XV.—*Camphoroxime. Part I. Conversion of Camphoroxime into Methylcamphorimine and into Camphenylnitramine.*

By MARTIN ONSLOW FORSTER, Ph.D.

IN studying the properties of the methyl ether of camphoroxime—a substance which is readily obtained on heating the oxime in a reflux apparatus with sodium methoxide, methylic iodide, and methylic alcohol—it became of interest to ascertain whether ethers are produced under the direct influence of alkylic iodide on camphoroxime. The latter was therefore heated with methylic iodide in sealed tubes at temperatures above 100°, and it was found that, under these

circumstances, the product consisted of the hydriodide of a base, which proved to be the methyl derivative of camphorimine.

Camphorimine was first obtained by Tiemann on treating camphoroxime with nitrous acid (*Ber.*, 1895, 28, 1080), which gives rise simultaneously to camphorimine nitrate and camphenylnitramine. The identity of the product of the action of methylic iodide on camphoroxime with methylcamphorimine, which, according to Tiemann, has the constitution

was at once suggested by the conversion of the former into camphor and methylamine under the influence of concentrated hydrochloric acid at high temperatures, the point being placed beyond doubt by comparison with a specimen of the methyl derivative prepared directly from camphorimine by the method described in a recent paper by Mahla and Tiemann (*Ber.*, 1896, 29, 2809). As the examination of methylcamphorimine was almost completed when Mahla and Tiemann's paper appeared, and its properties have not yet been described, these are recorded in the present communication.

Although camphorimine is a comparatively unstable substance, which undergoes partial decomposition at its melting point (95°), and evolves ammonia when exposed to the air for a considerable period (*loc. cit.*), the methyl derivative, which boils at 203°, may be preserved indefinitely without change; as already stated, however, the base gives rise to camphor when heated with concentrated hydrochloric acid in sealed tubes, and the same change takes place when an acid solution of the hydrochloride is evaporated on the water bath. Camphor is also regenerated when an aqueous solution of methylcamphorimine methiodide is treated with cold, dilute caustic soda, or boiled with sodium carbonate; the quantity obtained in this way approximates to the theoretical proportion. Methylcamphorimine immediately decolorises bromine when the solution in chloroform is treated with the halogen in the same medium, an additive compound being formed. This behaviour, however, cannot be regarded as evidence of the unsaturated linking between carbon and nitrogen, because a solution of iodine gives rise to a similar product; moreover, the dibromide, obtained in the manner described, readily loses bromine when treated with warm, dilute hydrochloric acid, and is therefore most probably a perbromide in which both bromine atoms are attached to nitrogen.

It has been pointed out by Tiemann (*loc. cit.*) that the production of camphorimine and camphenylnitramine, by the action of nitrous acid on camphoroxime, admits of explanation on the assumption that the

nitrite of camphoroxime, $C_{10}H_{16} \cdot NOH, HNO_2$ —which is probably incapable of existence in the free state—constitutes the intermediate product of the change, and undergoes molecular rearrangement, yielding the nitrate of camphorimine, $C_{10}H_{16} \cdot NH, HNO_3$; the greater portion, on the other hand, loses the elements of water, and becomes converted into camphenylnitramine, $C_{10}H_{15} \cdot NH \cdot NO_2$. No simple explanation of the direct production of methylcamphorimine hydriodide by the action of methylic iodide on camphoroxime is apparent at present, and this curious result was certainly not anticipated at the time the experiments were undertaken; as expressed by the equation $C_{10}H_{16} \cdot NOH + CH_3I = C_{11}H_{19}N, HI + O$, one methylic group is introduced into the oxime, and an atomic proportion of oxygen eliminated from the product. I have been unable to meet with the record of any experiments in which oximes have been submitted to the direct action of alkylic iodides, excepting those of Luxmoore (*Trans.*, 1896, 69, 185), who obtained the hydriodide of benz-antialdoxime nitrogen methyl ether on heating the oxime with methylic iodide; attempts to apply this action to the preparation of the alkyl isoximido-derivative of benzophenone were unsuccessful (footnote, *loc. cit.*). Whilst the production of the hydriodide of benz-antialdoxime nitrogen methyl ether constitutes an additive action, involving a change in the valency of nitrogen, no such simple course is followed in the action of methylic iodide on camphoroxime, and in view of the fact that the yield of methylcamphorimine hydriodide does not approximate to the amount required by theory, it would be premature to discuss the mechanism of the change until fresh evidence is forthcoming.

EXPERIMENTAL.

Although the first experiments which led to the direct conversion of camphoroxime into methylcamphorimine were carried out at temperatures approaching 200° , it is unnecessary to heat the contents of the tube above 100° . Ten grams of camphoroxime are enclosed in a hard glass tube with 20 grams of methylic iodide, and heated during 1—2 hours at 120 — 140° : on opening the capillary, there is a considerable escape of gas, and the tube contains a dark-brown oil, impregnated with a crystalline deposit of methylcamphorimine hydriodide. The viscous liquid, which has the odour of campholenitrile, is allowed to drain as completely as possible from the hydriodide, which is then transferred to the filter pump, washed several times with ether, and finally with alcohol; the quantity of salt obtained from 10 grams of camphoroxime amounts to 7.5 grams. The recrystallised hydriodide is dissolved in hot water and treated with caustic soda, which liberates the base as a

pale yellow oil ; the liquid is extracted with ether, which is then dried with caustic potash, and removed by distillation.

Methylcamphorimine is a limpid, almost colourless oil, which boils at 203° (uncorr.) under a pressure of 757 mm., and has the sp. gr. = 0.9226 at 22.75° ; it is levorotatory, and the mean of seven concordant readings in a 2 decimetre tube gave $\alpha_D = -43.39'$ at 22.75° , whence the specific rotatory power $[\alpha]_D = -23.6^{\circ}$. The base has the odour of piperidine, and the vapour produces dense white fumes with hydrogen chloride; it is readily volatile in an atmosphere of steam, and on boiling it with water the odour suggests both camphor and ammonia. The vapour is inflammable, and will ignite at the mouth of the test-tube in which water is boiled along with the base.

Although a preliminary examination of this substance pointed to the formula $C_{12}H_{19}N$ (Proceedings, 1895, 146), the preparation of the compound on a larger scale, and the investigation of new derivatives, have established the formula $C_{11}H_{19}N$ as representing its composition. The following results were obtained on analysis.

0.2222 gave 0.6480 CO_2 , and 0.2266 H_2O . C = 79.53; H = 11.33.

0.1419 „ 0.4159 CO_2 , and 0.1476 H_2O . C = 79.93; H = 11.55.

$C_{11}H_{19}N$ requires C = 80.00; H = 11.51 per cent.

Methylcamphorimine has no reducing action on ammoniacal silver or Fehling's solutions; unlike camphorimine, it does not yield camphor when treated with a hot solution of sodium hydrogen sulphite. It is indifferent towards an acid solution of potassium permanganate, an ice-cold solution of the oxidising agent merely precipitating the crystalline permanganate, which separates in lustrous, violet scales, and becomes brown when exposed to the air; a neutral solution is reduced on boiling, but dilute nitric acid has no immediate action on the substance.

Scission of Methylcamphorimine.—When a solution of camphorimine in cold, alcoholic, oxalic acid is kept for some days, it is found that a certain amount of camphor is formed, and it is also produced when an acid solution of the hydrochloride is heated on the water bath; the quantity of camphor obtained in this way, however, is comparatively small, the greater proportion of the base being easily recovered on treating the filtered liquid with alkali. The hydrolytic action proceeds almost quantitatively, however, when the base is heated with concentrated hydrochloric acid.

Three c.c. of methylcamphorimine were heated in a sealed tube with 10 c.c. of concentrated hydrochloric acid for 2 hours at $180-200^{\circ}$, it having been previously ascertained that no separation of camphor occurs at 120° . After being submitted to the higher temperature, the tube was found to contain a solid cake of camphor; the contents were therefore transferred to a distilling flask in which steam was driven through

the liquid, and a quantity of camphor weighing 2 grams was carried over. Assuming the action to take place in accordance with the equation

2.6 grams of camphor should have been expected. The residual liquid was filtered, concentrated on the water bath, and extracted with chloroform in order to remove a small quantity of methylcamphorimine hydrochloride which escapes hydrolysis; the solution answered to the qualitative tests for methylamine hydrochloride, remaining clear on treatment with soda, and yielding a gaseous base which fumed with hydrogen chloride, and burnt readily. On mixing the liquid with a solution of platinum tetrachloride, an orange-coloured platinochloride was obtained. This was analysed with the following result.

0.0504 gave 0.0206 Pt. Pt = 40.9.

0.0407 „ 0.0167 Pt. Pt = 41.0.

$(\text{CH}_3\cdot\text{NH}_2)_2\text{H}_2\text{PtCl}_6$ requires Pt = 41.3 per cent.

The camphor obtained in this manner was identified by conversion into the oxime, which melted at 118° , and did not depress the melting point of purified camphoroxime when mixed with it.

Methylcamphorimine hydrochloride, $\text{C}_{11}\text{H}_{19}\text{N}\cdot\text{HCl}$, is prepared by dissolving the base in hydrochloric acid, and extracting the liquid with chloroform, which on evaporation deposits the salt as a friable, amorphous mass; it is very readily soluble in alcohol and water, crystallising slowly from the latter in colourless needles. It melts and effervesces at 270° , and becomes yellow on exposure to the air.

0.1308 gave 0.0943 AgCl. Cl = 18.0.

0.1203 „ 0.0866 AgCl. Cl = 17.8.

$\text{C}_{11}\text{H}_{19}\text{N}\cdot\text{HCl}$ requires Cl = 17.6 per cent.

Methylcamphorimine hydriodide, $\text{C}_{11}\text{H}_{19}\text{N}\cdot\text{HI}$, is obtained from camphoroxime in the manner already described; it is also produced when potassium iodide is added to an aqueous solution of methylcamphorimine hydrochloride, separating from the liquid in lustrous needles; it is identical with the substance obtained by Tiemann on treating an ethereal solution of camphorimine with methylic iodide (*loc. cit.*), and crystallises from water and alcohol in long, colourless, lustrous needles, which become yellow on exposure to air. It darkens above 200° , and melts with effervescence above 285° . The salt was analysed with the following results.

0.2131 gave 0.3560 CO_2 , and 0.1387 H_2O . C = 45.56; H = 7.23.

0.1853 „ 0.3082 CO_2 , and 0.1170 H_2O . C = 45.36; H = 7.01.

0.4626 „ 17.2 c.c. moist nitrogen at 16° and 761 mm. N = 4.3.

0.2583 „ 0.2081 AgI. I = 43.50.

0.2126 „ 0.1712 AgI. I = 43.48.

$\text{C}_{11}\text{H}_{19}\text{N}\cdot\text{HI}$ requires C = 45.05; H = 6.82; N = 4.7; I = 43.34 per cent.

Methylcamphorimine platinochloride, $(C_{11}H_{19}N)_2, H_2PtCl_6$, separates in woolly masses of pale yellow needles on adding aqueous platinum tetrachloride to the alcoholic hydrochloride; the crystals rapidly become transparent and orange-coloured. Recrystallised from absolute alcohol, it melts and effervesces at 219.5° .

0.2542 gave 0.0665 Pt. Pt = 26.16.

0.1895 „ 0.0493 Pt. Pt = 26.02.

0.1816 „ 0.0475 Pt. Pt = 26.15.

0.5130 „ 17.9 c.c. of moist nitrogen at 15.5° and 769 mm. N = 4.12.

$(C_{11}H_{19}N)_2, H_2PtCl_6$ requires Pt = 26.28; N = 3.79 per cent.

Methylcamphorimine methiodide, $C_{11}H_{19}N, CH_3I$, rapidly separates from a mixture of the base with an equal weight of methylic iodide, until a solid mass of crystals is obtained; the substance is precipitated in minute, lustrous leaflets on adding ether to the solution in chloroform, whilst from benzene containing a very small proportion of absolute alcohol it crystallises in lustrous, square plates, and melts at $231-232^\circ$ without undergoing decomposition.

0.3476 gave 0.2634 AgI. I = 40.92.

0.2648 „ 0.2015 AgI. I = 41.09.

$C_{11}H_{19}N, CH_3I$ requires I = 41.36 per cent.

The methiodide dissolves sparingly in hot benzene, and is insoluble in ether and petroleum, but dissolves very readily in methylic and ethylic alcohols and acetone, crystallising from the latter in stout needles. When crystallised from ethylic acetate, it yields lustrous, transparent leaflets, which effloresce in the desiccator.

Methylcamphorimine picrate crystallises from absolute alcohol in slender, sulphur-yellow needles, and melts at 190° . The *chromate* crystallises from hot water in square, orange-coloured plates, and becomes purple when exposed to light. The *mercurichloride* is obtained on adding excess of mercuric chloride to an aqueous solution of the hydrochloride; it is readily soluble in water, and separates in slender, white needles, melting at $126-128^\circ$.

The substance dissolves readily in water, and on adding cold, dilute caustic soda to the solution, a precipitate of camphor immediately separates; the same effect is produced by hot sodium carbonate.

Methylcamphorimine perbromide, $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ C:NBr_2Me \end{smallmatrix}$, is prepared by

treating a solution of the base in petroleum with one molecular proportion of bromine dissolved in the same medium, the colour of the halogen being immediately destroyed; no hydrogen bromide is liberated, and the perbromide separates as a pale yellow, amorphous precipitate, which is collected, washed with petroleum, and dried in the desiccator.

It does not dissolve readily in cold absolute alcohol, but, on warming, a red solution is obtained; when this is diluted, the perbromide separates in lustrous, reddish needles, and melts at $133-134^{\circ}$.

The perbromide is insoluble in cold water, but very readily dissolves in chloroform. When the substance is treated with boiling water, it gradually passes into solution, yielding methylcamphorimine hydrobromide, whilst cold, aqueous alkali also removes the bromine, and regenerates the base; hot dilute hydrochloric acid eliminates bromine, and gives rise to methylcamphorimine hydrochloride.

Concurrently with the examination of methylcamphorimine, attention has been paid to the behaviour of camphoroxime towards oxidising agents, and although the experiments have not thrown any fresh light on the nature of the substance, the results are not altogether devoid of interest.

Action of Nitric Acid on Camphoroxime.

By heating camphoroxime for some time with nitric acid of sp. gr. = 1.38 diluted with an equal volume of water, Koenigs obtained camphoric and isocamphoric acids, along with a nitrogenous compound which is stated to melt at $215-218^{\circ}$, evolving red gas and hydrogen cyanide (*Ber.*, 1893, 26, 2340); I find, however, that if a more dilute acid is employed, and the action is arrested after a few minutes, camphenylnitramine, $C_{10}H_{16}N_2O_2$, is obtained almost exclusively, along with about 2 per cent. of a substance which crystallises from alcohol in six-sided plates, and melts, evolving red gas, at 222° , being probably identical with the compound mentioned by Koenigs (*loc. cit.*).

Camphoroxime is dissolved in 10 parts of dilute nitric acid (sp. gr. = 1.42, mixed with five volumes of water), the liquid being warmed on the water bath in a reflux apparatus until a clear, colourless solution is obtained; on heating it by means of a Bunsen flame, it is noticed that, as the temperature rises, the liquid gradually acquires a green tint, and then suddenly becomes turbid, owing to the separation of a green oil. At this stage, red nitrous fumes are liberated in small quantity, and a brisk action then sets up, continuing for some time without further application of heat. After about 20 minutes, when the oil—which is now colourless, and has a faint odour of camphor—becomes semi-solid if cooled, it is extracted with ether, the extract washed with dilute caustic soda until the alkaline washings are colourless, freed from mineral matter by repeated agitation with water, and finally dried with calcium chloride; on evaporation, the solvent deposits a translucent, camphor-like mass, which is then submitted to distillation in an atmosphere of steam. The solid distillate, which melts at 44° , gives Liebermann's reaction, and dissolves readily

in alcoholic potash, ether precipitating the potassium derivative of camphenylnitramine from the liquid; on decomposing this potassium derivative with hydrochloric acid, and comparing the product with camphenylnitramine obtained by the action of nitrous acid on camphoroxime (Angeli and Rimini, *Ber.*, 1895, 28, 1078; also Tiemann, *ibid.*, 28, 1080, and 29, 2810), they were found to be identical.

Employing 50 grams of camphoroxime, 35 grams of camphenylnitramine were obtained, and when this quantity of substance had been carried over by the steam, it was found that the distillate no longer fused in warm water, but remained as a solid deposit in the tube of the condenser, even during the passage of steam. The quantity of substance exhibiting this property, however, amounted to less than one gram, and consequently was not further investigated; it gives Liebermann's reaction, crystallises from alcohol in lustrous, six-sided plates, melting sharply at 222° with brisk evolution of red fumes, and differs from camphenylnitramine in its behaviour towards concentrated sulphuric acid, which does not liberate gas from the substance.

Camphenylnitramine is also produced when nitrogen peroxide acts on camphoroxime. On dissolving 10 grams in chloroform, cooling the liquid by immersion in a mixture of ice and salt, and submitting it to a current of the gas obtained by heating lead nitrate, the solution assumed a green tint, and on evaporating the chloroform, a yellow oil was deposited; the product was distilled in an atmosphere of steam, 5.5 grams of camphenylnitramine being obtained. Scholl and Born have also studied the behaviour of camphoroxime towards nitrogen peroxide, and obtained camphorimine nitrate (*Ber.*, 1895, 28, 1361), the product, that is, of the action of nitrous acid on camphoroxime.

Assuming that camphenylnitramine has the structure

ascribed to it by Tiemann (*Ber.*, 1896, 29, 2810), it is possible to explain the production of this substance by the action of nitrogen peroxide on camphoroxime in the following manner.

This scheme depends on elimination of the elements of nitric acid from an intermediate additive compound of nitrogen peroxide and

camphoroxime ; the action of dilute nitric acid, however, is less easy to follow, and considering the somewhat complex course which is probably pursued, it would be unprofitable to discuss the change until it has been more closely investigated.

Action of Potassium Permanganate on Camphoroxime.

In the paper already quoted, Koenigs alludes to the production of camphoric and nitrous acids on oxidising camphoroxime with an alkaline solution of potassium permanganate ; a very different result has been obtained, however, by employing an acidified solution of the oxidising agent.

Ten grams of recrystallised camphoroxime are dissolved in 200 c.c. of cold, dilute sulphuric acid, containing one part of the concentrated acid and seven parts of water ; the filtered liquid is cooled by immersion in crushed ice, and treated with a 3 per cent. solution of potassium permanganate in dilute sulphuric acid, which is cooled to about 0°, and added to the liquid in small quantities at a time. After the first few c.c. are decolorised, the colour becomes discharged immediately the oxidising agent is added, and this continues until a considerable quantity of the solution has been reduced ; during treatment with the agent, the liquid acquires a green tinge, and a bright green oil slowly separates, and solidifies to a sticky, opaque mass. The substance obtained in this manner does not admit of further purification, as it is excessively unstable. It has a somewhat pungent odour, and when exposed to the air, rapidly deliquesces, losing its bright tint, and becomes translucent and yellow, the product yielding camphor on distillation with steam ; the green substance changes in the same way when left in the desiccator, and yields camphor immediately when heated with aqueous alkali, being insoluble in the cold agent. The camphor obtained in this manner was identified by conversion into the oxime, which melted at 118°, and did not depress the melting point of purified camphoroxime when mixed with it.

The product of the action of an acidic solution of potassium permanganate on camphoroxime has the properties of a very unstable nitroso-derivative. It is readily soluble in alcohol and acetic acid, yielding bright emerald green solutions, which rapidly become colourless when boiled ; the solution in acetic acid also loses its bright green colour when treated with aniline dissolved in the same medium, passing through olive green, and greenish-brown, to brownish-red. On adding a mixture of finely-powdered ice and zinc dust to an ice-cold solution of the substance in glacial acetic acid, the green colour is rapidly destroyed, and on filtering off the zinc, and rendering the liquid alkaline with soda, a current of steam carries over a considerable quantity of camphor.

200 YOUNG AND ANNABLE: FORMATION OF SUBSTITUTED

The formation of a nitroso-derivative on oxidising camphoroxime is probably due to the double linking between carbon and nitrogen. It is conceivable that an intermediate compound arises from the initial action of the agent, and losing the elements of water, is converted into an unstable nitroso-derivative, as represented by the following scheme.

Elimination of the elements of hyponitrous acid from a substance of this constitution would lead to the production of camphor.

Oxidised camphoroxime gives Liebermann's reaction ; when the alcoholic solution is boiled, the odour of aldehyde becomes perceptible, and the liquid exerts a vigorous reducing action on an ammoniacal solution of silver nitrate.

ROYAL COLLEGE OF SCIENCE, LONDON.
SOUTH KENSINGTON.