LXVII.—*Studies in the Camphane Series. Part II.*
Nitrocamphene, Aminocamphene, and Hydroxycamphene.

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AMONG the changes which 1:1-bromonitrocamphane is capable of undergoing, not the least interesting is that which involves the removal of hydrogen bromide. By this means there is produced an unsaturated nitro-compound, which, in accordance with the suggestion made in a previous paper (Trans., 1900, 77, 251), will be called 1-nitrocamphene.

The noteworthy point in a study of this compound is the fact that its production lays open a way to hydroxycamphene, the enolic modification of camphor, and the present communication gives an account of the steps by which hydroxycamphene has been obtained.

Owing to the susceptibility of camphene to the action of oxidising agents, nitro-derivatives of this hydrocarbon have been hitherto unknown, the nearest approach to compounds of that type being camphene

nitronitrosite, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C}(\text{NO}) \cdot \text{NO}_2 \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{NO}_2 \end{array}$, and camphene nitrosite,

obtained by Jagelki from camphene and nitrous acid (*Ber.*, 1899, 32, 1498). These, however, being saturated, are not genuine camphene derivatives, but belong rather to the camphane series. The first representative of the nitrocamphenes has been prepared by heating an alcoholic solution of 1:1-bromonitrocamphane with silver nitrate. Although melting at 56°, the substance displays extraordinary readiness to crystallise; it is an unsaturated compound, yielding additive derivatives with bromine, hydrogen iodide, and hydrogen bromide. As might be anticipated, the last-named gives rise to a bromonitrocamphane which is distinct from 1:1-bromonitrocamphane, and as it yields neither camphoroxime nor bornylamine on reduction, must have the constitution of a 2-bromo-1-nitrocamphane, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CHBr} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{NO}_2 \end{array}$.

When 1-nitrocamphene is heated with zinc dust and glacial acetic acid, the nitro-group alone is reduced, and the unsaturated link remaining unaltered, 1-aminocamphene is obtained. This base is not the first of the aminocamphenes. Duden and Macintyre (*Annalen*, 1900,

313, 59) have recently prepared 2-aminocamphene, or camphenamine; through the agency of phosphorus pentachloride, they replaced the hydroxyl in aminoborneol by chlorine, and obtained camphenamine from the product by the action of caustic soda.

1-Aminocamphene is quite distinct from camphenamine. It is a translucent solid which melts at 46° and boils at $191\text{--}192^\circ$ under atmospheric pressure; unlike the isomeride, it is strongly dextro-rotatory. When it is heated with acetic anhydride, camphor is produced, a result which must be due to a capacity, also exhibited by camphene itself, for assimilating the elements of acetic acid:

The chief interest attaching to 1-aminocamphene is due to its conversion into 1-hydroxycamphene under the influence of nitrous acid. When the sulphate of the base, dissolved in water, is heated with potassium nitrite, nitrogen is liberated, and the hydroxy-compound is produced. The substance crystallises in long needles, has a faint, camphor-like odour, and melts at 74° ; although indifferent towards alkalis, warm dilute mineral acids convert it immediately into ordinary camphor yielding an oxime of normal rotatory power.

The complete cycle of changes by which camphor has been converted into the tautomeric hydroxy-compound and then regenerated from the latter is represented by the following formulæ:

Hydroxycamphene is an unexpectedly stable substance, and shows no tendency to change into camphor excepting under the influence of acids. It may be distilled under atmospheric pressure without suffer-

ing alteration, and, unlike the enolic modifications of diketones or of ketonic esters, is quite indifferent towards ferric chloride.

In view of these peculiarities, the substance and its derivatives are being subjected to further investigation.

EXPERIMENTAL.

One hundred grams of 1:1-bromonitrocamphane were dissolved in 1000 c.c. of absolute alcohol and heated in a reflux apparatus with 110 grams of powdered silver nitrate, which was added in quantities of 10 grams at intervals of about 2 hours. Twice before the operation was complete the liquid was filtered from silver bromide, and when the clear solution no longer became turbid on being heated alone, alcohol was boiled off by means of a water-bath. The viscous oil remaining in the flask was then distilled in a current of steam, yielding a colourless, crystalline substance which was readily fusible, and very volatile in steam. The product was filtered, drained on porous earthenware, and treated with a very small quantity of cold alcohol, in which the crude material was freely soluble; the alcohol removed an oily by-product, and when the solid had been filtered from this, it became safe to dissolve it in a small quantity of hot alcohol, from which it crystallised readily on cooling. The yield of nitrocamphene is disappointing, and is liable to wide fluctuations if the foregoing process is not followed closely, but under favourable circumstances 35 grams of the recrystallised nitro-derivative may be obtained from 100 grams of bromonitrocamphane, scarcely more than 50 per cent. of the theoretical amount.

It will be noticed that the quantity of silver nitrate employed in the preparation of nitrocamphene considerably exceeds the amount required by the equation

it approaches, indeed, two molecular proportions, but experiment has shown that a result of using smaller quantities is the contamination of the product with unchanged bromonitrocamphane. Doubtless the excess of silver nitrate in part explains the diminution in yield, as it probably exerts an oxidising action. The same effect is of course produced by the nitric acid set free; the latter is largely appropriated by the alcohol, which becomes converted into ethyl nitrite, but as 100 grams of bromonitrocamphane liberate 24 grams of nitric acid, a considerable portion of the product must suffer oxidation. An attempt has been made to overcome this difficulty by the employment of silver oxide or silver acetate, but neither of these substances lends itself to

the removal of hydrogen bromide from bromonitrocamphane; both, it is true, are converted into silver bromide, but the change is so slow, and so far from complete, as to offer no hope of economising silver by this modification of the process. Another reason for the large excess of silver nitrate required in practice is revealed by the fact that a certain amount leaves the solution without precipitating the bromide, but merely combined with that salt. In the earlier experiments, it was customary to add the silver nitrate in quantities of 20—30 grams, until it was noticed that the precipitate differed from silver bromide in appearance; on examination, it proved to consist of the molecular compound of silver bromide with silver nitrate.

Nitrocamphene dissolves readily in hot alcohol, crystallising in long, hard, striated prisms resembling α -bromocamphor; it melts at 56° , and boils under atmospheric pressure without undergoing alteration, but although so readily fusible, its tendency to crystallise is unusually pronounced. On analysis:

0.1517 gave 0.3702 CO_2 and 0.1130 H_2O . $\text{C} = 66.55$; $\text{H} = 8.28$.

$\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{C} = 66.29$; $\text{H} = 8.28$ per cent.

It is quite colourless, and has a faint odour which becomes very intense when the vapour is carried off with steam, then resembling that of 1:1-bromonitrocamphane; the substance is insoluble in water, but dissolves very readily in cold benzene, petroleum, chloroform, or ethyl acetate. It gives Liebermann's reaction for nitroso-derivatives.

A solution containing 0.5062 gram of nitrocamphene in 25 c.c. of absolute alcohol at 21° gave $\alpha_D + 4.32'$ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D + 112.0^\circ$; 1 gram dissolved in 25 c.c. of benzene at 21° gave $\alpha_D + 11.0'$ in the same tube, corresponding to $[\alpha]_D + 137.5^\circ$.

Nitrocamphene undergoes no change when treated with boiling acetic anhydride in a reflux apparatus during several hours.

Twenty c.c. of fuming hydrobromic acid (sp. gr. 1.83) were placed in a large, wide mouthed weighing bottle, and 5 grams of finely powdered nitrocamphene were quickly added to the liquid, which was stirred thoroughly during the operation. No rise of temperature took place, but the suspended solid soon hardened and became compact. After a couple of hours, during which the substance was thoroughly incorporated with the acid, a considerable quantity of water was added, and the filtered product was washed several times.

2-Bromo-1-nitrocamphane crystallises from alcohol in fern-like

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aggregates of white needles, and melts at 178° to a colourless liquid which evolves gas. On analysis :

0.1875 gave 0.1368 AgBr. Br = 31.05.

$C_{10}H_{16}O_2NBr$ requires Br = 30.53 per cent.

In appearance the substance closely resembles 1:1-bromonitrocamphane, forming a tough, camphor-like mass when compressed; its odour, however, is scarcely perceptible, and it does not distil at all readily in steam. It gives Liebermann's reaction, and the alcoholic solution immediately yields a precipitate of silver bromide when warmed with silver nitrate.

A solution containing 0.5089 gram dissolved in 25 c.c. of benzene at 21° gave $\alpha_D^{21} + 9'$ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D^{21} + 3.7^{\circ}$.

The behaviour of 2-bromo-1-nitrocamphane towards concentrated sulphuric acid at once differentiates it from the isomeride; whilst the latter loses the elements of water, and gives rise to the anhydride, $C_{10}H_{14}ONBr$ (Trans., 1899, 75, 1141), the new derivative merely dissolves in the acid, from which it is precipitated on dilution with water.

When a solution of bromine in chloroform is added to nitrocamphene in the same solvent, the colour of the halogen persists, but if left in contact with the nitro-derivative during several hours, the bromine is gradually absorbed.

Five grams of nitrocamphene were dissolved in dry chloroform and cooled by immersion in melting ice; 4.5 grams of bromine dissolved in 20 c.c. of the solvent were then added, and the mixture allowed to remain in a stoppered bottle during 24 hours. The crystalline residue obtained on evaporating the chloroform was drained on porous earthenware and recrystallised twice from alcohol, which deposited long, flat, transparent needles melting at 195° to a colourless liquid evolving gas. On analysis :

0.1388 gave 0.1523 AgBr. Br = 46.69.

$C_{10}H_{15}O_2NBr_2$ requires Br = 46.91 per cent.

Dibromonitrocamphane dissolves very readily in cold chloroform, benzene, or ethyl acetate, but is only sparingly soluble in hot petroleum or cold alcohol; it gives Liebermann's reaction, but much less readily than the mono-halogen derivatives of nitrocamphane, requiring to be heated with the acid during a longer period than usual.

A solution containing 0.4942 gram dissolved in 25 c.c. of benzene at 19° gave $\alpha_D + 10'$ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D + 4.2^\circ$.

When left in contact with fuming hydriodic acid (sp. gr. 1.94) during 2 hours, nitrocamphene becomes completely converted into 2-iodo-1-nitrocamphane. This compound, after being washed thoroughly with water and twice crystallised from the minimum quantity of hot alcohol, forms lustrous, thin plates, which begin to darken at 100°, and melt to a deep brown liquid at 118°. On analysis:

0.2019 gave 0.1507 AgI. $I = 40.33$.

$C_{10}H_{16}O_2NI$ requires $I = 41.10$ per cent.

The compound is quite distinct from 1:1-iodonitrocamphane in appearance, but is quite as unstable; solutions of the substance in organic media spontaneously undergo change, a solution in benzene, for instance, becoming violet after an interval of a few hours. It is readily soluble in benzene and in ethyl acetate, being more sparingly soluble in alcohol; it is important to recrystallise the substance as quickly as possible in order to avoid loss. It gives Liebermann's reaction for nitroso-derivatives.

A solution containing 0.3557 gram dissolved in 25 c.c. of absolute alcohol at 20° gave $\alpha_D - 1.0'$ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D - 35.1^\circ$; 0.3676 gram dissolved in 25 c.c. of benzene at 18° gave $\alpha_D - 52'$ in the same tube, corresponding to $[\alpha]_D - 29.4^\circ$.

Twenty-five grams of recrystallised nitrocamphene were dissolved in 250 c.c. of glacial acetic acid to which 50 grams of zinc dust were then added. After remaining surrounded with cold water during 1 hour, the liquid was heated in boiling water during 2 hours, filtered from zinc, diluted with water, evaporated on the water-bath, and finally submitted to a current of steam, which carried over a small quantity of unaltered nitrocamphene. A concentrated solution of 75 grams of caustic soda in water was then added to the liquid, and the oil which rose to the surface was distilled in a current of steam. The base being somewhat soluble in cold water, concentrated potash was added to the aqueous distillate, which was then extracted with ether the solution was dried with solid potash, and evaporated, the residue being distilled under the ordinary pressure.

1-Aminocamphene is a translucent solid closely resembling camphene in appearance. It melts at 46° , and boils at $191\text{--}192^{\circ}$ under 758 mm. pressure; the odour resembles that of bornylamine, but is more distinctly ammoniacal. On analysis:

0.1773 gave 0.5179 CO_2 and 0.1767 H_2O . $\text{C} = 79.55$; $\text{H} = 11.07$.

$\text{C}_{10}\text{H}_{17}\text{N}$ requires $\text{C} = 79.47$; $\text{H} = 11.25$ per cent.

A solution containing 0.4453 gram dissolved in 25 c.c. of absolute alcohol at 22° , gave $\alpha_D + 2^{\circ} 7.5'$ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D + 59.7^{\circ}$; 0.4803 gram dissolved in 25 c.c. of benzene at 22° gave $\alpha_D + 1^{\circ} 40'$ in the same tube, corresponding to $[\alpha]_D + 43.4^{\circ}$.

The base is strongly alkaline towards litmus, and does not reduce an ammoniacal solution of silver nitrate; it instantaneously decolorises a solution of bromine in chloroform, and rapidly reduces a neutral solution of potassium permanganate.

The *sulphate* dissolves readily in water, from which it crystallises in lustrous leaflets which melt and evolve gas at 256° .

The *platinichloride* dissolves very readily in alcohol, and crystallises slowly in large, transparent, six-sided plates, pale red in colour; it melts and decomposes at 243° .

0.3300 gave 0.0879 Pt. $\text{Pt} = 26.64$.

$(\text{C}_{10}\text{H}_{17}\text{N})_2\text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 27.32$ per cent.

$(\text{C}_{10}\text{H}_{17}\text{N})_2\text{H}_2\text{PtCl}_6 + \text{H}_2\text{O}$ „ $\text{Pt} = 26.65$ „

The *benzoyl* derivative, easily prepared by the Schotten-Baumann method, is readily soluble in benzene, chloroform, or alcohol, but only sparingly so in petroleum; it crystallises from the last named solvent in white, silky needles melting at 157° .

0.1721 gave 0.5032 CO_2 and 0.1266 H_2O . $\text{C} = 79.73$; $\text{H} = 8.17$.

$\text{C}_{17}\text{H}_{21}\text{ON}$ requires $\text{C} = 80.00$; $\text{H} = 8.23$ per cent.

The substance behaves as an unsaturated compound towards bromine, which it decolorises immediately. A solution containing 0.3701 gram dissolved in 25 c.c. of absolute alcohol at 18° , gave $\alpha_D + 55'$ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D + 30.9^{\circ}$.

The *benzylidene* derivative is produced immediately on mixing the fused base with benzaldehyde, when water separates, and the viscous liquid rapidly solidifies. It is purified by melting it with a small quantity of alcohol, draining on porous earthenware the crystals obtained on cooling the liquid, and recrystallising the product from hot alcohol, which deposits it in transparent, six-sided plates melting at 63° .

0.1630 gave 0.5137 CO_2 and 0.1297 H_2O . $\text{C} = 85.95$; $\text{H} = 8.84$.

$\text{C}_{17}\text{H}_{21}\text{N}$ requires $\text{C} = 85.35$; $\text{H} = 8.79$ per cent.

The *picrate* crystallises rapidly on mixing alcoholic solutions of picric acid and the base. It is sparingly soluble in cold alcohol, but dissolves readily in the hot liquid, from which it separates in lustrous, canary-yellow needles. The salt melts to a brown liquid at 231° , and immediately evolves gas.

0.1032 gave 13.1 c.c. nitrogen at 15.5° and 753 mm. $N = 14.73$.

$C_{16}H_{20}O_7N_4$ requires $N = 14.73$ per cent.

The *phenylcarbamide* is at once produced on mixing ethereal solutions of the base and phenylcarbimide in molecular proportion. It crystallises from boiling alcohol in lustrous, white needles and melts at 213° .

0.1546 gave 0.4285 CO_2 and 0.1158 H_2O . $C = 75.57$; $H = 8.32$.

$C_{17}H_{22}ON_2$ requires $C = 75.55$; $H = 8.15$ per cent.

Action of Acetic Anhydride on 1-Aminocamphene.—With the object of preparing an acetyl derivative, the base was heated with glacial acetic acid and acetic anhydride in a reflux apparatus during 8 hours, the liquid being then poured into water. After several days the precipitated oil solidified, and was found to dissolve freely in light petroleum, from which it crystallised in lustrous plates melting at 79° . When the acetic acid filtrate from this substance was exactly neutralised with potash and distilled in a current of steam, a considerable proportion of camphor was obtained; this yielded an oxime of which the melting point and specific rotatory power were identical with those of ordinary camphoroxime; the aqueous liquid from which the camphor was distilled yielded ammonia when treated with alkali.

In preparing hydroxycamphene from aminocamphene, advantage was taken of the experience gained by Duden and Macintyre in their attempt to obtain a new camphor from camphenamine (*loc. cit.*).

Twenty-five grams of aminocamphene sulphate were dissolved in 250 c.c. of ice-cold water, and treated with 5.3 grams of potassium nitrite dissolved in the minimum quantity of water. After remaining at the ordinary temperature during 12 hours, no change had taken place, and the liquid was therefore heated on the water-bath during 4 hours in a reflux apparatus; throughout this period, nitrogen was slowly evolved, and an oil separated. This was distilled in a current of steam, and the product, which rapidly crystallised in the condenser, was drained on porous earthenware and dried in the desiccator. Only 6 grams of hydroxycamphene were obtained, but the unaltered base was easily recovered from the residue in the distilling flask by adding alkali.

Hydroxycamphene has a faint odour recalling that of borneol or camphor, and becoming intensified to a pleasant, refreshing perfume when the substance is heated with water. It melts at 74° , and boils at 212° under 750 mm. pressure. It is much too freely soluble in organic media to crystallise easily from these, but when the fused substance is allowed to cool slowly, it solidifies in long, tough, striated needles. Owing to its volatility, some difficulty was experienced in analysing the substance.

0.1425 gave 0.4131 CO_2 and 0.1305 H_2O . $\text{C} = 79.06$; $\text{H} = 10.17$.

0.1641 „ 0.4779 CO_2 „ 0.1539 H_2O . $\text{C} = 79.42$; $\text{H} = 10.42$.

$\text{C}_{10}\text{H}_{16}\text{O}$ requires $\text{C} = 78.95$; $\text{H} = 10.52$ per cent.

A solution containing 1.0059 grams, dissolved in 25 c.c. of absolute alcohol at 19° , gave $\alpha_D + 2^{\circ}45'$ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D + 34.1^{\circ}$; 0.53 gram dissolved in 25 c.c. of benzene at 20° gave $\alpha_D + 1^{\circ}15'$ in the same tube, corresponding to $[\alpha]_D + 29.5^{\circ}$.

Hydroxycamphene is indifferent towards hydroxylamine and semicarbazide. It reduces cold potassium permanganate freely, although at first the action is slow, owing to the sparing solubility of hydroxycamphene in water; a solution in chloroform instantly decolorises bromine in the same solvent, but the first few drops only are absorbed, probably because the small quantity of hydrogen bromide produced is sufficient to convert the remaining hydroxycamphene into camphor. Contrary to expectation, hydroxycamphene does not develop a red coloration with ethereal or alcoholic solutions of ferric chloride, and is equally indifferent towards copper acetate; it is quite stable in presence of alkalis, but warm, dilute mineral acids transform it immediately into ordinary camphor.

Action of Sulphuric Acid on Hydroxycamphene.—One gram of hydroxycamphene was dissolved in 10 c.c. of ice-cold sulphuric acid, the solution being poured immediately on crushed ice. The precipitate was collected washed, and heated in alcohol with hydroxylamine hydrochloride and caustic soda; on evaporating the alcohol, diluting with water, neutralising with dilute sulphuric acid, and recrystallising from petroleum, a specimen of camphoroxime was obtained melting at 119° , and giving $[\alpha]_D - 40.2^{\circ}$ in absolute alcohol.

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