CLV.—*The Preparation and Properties of Dihydropinylamine (Pinocamphylamine).*

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THE chief product of the reduction of nitrosopinene by the action of zinc and acetic acid is pinyllamine which was first obtained by Wallach and Lorentz (*Annalen*, 1892, 268, 197). In addition to pinyllamine, however, there is always formed a saturated ketone, pinocamphone, $C_{10}H_{16}O$, isolated for the first time and studied by J. A. Smythe (*Inaug. Diss. Göttingen*, 1898, 16), who obtained a yield corresponding to 22 per cent. of the nitrosopinene employed. The oxime derived from this ketone has been described by Wallach (*Annalen*, 1898, 300, 286) and the product of its reduction by alcohol and sodium is the saturated base dihydropinylamine, or, as it is called by Wallach, pinocamphylamine (*Annalen*, 1900, 313, 367). Assuming G. Wagner's formula for pinene, the following expressions represent the course of these changes and the constitution of pinocamphylamine:

Smythe (*loc. cit.*, 36) attempted the direct reduction of pinyllamine by means of amyl alcohol and sodium, but without much success, the amount of the saturated base obtained being too small for complete purification. Wallach contented himself with preparing and analysing the carbamide (m. p. 204°) and the acetyl compound (m. p. 120°).

We find that dihydropinylamine may be prepared easily and in con-

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siderable quantity by the direct reduction of nitrosopinene by means of boiling amyl alcohol and sodium, or even by the use of ethyl alcohol and sodium, although in the latter case the yield is much smaller.

Preparation of Dihydropinylamine and its Hydrochloride.—Twenty grams of nitrosopinene were dissolved in boiling amyl alcohol and 24 grams of sodium added in small pieces. After the dissolution of the metal, hydrochloric acid was added in slight excess and the amyl alcohol distilled off in steam. The residue was rendered strongly alkaline with potash, submitted to steam distillation, the distillate extracted with ether, and the base precipitated from the ethereal solution in the form of hydrochloride by passing in gaseous hydrogen chloride. In the most successful experiments, 80 per cent. of the theoretical amount of hydrochloride was obtained.

The hydrochloride is sparingly soluble in water, easily so in alcohol, and crystallises in silky needles which melt and decompose at a temperature above 300°. It sublimes readily and is saturated.

Crystallised from water, the hydrochloride was found to contain two molecules of water of crystallisation. The results of analysis were as follows:

C = 52.98; H = 10.95; N = 6.54; Cl = 15.36; H_2O (at 110°) = 16.28.

$C_{10}H_{17}NH_2 \cdot HCl \cdot 2H_2O$ requires C = 53.19; H = 10.72; N = 6.22;

Cl = 15.71; and H_2O = 15.95 per cent.

The hydrochloride precipitated from ether and recrystallised from alcohol was anhydrous. It contained Cl = 18.58, whilst $C_{10}H_{17}NH_2 \cdot HCl$ requires Cl = 18.69 per cent.

The free base is a colourless liquid boiling at 198—199°, having an odour very like that of pinylamine.

Platinichloride.—This compound crystallises from alcohol in glistening, orange-yellow plates, insoluble in water and only slightly soluble in cold alcohol or ether.

It contained Pt = 27.02, whilst $(C_{10}H_{17}NH_2)_2H_2PtCl_6$ requires Pt = 27.20 per cent.

Picrate.—This was prepared by dissolving the hydrochloride in warm dilute alcohol, and adding the requisite quantity of picric acid. It crystallises in plates which are moderately soluble in water and melt at 208°.

Analysed, it yielded C = 50.51 and H = 6.36.

$C_{10}H_{17}NH_2 \cdot C_6H_3(NO_2)_3OH$ requires C = 50.10 and H = 6.05 per cent.

Nitrate.—A small quantity of the base was dissolved in acetic acid and a saturated solution of sodium nitrate added. The crystals which were deposited were recrystallised from water, in which the salt is moderately soluble.

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The nitrate crystallises in prisms which are easily soluble in alcohol. On being heated it begins to decompose at 176° , and melts with evolution of gas at 180° . It was found to contain $N=12.90$; $C_{10}H_{17}NH_2 \cdot HNO_3$ requiring $N=12.98$ per cent.

Oxalate.—A hot concentrated solution of oxalic acid was added to a dilute alcoholic solution of the base. The salt crystallises in small plates which are only slightly soluble in cold water. It melts at 275° .

Analysed, it gave $N=7.21$, whilst $(C_{10}H_{17}NH_2)_2 \cdot H_2C_2O_4$ requires $N=7.08$ per cent.

Acetyl Derivative.—This was prepared by warming the base with acetic anhydride for about an hour and pouring the product into water. The solid which separated crystallised from petroleum in fine needles which melted at $108-110^{\circ}$, and, although recrystallised several times, could not be obtained with a higher melting point. The melting point of acetyl pinocamphylamine is stated by Wallach to be 120° (*Annalen*, 1900, 313, 368).

Analysis gave $N=7.55$, whilst $C_{10}H_{17} \cdot NH \cdot CO \cdot CH_3$ requires $N=7.19$ per cent.

Benzoyl derivative, prepared by the use of benzoyl chloride and potassium hydroxide, crystallises from alcohol in clusters of needles and melts at 144° .

The benzoyl compound, prepared from the base made from pinocamphone, melts at 144° , and a mixture of the two benzoyl compounds also melts at the same temperature.

Analysis gave $N=5.55$, $C_{10}H_{17} \cdot NH \cdot CO \cdot C_6H_5$ requiring $N=5.46$ per cent.

Carbamide.—The hydrochloride of the base mixed with an aqueous solution of potassium cyanate was warmed on the water-bath until the compound separated out. From dilute alcohol it crystallises in fine needles which melt at 204° , the melting point of the pinocamphyl urea prepared by Wallach.

Analysis gave $N=14.22$, whilst $C_{10}H_{17} \cdot NH \cdot CO \cdot NH_2$ requires $N=14.30$ per cent.

From the comparison of the benzoyl derivative and the carbamides, there can be no doubt about the identity of the base prepared by the direct reduction of nitrosopinene with that obtained through the intermediate steps represented by pinocamphone and its oxime. This is further shown by the production of the alcohol from dihydropinylamine and comparison with pinocampeol obtained by reduction of

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pinocamphone by sodium in the presence of moist ether (Smythe, *loc. cit.*, 21). From dihydropinylamine it was obtained by warming an aqueous solution of the hydrochloride of the base with the calculated quantity of sodium nitrite. The yellow oil which was precipitated was separated by steam distillation, dried, and distilled under reduced pressure. The boiling point at 15 mm. was found to be 103°, that of pinocampeol at the same pressure being, according to Smythe, 104—105°.

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