XLI.—*Pinene isoNitrosocyanide and its Derivatives.*

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A BRIEF description of the cyanide and some of its reactions has been given in the "Preliminary notice of some new derivatives of pinene and other terpenes," by the same authors (Proc., 1902, 18, 161).

Pinene isoNitrosocyanide.—In order to prepare this compound, a number of flasks are each charged with 20 grams of pinene nitrosochloride, 8 grams of finely-powdered potassium cyanide, and 75 c.c. of alcohol (84 per cent.), and the mixture left at the ordinary temperature with frequent shaking for at least twenty-four hours. Eight grams of cyanide and 30 c.c. of alcohol are then added, and the mixture slowly heated to the boiling point and kept at that temperature until the reaction is finished. Sufficient heat is developed to keep the alcohol boiling for a few minutes. The mixture is then poured into about six times its volume of cold water and left for a few hours. The nitrosocyanide is precipitated, and may be purified by crystallisation from alcohol. The nitrosochloride yields rather less than half its weight of the cyanide. The by-products are viscid and do not crystallise even after long standing.

This compound crystallises in thick, colourless prisms which melt at 171° . When crystallised from ether and occasionally from other solvents, it readily yields large, transparent prisms, which exhibit triboluminescence in a remarkable degree. On decanting the mother liquor from the crystals, flashes of light accompanied by a crackling sound were several times noticed. These phenomena seem to be dependent on the size and transparency of the crystals. The opaque crystals which are often formed give no flash when crushed.

This nitrosocyanide is soluble in dilute alkali, and is unchanged by boiling with a concentrated solution of caustic potash, being precipitated unaltered on addition of an acid. Boiled with dilute hydrochloric acid, it yields hydroxylamine and uncrystallisable products. It behaves as a saturated compound towards bromine, and is not oxidised by alkaline permanganate. The nitrosocyanide and its derivatives are optically inactive.

0.1948 gave 0.4916 CO_2 and 0.1436 H_2O . $\text{C} = 68.83$; $\text{H} = 8.19$.

0.2220 „ 28.4 c.c. moist nitrogen at 24° and 766 mm. $\text{N} = 14.47$.

$\text{C}_{11}\text{H}_{16}\text{ON}_2$ requires $\text{C} = 68.75$; $\text{H} = 8.33$; $\text{N} = 14.58$ per cent.

Dissolved in benzene, it gave by the cryoscopic method a molecular weight 188, whilst the formula $\text{C}_{10}\text{H}_{15}(\text{:NOH})\cdot\text{CN}$ corresponds with 192.

The only compound of the kind which appears to have been investigated is the cyanide obtained by Wallach from amylene nitrosate (*Annalen*, 1888, **248**, 164). That compound is, however, fairly easily hydrolysed by caustic potash, yielding the corresponding amide and acid. This difference of behaviour can only be attributed to the difference of constitution of the parent hydrocarbons, amylene being an open chain, whilst pinene has a cyclic structure. In both compounds, the oxime and nitrile groups are in the ortho position relatively to each other.

Methyl Ether of Pinene isonitrosocyanide.—Five grams of pinene isonitrosocyanide, 2 grams of caustic soda, and 5 grams of methyl iodide were dissolved in 100 c.c. of methyl alcohol and boiled for six hours. After evaporation of the alcohol, the residue was washed with water and crystallised from petroleum. Large, colourless prisms were obtained melting at 67°.

0.2611 gave 31.4 c.c. moist nitrogen at 19° and 750 mm. $N = 13.64$.

$C_{12}H_{18}ON_2$ requires $N = 13.60$ per cent.

Benzoyl Ester.—Treated with benzoyl chloride and caustic soda, the cyanide yields a benzoyl derivative which, after crystallising from alcohol, melts at 102°.

Nitro-compound, $C_{10}H_{15}(NO_2)_2 \cdot CN$.—When pinene isonitrosocyanide is added to a cooled mixture of equal volumes of nitric acid (sp. gr. 1.42) and acetic anhydride, it dissolves with evolution of red fumes, and on diluting with water a compound is precipitated which may be crystallised from a mixture of ether and light petroleum. It melts at 105° with evolution of red fumes. This compound responds to Liebermann's test, but is insoluble in aqueous alkalis. The same compound is produced when gaseous nitrogen peroxide is passed into a cooled solution of the cyanide in chloroform.

0.1187 gave 0.2258 CO_2 and 0.0676 H_2O . $C = 51.87$; $H = 6.35$.

0.1241 „ 18.4 c.c. moist nitrogen at 17° and 757 mm. $N = 17.07$.

$C_{11}H_{15}O_4N_3$ requires $C = 52.17$; $H = 5.92$; $N = 16.60$ per cent.

Dissolved in benzene, it gave, by the cryoscopic method, the molecular weight 248: the above formula requires 254.

When the nitro-compound is reduced by zinc and acetic acid or by hydrogen sulphide, the original isonitrosocyanide is reproduced. Reduction by sodium and alcohol leads to the evolution of much ammonia and formation of pinylamine. These reactions appear to indicate that in the formation of this compound the oxime group is oxidised, and that the second nitro-group is attached to the same carbon atom as the first, $:C:N \cdot OH$ becoming $:C \begin{smallmatrix} \nwarrow NO_2 \\ \nearrow NO_2 \end{smallmatrix}$.

Pinene isoNitrosocarboxylamide, $C_{10}H_{15}(:NOH) \cdot CO \cdot NH_2$.—A solution of the cyanide in three to four times its weight of concentrated sulphuric acid, kept at a temperature about 80° for two hours, yields this compound, with little loss, on diluting the acid with water. The mother liquor gives a small additional quantity of the amide, and a small purple precipitate which is soluble in alcohol, forming a bright red solution. The amide crystallised from alcohol yields colourless prisms which melt at 220° with decomposition. The amide is slightly soluble in dilute alkali, but is unaltered by strong boiling caustic soda. It is soluble in concentrated hydrochloric acid, and is partly precipitated unchanged on dilution with water. It is unaffected by bromine or alkaline hypobromite.

- I. 0.1132 gave 0.2602 CO_2 and 0.0857 H_2O . C = 62.67; H = 8.41.
 II. 0.1712 „ 0.3943 CO_2 „ 0.1318 H_2O . C = 62.80; H = 8.55.
 III. 0.2629 „ 32.6 c.c. moist nitrogen at 24.5° and 767 mm.
 N = 13.78.
 IV. 0.1901 gave 22.7 c.c. moist nitrogen at 24° and 762 mm.
 N = 13.43.
 $C_{11}H_{18}O_2N_2$ requires C = 62.85; H = 8.57; N = 13.3.

Methyl Ether, $C_{10}H_{15}(:NO \cdot CH_3) \cdot CO \cdot NH_2$.—Prepared in the same manner as the ether of the cyanide, it crystallises from methyl alcohol in large, colourless prisms melting at 145° . The same compound is obtained when the caustic soda in the process is replaced by silver oxide.

- 0.1230 gave 14.4 c.c. moist nitrogen at 25° and 764 mm. N = 12.6.
 $C_{12}H_{20}O_2N_2$ requires N = 12.5 per cent.

Benzoyl Ester, $C_{10}H_{15}(:NO \cdot C_7H_5O) \cdot CO \cdot NH_2$.—This compound was prepared by the aid of benzoyl chloride and caustic soda in the usual manner. It forms colourless crystals which melt at 197° , and on saponification by means of alcoholic soda yield the unaltered amide. The benzoyl compound is incapable of interacting with methyl iodide and silver oxide.

- 0.1260 gave 10.6 c.c. moist nitrogen at 25° and 764 mm. N = 9.05.
 $C_{18}H_{22}O_3N_2$ requires N = 8.91 per cent.

Pinene *isonitrosocarboxylic acid* corresponding with the amide has not been obtained. When the amide is heated to 100° with about four times its weight of 20 per cent. hydrochloric acid, it dissolves, and after a time a viscid oil separates in considerable quantity. The acid solution evaporated to dryness leaves abundance of ammonium chloride mixed with unchanged amide. On distillation in steam, part of the oil passes over and forms a nearly colourless liquid which floats on

water and is very soluble in alkalis. It contains no nitrogen and appears to consist of the ketonic acid $\text{O}:\text{C}_{10}\text{H}_{15}:\text{CO}_2\text{H}$, which would result from the hydrolysis of both the amide and oxime groups. No crystalline compounds could be obtained from it, nor would it react with hydroxylamine in alkaline solution. It gives no colour with ferric chloride.

Pinene Carboxylic Amide Pseudoxime or Lactam.—When a solution of the amide in concentrated sulphuric acid is heated to 100° for about six hours, a further change occurs, and the colour of the solution darkens considerably. Care is necessary to avoid any rise of temperature above 100° , otherwise the product is destroyed with evolution of sulphur dioxide. On diluting the liquid with water and neutralising with ammonia, crystals are deposited which, after recrystallisation from alcohol, melt at 209° . This compound has the same composition as the amide, together with a molecule of water of crystallisation. It is insoluble in cold alkali, but on boiling with concentrated solution of caustic soda it gradually dissolves, while ammonia is evolved. It gives no methyl derivative.

- I. 0.1274 gave 0.2672 CO_2 and 0.1014 H_2O . $\text{C} = 57.3$; $\text{H} = 8.86$.
 II. 0.1670 „ 0.3564 CO_2 „ 0.1304 H_2O . $\text{C} = 58.2$; $\text{H} = 8.67$.
 III. 0.1572 „ 17 c.c. moist nitrogen at 16° and 769 mm. $\text{N} = 12.75$.
 IV. 0.1736 at 110° lost 0.0142, and 0.2294 at 110° lost 0.0186.
 $\text{H}_2\text{O} = 8.1$ and 8.1 .
 $\text{C}_{11}\text{H}_{18}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{O}$ requires $\text{C} = 57.9$; $\text{H} = 8.7$; $\text{N} = 12.28$; $\text{H}_2\text{O} = 7.9$
 per cent.

Pinene Carboxylic Acid Pseudoxime or Lactam.—This compound is obtained by boiling the amide just described with concentrated aqueous solution of caustic soda till evolution of ammonia ceases, then neutralising with hydrochloric acid. The acid recrystallised from alcohol forms small, colourless prisms which contain water of crystallisation and melt at 220° . Its alkali salts are very soluble in water.

The acid does not react with hydroxylamine in alkaline solution.

- I. 0.2012 heated at 110° lost 0.0156. $\text{H}_2\text{O} = 7.75$.
 II. 0.1850 gave 0.3870 CO_2 and 0.1373 H_2O . $\text{C} = 57.05$; $\text{H} = 8.25$.
 III. 0.1059 „ 0.2210 CO_2 „ 0.0796 H_2O . $\text{C} = 56.92$; $\text{H} = 8.35$.
 IV. 0.1678 „ 9.0 c.c. moist nitrogen at 18° and 765 mm. $\text{N} = 6.24$.
 $\text{C}_{11}\text{H}_{17}\text{O}_3\text{N} \cdot \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 7.86$; $\text{C} = 57.6$; $\text{H} = 8.29$; $\text{N} = 6.11$
 per cent.

0.4829 titrated with $N/10$ caustic soda required for its neutralisation 20 c.c., corresponding with 0.800 NaHO , instead of 0.843 as required by theory.

Salts.—The acid suspended in absolute alcohol and saturated with

ammonia gas dissolves, and the solution by spontaneous evaporation leaves flat prisms of the ammonium salt. The ammonium salt, dissolved in water and mixed with the calculated amount of silver nitrate, gives the silver salt as a white, crystalline precipitate which is somewhat sensitive to light.

0.3214 gave on heating 0.1088 of silver corresponding with 33.85 per cent. : $C_{11}H_{16}O_3NAg$ requires $Ag = 33.96$.

The methyl ester was prepared from the silver salt by action of methyl iodide diluted with ether. It melts at 132° .

0.1190 gave 6.8 c.c. moist nitrogen at 23° and 756 mm. $N = 6.37$.

$C_{12}H_{19}O_3N$ requires $N = 6.22$ per cent.

When the acid is heated to about 120° with 20 per cent. hydrochloric acid, a colourless solution is formed, which, on evaporation to dryness, gives a white, crystalline residue soluble in water. No gas is evolved on opening the tube. The compound crystallises from water in long prisms, and was found to consist of the hydrochloride of an amino-acid.

After drying at 100° , the crystals, by direct titration with silver nitrate, were found to contain 13.64 per cent. of chlorine. The formula $C_{11}H_{19}O_4N.HCl$ requires $Cl = 13.37$ per cent.

An attempt to obtain this compound by heating the amide, instead of the acid, with hydrochloric acid failed, as only uncrystallisable products were formed. This amino-acid is now undergoing investigation.

Theoretical.

Pinene being represented by the following expression,

the nitrosochloride and compounds derived from it may be represented by the following formulæ :

Amide pseudoxime (m. p. 209°),

Acid pseudoxime (m. p. 220°),

The amino-acid is derived therefrom by opening the ring, thus :

It is hoped that the further study of the products of this change may throw light on the constitution of pinene.

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