LXXXVI.—*The Action of Magnesium Methyl Iodide on Pinene Nitrosochloride.*

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WITH the object of further studying pinene nitrosochloride and the circumstances in which the nitroso-derivatives of pinene retain the bimolecular constitution, it was thought that some interest would attach to the replacement of the chlorine of the nitrosochloride by an alkyl group. For this purpose, the use of Grignard's reagent at once suggested itself, and the anticipated reaction has been accomplished. The resulting oxime possesses well developed basic properties, as it readily forms a stable hydrochloride. The proportions of materials employed and the conditions of experiment have been varied in successive operations, but the yield of the oxime remains very small, amounting to less than 10 per cent. of the nitrosochloride used. The by-products are chiefly uncrystallisable and become brown on exposure to the air. They include, however, a notable quantity of an interesting saturated base produced by the interaction of the magnesium alkyl iodide with the oxygen of the nitroso-group, the chlorine of the nitrosochloride remaining undisturbed. The products are represented by the following formulæ :

The unimolecular constitution of this base appears to dispose of any idea that the two molecules of which the nitrosochloride consists are united by the chlorine as well as by the nitroso-group present in each. If the chlorine atoms formed a part of the link it might be expected that the base, which retains the chlorine atom, would be similarly bimolecular.

The chlorinated base readily parts with the elements of hydrogen

chloride, yielding an unsaturated base which is identical with dimethylpinylamine,

It is remarkable that the chlorine of the chlorinated base is not exchangeable for methyl by the further action of the magnesium methyl iodide used in excess, even at a temperature exceeding 100° . This is a further example of the mutual influence of the groups occupying the ortho-position in these compounds, which is indicated also by the effect produced by the chlorine atom in preventing the conversion of the neighbouring nitroso-group into the oxime form (compare *Trans.*, 1904, 85, 764).

EXPERIMENTAL.

A solution of magnesium methyl iodide in ether was first prepared by mixing together 3.5 grams of magnesium powder, 25 grams of methyl iodide, and 75 c.c. of dry ether. The clear solution was then added in small quantities to 15 grams of pinene nitrosochloride made into a thin paste with dry ether. After standing at the ordinary temperature some twelve hours, the mixture was heated to the boiling point of the ether for about an hour. A small quantity of alcohol was then added, and the precipitated magnesium hydroxide dissolved by adding a strong aqueous solution of ammonium chloride. After evaporating off the ether, the residual viscid substance was washed with cold water and was then redissolved in ether and shaken in a separating funnel with a small quantity of very dilute hydrochloric acid. The ethereal and acid solutions were then separated. The former on addition of light petroleum gave a white, crystalline precipitate which proved to be the oxime.

The acid solution, rendered slightly alkaline by caustic potash and extracted with ether, yielded large, thick, rhombic prisms melting at 122° and consisting of the chlorinated base.

The by-products from both ethereal solutions were viscid and yellow substances, darkening on exposure to the air, from which nothing definite could be obtained.

The Oxime, $\text{C}_{10}\text{H}_{15}(\text{CH}_3):\text{NOH}$.

The oxime was readily soluble in cold alcohol, ether, benzene, acetone, ethyl acetate, and chloroform, but almost insoluble in petroleum even when hot. After recrystallisation from a mixture of chloroform and petroleum, it was obtained in prismatic needles melting at 193° .

0·2026 gave 13·9 c.c. moist nitrogen at 21° and 768 mm. $N = 7·94$.

$C_{11}H_{19}ON$ requires $N = 7·73$ per cent.

0·0310 in 13·2 benzene gave $\Delta t = 0·06^\circ$. M. W. = 191.

0·0858 " " " $\Delta t = 0·17^\circ$. M. W. = 187.

The unimolecular formula $C_{11}H_{19}ON$ requires 181.

This compound is soluble in warm dilute caustic potash, also in warm dilute hydrochloric acid, yielding a definite hydrochloride which, after recrystallisation from alcohol, gave the following results :

0·2112 gave 0·1402 AgCl. $Cl = 16·42$.

$C_{11}H_{19}ON, HCl$ requires $Cl = 16·32$ per cent.

The *benzoyl* derivative, prepared by the conjoint action of benzoyl chloride and caustic potash solution, crystallises from petroleum in plates which melt at 118°.

The *methyl ether*, $C_{10}H_{15}(CH_3)NO \cdot CH_3$, was obtained by boiling the oxime dissolved in methyl alcohol with methyl iodide and caustic potash. On pouring the solution into water, the ether was precipitated and was crystallised from methyl alcohol ; it forms small, prismatic needles which melt at 62°.

0·2112 gave 13·7 c.c. moist nitrogen at 21° and 769·5 mm. $N = 7·48$.

$C_{12}H_{21}ON$ requires $N = 7·18$ per cent.

Action of Acids on the Oxime.

Two grams, heated in a sealed tube with excess of 20 per cent. hydrochloric acid for about two hours, gave a solution which reduced Fehling's solution, and when submitted to steam distillation gave a sweet-scented oil. The quantity was insufficient for detailed study, but obviously consisted of the corresponding ketone. This was confirmed by mixing it with hydroxylamine and caustic soda, with the addition of a little alcohol, when, after some time, needles of the original oxime were deposited.

The oxime dissolves in warm concentrated sulphuric acid with production of a red colour, which, on admixture of water, disappears, and a precipitate is formed of the original oxime.

Examination of the Chlorinated Base.

The chloro-base was analysed after crystallisation from ether.

0·1564 gave 0·3820 CO_2 and 0·1460 H_2O . $C = 66·44$; $H = 10·36$.

0·0951 gave 0·0634 AgCl. $Cl = 16·51$.

0·2340 gave 14·0 c.c. moist nitrogen at 22° and 754·5 mm. $N = 6·73$.

$C_{12}H_{22}NCl$ requires $C = 66·82$; $H = 10·20$; $Cl = 16·47$; $N = 6·50$ per cent.

0.0708 in 12.9 benzene gave $\Delta t = 0.12^\circ$. M. W. = 224.1.

0.1362 „ „ „ $\Delta t = 0.23^\circ$. M. W. = 224.9.

The unimolecular formula $C_{12}H_{22}NCl$ requires M. W. = 215.5.

With the object of obtaining the base $C_7H_{12} \begin{smallmatrix} < C(CH_3)_2 \\ | \\ CHN(CH_3)_2 \end{smallmatrix}$, which would result from the exchange of the chlorine for a methyl group, the pure chloro-base, dissolved in ether, was mixed with an excess of magnesium methyl iodide. It was found, however, that no interaction occurred either at the ordinary temperature or at the boiling point, or when the temperature of ebullition was raised to 60° by addition of toluene. A fresh ethereal solution of the base and reagent, sealed up and heated to about 110° , deposited a liquid and a small quantity of viscid matter, but nothing could be obtained from the product except a minute quantity of volatile alkaline matter, which was too small in amount to permit of its separation from the brown, viscous substances chiefly produced.

The *hydrochloride*, which was prepared by dissolving the base in ether and passing hydrogen chloride into the solution, forms small needles.

0.2887 required 11.6 c.c. of standard silver nitrate, of which 1 c.c. = 0.003548 Cl. Cl = 14.29 per cent.

$C_{12}H_{22}NCl, HCl$ requires Cl (of HCl) = 14.14 per cent.

Action of Alcoholic Potash on the Base.

Five grams of the chlorinated base dissolved in alcohol were boiled with 1.5 grams of caustic potash until the reaction was completed as indicated by the precipitation of potassium chloride. On adding to the liquid a small quantity of water, colourless crystals separated out, which, after recrystallisation from diluted alcohol, melted at 112° .

0.2038 gave 14.2 c.c. of moist nitrogen at 25° and 761 mm. N = 7.83.

$C_{12}H_{21}N$ requires N = 7.82 per cent.

The *hydrochloride* of this *unsaturated base* was obtained in the form of small, white needles by dissolving the base in ether and passing dry hydrogen chloride into the solution.

0.2009 required 9.4 c.c. $N/10$ $AgNO_3$. Cl = 16.59.

0.2742 „ 12.8 c.c. $N/10$ $AgNO_3$. Cl = 16.56.

$C_{12}H_{21}N, HCl$ requires Cl = 16.47 per cent.

As this base was presumably identical with dimethylpinylamine, it was thought probable that it would yield a nitrate more or less resembling the nitrate of pinylamine, which is distinguished by its

slight solubility in water; this was found to be the case. The unsaturated base, dissolved in the smallest possible quantity of hydrochloric acid, gives, on the addition of a solution of sodium nitrate, a precipitate of small prisms which resemble the pinylamine nitrate in solubility.

In order to compare the new base with dimethylpinylamine, which has not hitherto been described, six grams of pinylamine were dissolved in methyl alcohol and heated with an excess of methyl iodide at 100° for some hours. After evaporating off the excess of methyl iodide, the liquid was poured into dry ether. A white, crystalline precipitate of the hydriodide was deposited, whilst the mother liquor retained a yellow, viscid oil.

The hydriodide is very soluble in water and gave an immediate precipitate with silver nitrate.

0.2168 gave 0.1664 AgI. $I = 41.40$.

$C_{12}H_{21}N, HI$ requires $I = 41.43$ per cent.

The nitrate was prepared by adding a concentrated solution of sodium nitrate to a solution of the hydriodide.

0.1485 gave 15.0 c.c. moist nitrogen at 19° and 765 mm. $N = 11.87$.

$C_{12}H_{21}N, HNO_3$ requires $N = 11.57$ per cent.

Dimethylpinylamine.

On dissolving the hydriodide in water and adding caustic potash, the base is precipitated as a white, crystalline solid. Dimethylpinylamine crystallises from ether in small prisms which melt at 112° and which, when mixed with the unsaturated base described above, cause no depression of the melting point. Hence the identity of the two substances may be regarded as established.

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