the formula $C_{10}H_{16} \cdot NO \cdot NH \cdot C_7H_7$ corresponds with 272.

On the other hand, the piperidynitrolamine gave in one series of experiments 215, 209, and 214 as the value of the molecular weight. A second specimen gave 196 and 212. The simple formula $C_{10}H_{16} \cdot NO \cdot NC_5H_{10}$ corresponds with 250.

Determinations of the molecular weight of the nitrosocyanide (Tilden and Burrows, Proc., 1902, 18, 161) gave 188 and 189, the formula $C_{10}H_{16} \cdot NO \cdot CN$ requiring 192.

Hence it appears that when in the nitrosochloride the chlorine is replaced by cyanogen or by the piperidine residue, the compound becomes monomolecular and reacts as an oxime. The chlorine in the nitrosochloride therefore controls the hydrogen of the secondary carbon to which the NO group is attached, preventing the formation of the *isonitroso*-compound.

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