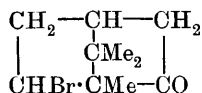


LXXXVI.—*Studies in the Camphane Series. Part IX.*  
*Comparison of Bromonitrocamphane with Bromo-*  
*nitrocamphor.*

By MARTIN ONSLOW FORSTER.

ALTHOUGH the recorded observations which relate to camphor and its derivatives are now exceedingly numerous, the vast majority have reference to changes occurring in that ring which contains the carbonyl group. Reliable methods for replacing hydrogen atoms in the second ring; and for recognising the position of substituents when introduced, remain to be discovered, and the interest attaching to derivatives of the class indicated will be very considerable.

The series of operations by which  $\beta$ -bromocamphor has been obtained from camphoroxime (Forster, *Trans.*, 1901, 79, 644, and this vol., 264) and the evidence furnished in favour of the expression



for the first named substance, suggested a possible means of replacing hydrogen in the remaining methylene group of the second ring. The change in question depends on the removal of hydrogen bromide from bromonitrocamphane,  $\text{C}_{10}\text{H}_{16}\text{Br}\cdot\text{NO}_2$ , the resulting nitro-derivative,  $\text{C}_{10}\text{H}_{15}\cdot\text{NO}_2$ , being then converted into a hydroxylic isomeride of camphor,  $\text{C}_{10}\text{H}_{15}\cdot\text{OH}$ ; addition of bromine to this compound, followed by elimination of hydrogen bromide, gave rise to  $\beta$ -bromocamphor. It was hoped, therefore, that by corresponding steps from  $\alpha\alpha$ -bromonitrocamphor, the hydroxy-derivative of a dehydrogenised camphor,  $\text{C}_{10}\text{H}_{13}\text{O}\cdot\text{OH}$ , might be obtained, from which a bromocamphorquinone,  $\text{C}_8\text{H}_{13}\text{Br} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix}$ , would result on addition of bromine, followed by removal of hydrogen bromide.

On heating bromonitrocamphor with alcoholic silver nitrate, however, an unexpected change ensued. Instead of yielding an unsaturated nitro-compound, the bromonitro-derivative was converted into camphorquinone, silver bromide being precipitated; the yield of quinone amounted to little more than 25 per cent. of the theoretical, but the oily bye-product was not reducible to the expected amine. This is the first occasion on which direct conversion of bromonitrocamphor into the quinone has been observed, but Lapworth (*Trans.*, 1896, 69, 322) has obtained 5 per cent. of camphorquinone by heating small quantities of  $\alpha\alpha$ -chloronitrocamphor during several hours at 200°. The yield by this process would appear to be less satisfactory than by the one described in the present communication, and, although it cannot be claimed that the new method has the advantage of that described by Claisen and Manasse in point of convenience, the fact that *isonitrosocamphor* is ten times more expensive than  $\alpha$ -bromocamphor renders the cost of producing a given weight of camphorquinone from each source approximately the same.

In view of this difference between  $\alpha\alpha$ -bromonitrocamphor and 1:1-bromonitrocamphane, it appeared of interest to compare the behaviour of these substances towards phenylhydrazine, with the result that the latter, acting on bromonitrocamphor, has been found a most convenient agent for the preparation of nitrocamphor. When the base acts under regulated conditions, 84 per cent. of the theoretical quantity of nitrocamphor is obtained in such a condition that a single crystallisation from petroleum yields a colourless product melting at 103° and giving  $[\alpha]_D - 123.8^\circ$  in a 10 per cent. solution in benzene. This method of preparing nitrocamphor appears to be a distinct improvement, both in quantity and quality of the material, on the process described by Lowry (*Trans.*, 1898, 73, 995).

During the preparation of nitrocamphor by the action of phenylhydrazine on bromonitrocamphor, there is produced, in addition to camphor phenylhydrazone, a small quantity of a crystalline substance having the empirical formula  $C_{16}H_{20}ON_2$ . From the circumstances attending the formation of this compound, the possibility of its being the phenylhydrazone of camphorquinone suggested itself, and direct comparison with that substance, which has been described by Claisen and Manasse (*Annalen.*, 1893, 274, 87), shows that chemically the substances are unquestionably identical. There is, however, a difference between them which reveals itself in the crystalline form, but whether this distinction is due merely to physical structure or depends on stereoisomerism is a question which can be decided only when more of the substance becomes available. Unfortunately, it is produced in quantities amounting to less than 4 per cent. of the material employed.

The action of phenylhydrazine on 1:1-bromonitrocamphane is

analogous to the change which the camphor derivative undergoes. Reduction takes place, and 1-nitrocamphane is produced, but the yield is not satisfactory, although the compound is obtained in a purer form than has been possible hitherto. Nitrocamphane prepared by this method melts at  $157^{\circ}$  instead of  $147\text{--}148^{\circ}$  (Trans., 1900, **77**, 257), and has  $[\alpha]_D + 27.0^{\circ}$  in benzene, and  $[\alpha]_D + 7.4^{\circ}$  in absolute alcohol instead of  $20.4^{\circ}$  and  $4.6^{\circ}$  respectively.

#### EXPERIMENTAL.

##### *Action of Alcoholic Silver Nitrate on $\alpha\alpha$ -Bromonitrocamphor.*

When an alcoholic solution of  $\alpha\alpha$ -bromonitrocamphor is heated in a reflux apparatus with finely powdered silver nitrate, the liquid remains clear during a considerable period, and the formation of silver bromide, even when started, proceeds very slowly; the camphor derivative is therefore much less sensitive to this agent than bromonitrocamphane. As action proceeds, the liquid becomes yellow, owing to formation of camphorquinone, but the quantity of this substance varies considerably according to the amount of silver nitrate employed and the rate at which it is added. After numerous experiments, the following conditions were found to yield the maximum proportion of the quinone.

Fifty grams of bromonitrocamphor were heated in a reflux apparatus with 400 c.c. of absolute alcohol during 30 hours, finely powdered silver nitrate being added in quantities of 2—3 grams at intervals of 1—2 hours. From time to time the liquid was filtered, the precipitate amounting to 34 grams, this being almost exactly the calculated quantity. Forty grams of silver nitrate were added in this way, and when the formation of silver bromide ceased, the filtered liquid was evaporated to a small bulk and allowed to cool; 5 grams of silver nitrate then separated and were filtered off, the oily mother liquor, which was intensely yellow, being then distilled in a current of steam. The distillate consisted of camphorquinone associated with a colourless oil, which was separated from the former with the aid of a filter-pump. After being drained on porous earthenware, the quinone weighed 7 grams, and a further quantity of 1 gram was obtained by agitating the aqueous distillate and oily filtrate with ether, drying the extract with calcium chloride, and boiling off the ether, the residue from which deposited crystals of the quinone.

The nature of the liquid bye-product has not been determined. Ten grams were obtained in the experiment described, and the substance was found to be saturated and contained nitrogen. On dissolving it in glacial acetic acid and heating the solution with zinc dust, only an inconsiderable proportion of basic product was obtained, the major

portion of the material being apparently unchanged. The attempt to prepare the nitro-derivative of a dehydrogenised camphor was therefore unsuccessful

*Action of Phenylhydrazine on  $\alpha\alpha$ -Bromonitrocamphor.*

The uncontrolled action of phenylhydrazine on  $\alpha\alpha$ -bromonitrocamphor is extraordinarily vigorous. If a few grams of the base are added to the same quantity of the camphor derivative, the pasty mixture rapidly becomes hot, torrents of pungent, white fumes are liberated, and a dark brown tar is produced. Preliminary experiments showed, however, that under properly regulated conditions a satisfactory yield of nitrocamphor may be obtained.

Fifty grams of bromonitrocamphor, giving  $[\alpha]_D - 20.7^\circ$  in a 20 per cent. chloroform solution, were placed in a porcelain beaker and treated with 40 grams of phenylhydrazine, added in quantities of about 5 grams at a time. Soon after adding the base, the mixture became pasty, developed heat, and set up a continuous evolution of gas. When the action seemed in danger of becoming too vigorous, the product was cooled, and the effect of one quantity of the base was allowed to subside before further addition was made. Throughout the treatment, which lasted 1 hour, phenylhydrazine hydrobromide was produced, and at the end of the operation the contents of the beaker were quite hard.

Ether was added in sufficient quantity to dissolve all excepting the hydrobromide, which, when filtered and washed, weighed only 24 grams although 34.2 grams would represent one molecular proportion. The ethereal solution was extracted with dilute hydrochloric acid, which removed 8 grams of unused phenylhydrazine. The liquid was then shaken vigorously with a moderately concentrated solution of sodium carbonate as long as carbon dioxide was liberated, and then evaporated, depositing 10 grams of a deep red oil, from which 2 grams of a crystalline substance quickly separated.

The sodium carbonate solution was washed with ether, heated on the water-bath, cooled, and acidified with hydrochloric acid, which precipitated nitrocamphor in a pale yellow, crystalline form, showing no tendency to be oily; it was filtered, washed, and treated with about 20 c.c. of cold alcohol, which left undissolved 30 grams of nitrocamphor as a pale yellow, crystalline powder, 35.7 grams being the calculated amount. One crystallisation from warm petroleum sufficed to convert the product into aggregates of lustrous, colourless, transparent crystals melting at  $103^\circ$  and giving  $[\alpha]_D - 123.8^\circ$  in a 10 per cent. solution in benzene. This value was obtained on examining the solution as soon as possible after dissolving the substance; during 3

hours' exposure to daylight it diminished to  $[\alpha]_D - 113^\circ$ , becoming constant at  $[\alpha]_D - 101.2^\circ$ .

*The Bye-product*,  $C_{16}H_{20}ON_2$ .—The deep red oil deposited by the ethereal solution from which nitrocamphor had been removed by agitation with sodium carbonate solution, consisted of camphor phenylhydrazone. After a short interval, separation of crystals occurred. These were filtered, washed with cold alcohol, and recrystallised twice from boiling alcohol, which deposited pale yellow, silky needles melting somewhat indefinitely at  $187\text{--}189^\circ$ :

0.1509 gave 0.4169  $CO_2$  and 0.1076  $H_2O$ .  $C = 75.35$ ;  $H = 7.92$ .

0.1703 „ 15.9 c.c of nitrogen at  $16^\circ$  and 765 mm.  $N = 10.95$ .

$C_{16}H_{20}ON_2$  requires  $C = 75.00$ ;  $H = 7.81$ ;  $N = 10.93$  per cent.

The substance has been obtained also in lustrous leaflets, and as it seemed probable that it might be camphorquinone phenylhydrazone, a specimen of this derivative was prepared from camphorquinone and phenylhydrazine. Claisen and Manasse (*Annalen*, 1893, 274, 87) state that the phenylhydrazone prepared by this method crystallises in yellowish prisms which melt at  $170\text{--}171^\circ$ , and add that it dissolves in sulphuric acid containing nitrous acid, developing a bluish-violet coloration which rapidly becomes red and finally dark yellow. The specimen which I prepared for the purpose of comparison crystallised in long, yellow, striated prisms melting at any temperature between  $183^\circ$  and  $190^\circ$ , according to the rate at which the temperature rose, the first-named being that observed when the acid is heated rather more slowly than usual. It dissolved in sulphuric acid containing nitrous acid, developing an intense red coloration which rapidly became purple and finally deep cherry-red. Concentrated nitric acid produced momentarily a brilliant purple coloration, the solution being brown.

The phenylhydrazone is a neutral substance and is indifferent towards Fehling's solution, even on boiling; if, however, it is heated for some time with concentrated hydrochloric acid, the liquid, when neutralised with potash, slowly reduces Fehling's solution when boiled with it. An alcoholic solution of the substance does not reduce cold ammoniacal silver nitrate, but on boiling the liquid, silver is precipitated, and the yellow colour intensified.

All these remarks apply to the bye-product of the reduction of bromonitrocamphor with phenylhydrazine, and when the purified substances are melted side by side or mixed, fusion occurs at the same moment. It is evident, therefore, that they are chemically identical, but differ in crystalline form.

*Action of Phenylhydrazine on 1:1-Bromonitrocamphane.*

The behaviour of bromonitrocamphane towards phenylhydrazine is very similar to that of bromonitrocamphor. If allowed to proceed spontaneously between equal quantities of the two substances, the action becomes uncontrollable, and white, pungent fumes are evolved, leaving only tarry products.

Fifty grams of bromonitrocamphane were therefore converted into a stiff paste with ether and treated with 50 grams of phenylhydrazine under the conditions prescribed for the camphor derivative; when this quantity of base had been added, the mixture was heated on the water-bath until the characteristic odour of bromonitrocamphane was no longer distinguishable. The product was then treated with ether and agitated with water, which removed 29 grams of phenylhydrazine hydrobromide, 36 grams being the calculated amount. After extracting the ethereal solution with 30 per cent. potassium hydroxide, which removed an inconsiderable proportion of dark brown, oily matter, it was treated with dilute hydrochloric acid, which removed 8 grams of unused phenylhydrazine.

On evaporating the ether, 32 grams of a dark red oil were deposited. A current of steam was passed through this product, which yielded 21 grams of nitrocamphane in the form of a reddish-yellow, crystalline distillate, instead of 35 grams required by theory. The product, however, when recrystallised twice from hot alcohol, was obtained in snow-white crystals melting at  $157^{\circ}$ , or  $10^{\circ}$  higher than the specimen prepared by the action of alcoholic potash; 0.5021 gram dissolved in 25 c.c. of benzene at  $20^{\circ}$  gave  $\alpha_D + 1^{\circ}5'$  in a 2-dm. tube, whence the specific rotatory power  $[\alpha]_D + 27.0^{\circ}$ , whilst 0.5043 dissolved in 25 c.c. of absolute alcohol at  $20^{\circ}$  gave  $\alpha_D + 18'$ , corresponding to  $[\alpha]_D + 7.4^{\circ}$  (compare Trans., 1900, 77, 257).

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