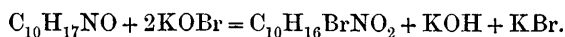


CXVII.—*Camphoroxime. Part III. Behaviour of Camphoroxime towards Potassium Hypobromite.*

By MARTIN ONSLOW FORSTER, Ph.D., D.Sc.

ON the failure of an attempt to prepare  $\alpha$ -bromocamphoroxime by the direct action of bromine on camphoroxime dissolved in glacial acetic acid (Trans., 1897, 71, 1030), I was led to study the behaviour of the oxime towards an alkaline solution of potassium hypobromite.

When treated with this agent, camphoroxime undergoes simultaneous bromination and oxidation, a quantitative yield of the compound,  $C_{10}H_{16}BrNO_2$ , being readily obtained if certain conditions are observed. The change is expressed by the equation



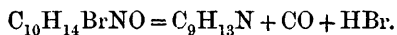
The new derivative is not an oxime, being indifferent towards benzoic chloride, but it contains a nitroso-group, produced by removal of hydrogen from the oximido-residue. It is remarkably indifferent towards aqueous potash, from which it may be distilled without undergoing apparent change, whilst hot concentrated nitric acid scarcely dissolves it, and, at first, has no perceptible action on it.

On dissolving the bromonitroso-derivative in concentrated sulphuric acid, the elements of water are withdrawn, and the compound  $C_{10}H_{14}BrNO$ , is produced. Unlike the substance from which it is obtained, this compound does not give Liebermann's reaction for nitroso-derivatives; moreover, cold concentrated nitric acid dissolves it immediately, whilst hot hydrochloric acid transforms it into an isomeride which yields a benzoyl derivative by the Schotten-Baumann method. These isomeric substances are optically inactive, although the initial compound is strongly lævorotatory.

Under the influence of hot caustic alkalis, the isomerides,  $C_{10}H_{14}BrNO$ , break up in a remarkable manner, yielding a nitrile of the empirical

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formula  $C_9H_{13}N$ . The production of such a compound involves elimination of carbon monoxide and hydrogen bromide in accordance with the equation,



The nitrile, when hydrolysed with alcoholic potash, yields the corresponding amide, which has the formula  $C_9H_{15}NO$ , and is therefore isomeric with the amides of isolaunonic and camphocenic acids; these, however, melt at  $129-130^\circ$  (G. Blanc, *Compt. rend.*, 1896, **123**, 749) and  $155^\circ$  (Jagelki, *Ber.*, 1899, **32**, 1506) respectively, whereas the new amide melts at  $90^\circ$ . Nevertheless, its relation to isolaunonolamide must of necessity be a close one, because hydrochloric acid converts it into that substance along with isolaunonic acid.

It has been shown that when sodium orthoethylic camphorate is submitted to electrolysis, the ethylic salt of campholytic acid is formed (Walker, *Trans.*, 1893, **63**, 495); the acid itself is also obtained by the action of nitrous acid on dihydroaminocampholytic acid, produced on eliminating carbon monoxide from  $\beta$ -camphoramidic acid,  $NH_2 \cdot CO \cdot C_8H_{14} \cdot COOH$ , by the agency of sodium hypobromite (Noyes, *Ber.*, 1895, **28**, 547). Electrolysis of sodium orthoethylic camphorate also yields isolaunonic acid, first described by Walker, who then called it camphothetic acid (*loc. cit.*); the production of this compound from sulphocamphylic acid was recorded about a month later by Koenigs and Hoerlin (*Ber.*, 1893, **28**, 811), from whom it received its present name.

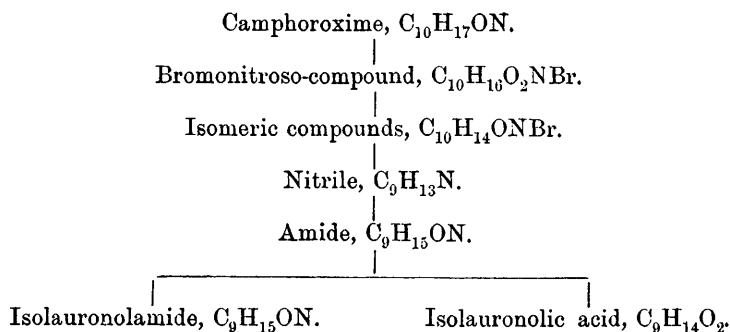
These isomerides, isolaunonic and campholytic acids, are now regarded as the *cis*- and *cistrans*-modifications respectively of a single acid, mainly because both contain an unsaturated linking in the  $\alpha\beta$ -position, and also on account of the readiness with which isolaunonic (*cis*-campholytic) acid is produced from the labile isomeride. Mere contact with cold dilute sulphuric acid at ordinary temperatures will suffice to convert the liquid campholytic acid into solid isolaunonic acid (Noyes, *Ber.*, 1895, **28**, 548), and in a private communication, Professor Walker informs me that an impure specimen of campholytic acid which has remained in his possession for some years, has now become almost entirely transformed into isolaunonic acid.

Neither the formula  $(CH_3)_2C \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \diagdown \quad \diagup \\ C(CH_3) : C \cdot COOH \end{smallmatrix}$  by which Blanc represents the structure of isolaunonic acid (*Bull. Soc. Chim.*, 1898, [iii], **19**, 534; compare also 1899, [iii], **21**, 830), nor the expression  $(CH_3)_2C \begin{smallmatrix} \text{CH}_2 - \text{C} \cdot COOH \\ \diagdown \quad \diagup \\ CH(CH_3) \cdot CH \end{smallmatrix}$ , adopted by W. H. Perkin, jun. (*Trans.*, 1898, **73**, 796), suggests any reason for supposing that one of the two possible structural isomerides which have the unsaturated linking in the

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$\alpha\beta$ -position would be more stable than the other. There is consequently every justification for the accepted view of the relation between campholytic and isolaunonic acids, and the readiness with which the new amide is converted into isolaunonolamide and isolaunonic acid renders it highly probable that the substance in hand is the hitherto unknown amide of campholytic acid. Up to the present, however, it has not been found possible to verify this anticipation experimentally, because the amide resists the action of alcoholic potash, and the employment of an acid as hydrolytic agent is obviously precluded; it is noteworthy that isolaunonolamide is described by Blanc as being very indifferent towards alcoholic potash.

The passage from camphoroxime to isolaunonic acid is represented in the following scheme:



As regards the constitution of the bromonitroso-compound and the isomerides obtained from it on withdrawing the elements of water, discussion at the present moment would be premature. Experiments on the behaviour of menthoneoxime, isonitrosocamphor, thymoquinone-oxime, and carvoxime towards alkaline hypobromite have been carried out for purposes of comparison, but no useful information has been obtained as yet from these sources. It is clear, however, that the initial substance does not belong to the class which includes bromonitrosopropane, obtained by Piloty from acetoxime and bromine in presence of pyridine (*Ber.*, 1898, 31, 452), because it contains more oxygen than camphoroxime, whereas the conversion of acetoxime into bromonitrosopropane merely involves removal of hydrogen and addition of bromine. There is every probability that the substance is a true bromonitroso-derivative containing the complex  $>CBr \cdot NO$ , the presence of the group,  $>C \cdot NOBr$  being rendered highly improbable by the stability of the compound towards aqueous alkali. The disposition of the oxygen atom which has been added to the molecule can be ascertained only by further study, and the work is being continued from this point of view.

## EXPERIMENTAL.

*Action of Potassium Hypobromite on Camphoroxime.*

A solution of potassium hypobromite was first prepared by dissolving 600 grams of caustic potash in 1000 c.c. of water, cooling the solution with crushed ice, and adding 400 grams of bromine to the well-stirred liquid. 100 grams of finely-powdered camphoroxime were next converted into a thin paste with 200 c.c. of water, and treated with 200 grams of caustic potash dissolved in 500 c.c. of water. The oxime, suspended and in part dissolved in the alkali, and cooled by fragments of ice, was finally mixed with the cold solution of hypobromite, which quickly transformed it into a pale green solid having a faint, pungent odour. After 24 hours, the product had risen to the surface in a compact mass, and the clear liquid was therefore removed with the aid of a syphon; the green solid was washed several times with water, and finally spread in thin layers on blotting paper.

On exposure to air, the substance became pale yellow, but retained its pungent odour. The yield approached that required by theory. When crystallised twice from hot alcohol, the compound was obtained in snow-white, fern-like aggregates, and melted at  $220^{\circ}$ , forming a colourless liquid which immediately began to turn red and evolve gas. The substance could not be powdered, because moderate pressure transforms it into tough, camphor-like masses; it was therefore cut into small fragments for analysis and dried at  $80^{\circ}$ .

0.2708 gave 0.4570  $\text{CO}_2$  and 0.1503  $\text{H}_2\text{O}$ .  $\text{C} = 46.02$ ;  $\text{H} = 6.16$ .

0.4048 „ 19.8 c.c. moist nitrogen at  $23^{\circ}$  and 769 mm.  $\text{N} = 5.57$ .

0.2376 „ 0.1693  $\text{AgBr}$ .  $\text{Br} = 30.32$ .

$\text{C}_{10}\text{H}_{16}\text{O}_2\text{NBr}$  requires  $\text{C} = 45.80$ ;  $\text{H} = 6.10$ ;  $\text{N} = 5.35$ ;  $\text{Br} = 30.53$   
per cent.

The new derivative from camphoroxime gives Liebermann's reaction for nitroso-compounds. It distils readily in an atmosphere of steam and is excessively soluble in benzene or petroleum. Concentrated nitric acid has no action on the substance, which merely fuses to a yellow oil when heated with it, and resolidifies on cooling; it is also indifferent towards boiling aqueous potash, from which it may be distilled without undergoing any apparent change.

A solution containing 0.2475 gram dissolved in 25 c.c. of absolute alcohol at  $23^{\circ}$  gave  $\alpha_D - 1^{\circ} 5'$  in a 2-dcm. tube, whence  $[\alpha]_D - 54.7^{\circ}$ . A solution of 0.5061 gram in 25 c.c. of benzene at  $21^{\circ}$  gave  $\alpha_D - 2^{\circ} 39.5'$  in the same tube, corresponding to  $[\alpha]_D - 65.6^{\circ}$ .

A determination of the molecular weight in benzene solution gave the following result:

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*Molecular weight of compound,  $C_{10}H_{16}O_2NBr = 262$ .*

Grams of benzene.	Grams of substance.	Grams of substance in 100 grams of solvent.	Depression of freezing point.	Molecular weight deduced.
16.66	0.2312	1.3875	0.292°	232.8
„	0.3352	2.0120	0.428	230.3
„	0.4372	2.6242	0.539	238.5

*Reduction of the Bromonitroso-compound.*—5 grams were dissolved in glacial acetic acid and treated with 5 grams of zinc dust while the liquid was cooled with ice. On diluting the filtered solution with water, a pale yellow oil separated, and after several days, colourless crystals were deposited. The oil had the odour of campholenitrile, which is generally produced when camphoroxime is heated with glacial acetic acid and zinc dust. The solid substance was dissolved in hot petroleum, which deposited the characteristic crystals of camphoroxime, melting at  $118^{\circ}$ ; a 3.2 per cent. solution in absolute alcohol gave  $[\alpha]_D - 41.1^{\circ}$ .

*Action of Concentrated Sulphuric Acid on the Bromonitroso-compound.*

A beaker containing 800 c.c. of concentrated sulphuric acid was surrounded with a freezing mixture. When the temperature of the acid had fallen below  $0^{\circ}$ , the bromonitroso-compound was added in small quantities at a time; meanwhile the liquid was well stirred and maintained at a temperature below  $10^{\circ}$ . An orange coloration was developed on first adding the substance, but the liquid rapidly became dark brown, and a highly scented, viscous oil rose to the surface. When 100 grams of material had been added, the oil was removed, and the acid allowed to flow in a thin stream on to finely crushed ice, which precipitated a pale yellow solid. The latter was collected, washed, spread on porous earthenware, and dissolved in the minimum quantity of boiling alcohol, which was then rapidly cooled. The yield was disappointing, as operations involving 200 grams of the bromonitroso-compound have never furnished more than 75 grams of the crystallised product, and on one occasion only 50 grams were obtained; the theoretical amount, allowing for the production of the fragrant oil, is 170 grams. In order to secure a comparatively good yield, it is absolutely essential to maintain the sulphuric acid in constant agitation while the bromonitroso-compound is being added; the latter rises to the surface of the acid if this remains undisturbed, where it becomes heated, and blackens, evolving gas. Even when

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the liquid is efficiently cooled and agitated, alcohol extracts from the crude product a considerable quantity of tarry matter.

The substance formed by dehydration of the bromonitroso-compound is sparingly soluble in cold, but readily in boiling alcohol, from which it crystallises in long, lustrous, transparent needles; it is readily soluble in benzene.

0.2460 gave 0.4382  $\text{CO}_2$  and 0.1322  $\text{H}_2\text{O}$ .  $\text{C} = 48.58$ ;  $\text{H} = 5.97$ .

0.2394 „ 12.3 c.c. moist nitrogen at  $21^\circ$  and 756 mm.  $\text{N} = 5.82$ .

0.1977 „ 0.1508 AgBr.  $\text{Br} = 32.46$ .

$\text{C}_{10}\text{H}_{14}\text{ONBr}$  requires  $\text{C} = 49.18$ ;  $\text{H} = 5.74$ ;  $\text{N} = 5.74$ ;  $\text{Br} = 32.79$   
per cent.

It has no definite melting point, but shrinks and darkens at about  $210^\circ$ , becoming completely charred at  $220^\circ$ ; it is slightly volatile on the water-bath, and sublimes in minute, transparent needles. The derivative does not give Liebermann's reaction, and is saturated towards bromine in chloroform, but a hot solution in dilute sulphuric acid quickly reduces potassium permanganate. Warm concentrated nitric acid decomposes it, liberating gas, but hot concentrated sulphuric acid and boiling pyridine are without action on it.

As already stated, this compound is destitute of rotatory power. A 4 per cent. solution in benzene and a 1 per cent. solution in alcohol were examined in a 2-dcm. tube and found to be inactive.

*Conversion of the Compound,  $\text{C}_{10}\text{H}_{14}\text{ONBr}$ , into an Isomeride.*

The compound,  $\text{C}_{10}\text{H}_{14}\text{ONBr}$ , was powdered and covered with concentrated hydrochloric acid, which was then boiled during several minutes; on dissolving the product in hot water and allowing the filtrated liquid to cool, colourless needles were deposited. This modification is also obtained by boiling an alcoholic solution of the compound with a few c.c. of concentrated hydrochloric acid, and crystallises from alcohol in large, transparent, six-sided plates; it melts at  $240^\circ$  to a colourless liquid which does not decompose, and is slightly volatile at  $100^\circ$ .

0.2548 gave 0.4596  $\text{CO}_2$  and 0.1347  $\text{H}_2\text{O}$ .  $\text{C} = 49.19$ ;  $\text{H} = 5.87$ .

0.3633 „ 18.1 c.c. moist nitrogen at  $24^\circ$  and 769 mm.  $\text{N} = 5.65$ .

0.2358 „ 0.1820 AgBr.  $\text{Br} = 32.84$ .

$\text{C}_{10}\text{H}_{14}\text{ONBr}$  requires  $\text{C} = 49.18$ ;  $\text{H} = 5.74$ ;  $\text{N} = 5.74$ ;  $\text{Br} = 32.79$   
per cent.

The substance does not give Liebermann's reaction, and behaves like a saturated compound towards bromine dissolved in chloroform, and also towards a hot solution of potassium permanganate; it under-

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goes no change when a solution in glacial acetic acid, or alcoholic hydrochloric acid, is boiled with zinc dust. It resembles the first modification in being optically inactive, but differs from it in its behaviour towards benzoic chloride, with which it yields a *benzoyl* derivative. This crystallises from alcohol in lustrous scales and melts at 174—176°.

0.2280 gave 0.1223 AgBr. Br = 22.82.

0.1998 „ 0.1070 AgBr. Br = 22.78.

$C_{17}H_{18}O_2NBr$  requires Br = 23.00 per cent.

*Behaviour of the Compounds,  $C_{10}H_{14}ONBr$ , towards Caustic Soda.*

A boiling, aqueous solution of caustic soda eliminates hydrogen bromide and carbon monoxide from the compound,  $C_{10}H_{14}ONBr$ , and from its isomeride, giving rise to a nitrile of the formula  $C_9H_{13}N$ .

100 grams of the finely powdered substance were heated with a solution of 40 grams of caustic soda in 300 c.c. of water; the operation was conducted in a reflux apparatus on the water-bath and continued during half an hour. A volatile oil soon appeared in the condenser, and the suspended solid aggregated to a pasty mass beneath the liquid. After the period specified, the condenser was rearranged for distillation, and a current of steam was passed through the alkali until the bromo-compound was completely decomposed. On extracting the distillate with ether, drying the extract with calcium chloride, and evaporating the ethereal solution, 50 grams of the nitrile were obtained; the aqueous residue in the distillation flask was concentrated on the water-bath and yielded 6 grams of the solid amide described below.

The nitrile is a limpid, colourless oil having an agreeable, camphor-like odour, it boils at 198—199° under 760 mm. pressure, and has a sp. gr. 0.9038 at 24°.

0.2213 gave 0.6466  $CO_2$  and 0.1940  $H_2O$ . C = 79.68; H = 9.74.

0.1560 „ 14.1 c.c. moist nitrogen at 20.5° and 764 mm. N = 10.37.

$C_9H_{13}N$  requires C = 80.00; H = 9.63; N = 10.37 per cent.

The substance reduces a cold solution of potassium permanganate instantly, and also decolorises bromine dissolved in chloroform. A specimen examined in a 2-dcm. tube was feebly dextrorotatory, giving  $\alpha_D + 0^\circ 46'$ , an angle so small, in view of the inactivity of the original compound, as to suggest the presence of some optically active impurity.

In view of the fact that the elements of hydrogen bromide and carbon monoxide are withdrawn from the compound,  $C_{10}H_{14}ONBr$ , by the action of caustic soda, it became necessary to test the alkaline

residue in the distillation flask for sodium formate. The liquid was accordingly acidified with dilute sulphuric acid, and a current of steam passed through it. Formic acid was recognised without difficulty in the distillate, which had a faint, pungent odour, and was strongly acid towards litmus; silver nitrate gave a precipitate undergoing immediate reduction on heating, and a specimen of the characteristic lead formate was obtained.

### *Hydrolysis of the Nitrile.*

25 grams of the nitrile were heated with a solution of 20 grams of caustic potash in alcohol during 30 hours in a reflux apparatus. Water was then added to the liquid, from which alcohol was removed by evaporation; a yellow oil floated on the surface, and rapidly crystallised as it cooled. The product was collected, drained on porous earthenware, and recrystallised from boiling light petroleum.

0.2117 gave 0.5479  $\text{CO}_2$  and 0.1913  $\text{H}_2\text{O}$ .  $\text{C} = 70.58$ ;  $\text{H} = 10.04$ .

0.1812 „ 0.4662  $\text{CO}_2$  „ 0.1613  $\text{H}_2\text{O}$ .  $\text{C} = 70.17$ ;  $\text{H} = 9.89$ .

0.2235 „ 18.4 c.c. moist nitrogen at  $24^\circ$  and 769 mm.  $\text{N} = 9.34$ .

$\text{C}_9\text{H}_{15}\text{ON}$  requires  $\text{C} = 70.59$ ;  $\text{H} = 9.80$ ;  $\text{N} = 9.15$  per cent.

The amide is scarcely soluble in cold, but dissolves more freely in boiling petroleum, from which it separates in highly lustrous needles melting at  $90^\circ$ ; it dissolves readily in alcohol, and is also soluble in boiling water, crystallising in flat, lustrous needles as the liquid cools.

*Behaviour towards Hydrochloric Acid.*—The recrystallised amide dissolved freely in cold concentrated hydrochloric acid, but on boiling the solution in a reflux apparatus it rapidly became turbid, owing to the separation of an oil; the latter immediately crystallised on cooling the contents of the flask. On collecting the product with the aid of a filter pump, it was found that crystallisation from boiling water containing a little sodium carbonate yielded a substance having the empirical formula of the original amide.

0.2000 gave 0.5145  $\text{CO}_2$  and 0.1759  $\text{H}_2\text{O}$ .  $\text{C} = 70.16$ ;  $\text{H} = 9.77$ .

$\text{C}_9\text{H}_{15}\text{ON}$  requires  $\text{C} = 70.59$ ;  $\text{H} = 9.80$  per cent.

Moreover, the compound crystallised in highly lustrous needles exactly resembling the substance from which it was obtained. It melted, however, at  $129$ — $130^\circ$ , the melting point of isolauronolamide (G. Blanc, *Compt. rend.*, 1896, 123, 749).

During the conversion of the amide melting at  $90^\circ$  into isolauronolamide, colourless crystals collected in the condenser. These were analysed, with the following result:

0.1714 gave 0.4399  $\text{CO}_2$  and 0.1408  $\text{H}_2\text{O}$ .  $\text{C} = 70.00$ ;  $\text{H} = 9.12$ .

$\text{C}_9\text{H}_{14}\text{O}_2$  requires  $\text{C} = 70.13$ ;  $\text{H} = 9.09$  per cent.



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The substance melted at  $132-133^{\circ}$ ; a solution in chloroform was indifferent towards bromine, but when dissolved in sodium carbonate, the acid decolorised potassium permanganate instantly. This is the behaviour of isolauronolic acid, and it was found that the melting point of the preparation obtained in the manner just indicated was not depressed by admixture with a specimen of isolauronolic acid sent to me for the purpose of comparison by Prof. W. H. Perkin.

The action of hydrochloric acid on the amide melting at  $90^{\circ}$  precludes the use of this agent for the purpose of hydrolysis. Unfortunately, however, alcoholic potash is almost without action on the substance. In one experiment, 10 grams were heated during 50 hours with a concentrated solution of caustic potash in alcohol, and practically the whole amount of the amide was recovered on dilution with water and evaporation. On heating 5 grams with 15 c.c. of a 50 per cent. aqueous solution of potash in a sealed tube at  $120^{\circ}$  during 6 hours, and removing the unaltered amide, the aqueous liquid yielded on acidification about 0.5 gram of an oily acid; for reasons already stated, it seems probable that this compound is campholytic acid (Walker, Trans., 1893, 63, 495), and further attempts to identify it are being made.

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