CCCCLXII.—*Derivatives of Phenylaminocamphor.*

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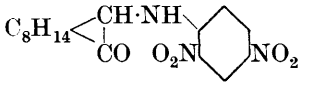
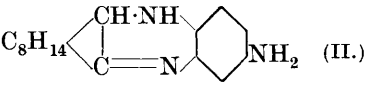
MANY derivatives of phenylaminocamphor have been prepared (Forster and Thornley, J., 1909, **95**, 942; Forster and Spinner, J., 1919, **115**, 889; Singh and Mazumder, *ibid.*, p. 566; Singh, Singh, Dutt, and Singh, J., 1920, **117**, 986) by the condensation of camphorquinone with various primary aromatic bases and reduction of the resultant unsaturated imino-compounds. Little, however, is known about the nitro-derivatives of phenylaminocamphor. Forster and Saville (J., 1921, **119**, 789) reported that, under ordinary conditions, direct nitration yields only a dinitro-compound.

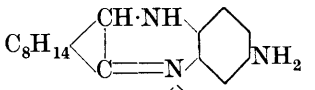
Aminocamphor reacts readily with 2 : 4-dinitrochlorobenzene to give 2 : 4-dinitrophenylaminocamphor in good yield. Ordinary methods failed to achieve reduction of one only of the two nitro-groups in this compound. Reduction was then carried out with sufficient stannous chloride to convert the dinitrophenylamino-camphor into the corresponding diamino-compound. The resulting base, however, did not have properties such as would be expected from a derivative of *m*-diaminobenzene. It was very stable towards oxidising agents even in alkaline solution, exhibited strong fluorescence when dissolved in organic solvents, and gave red solutions with dilute acids. These properties are typical of the dihydroquinoxalines and such a compound, *aminocamphanodihydroquinoxaline*, might readily be produced by the complete reduction of 2 : 4-dinitrophenylaminocamphor (I).

(I.)   (II.)

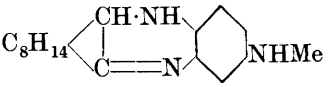
The diamino-compound was probably first produced and then underwent condensation, giving the dihydroquinoxaline (II).

The action of methyl iodide on the base gave a yellow and a red compound, in a proportion depending on the conditions of the experiment. The yellow substance was the quarternary salt (III),

and the red compound appeared to be the *hydriodide* of the methylated base (IV).



(III.)



(IV.)

Attempts to prepare *o*-nitrophenylaminocamphor from aminocamphor and *o*-chloronitrobenzene were unsuccessful. A colourless crystalline compound containing no nitro-group was obtained in all cases. Quantitative and qualitative experiments indicated that this was a derivative of dicamphorylamine. The same compound was obtained by the action of nitrobenzene on aminocamphor.

Experimental.

Aminocamphor was prepared by the electrolytic reduction of *iso*nitrosocamphor, a much easier method than that of Claisen and Manasse (*Annalen*, 1893, **274**, 90). The cathode compartment was filled with a solution of *iso*nitrosocamphor (40 g.) in caustic soda (10%) and the anode solution consisted of a saturated solution of sodium carbonate. Lead electrodes were used. The reduction gave almost the theoretical yield, and after the passage of 15 ampère-hours of current the aminocamphor separated at the surface of the liquid as an oil. It was extracted with ether and dried over fused potash, and the ether was removed in an atmosphere free from carbon dioxide. The product gave a dinitrophenyl derivative identical with that obtained from the aminocamphor prepared by Claisen and Manasse's method (*loc. cit.*).

2 : 4-*Dinitrophenylaminocamphor* (I).—Aminocamphor (30 g.) was heated with 200 c.c. of water on a water-bath, and 2 : 4-dinitrochlorobenzene (16 g.) gradually shaken in with vigorous stirring. The oil formed, which rapidly solidified, was collected when cold, washed with water, dried, and crystallised from acetone, giving golden-yellow needles (25 g.), m. p. 204°, $[\alpha]_D$ — 120·3° in chloroform ($c = 0{\cdot}985$; $l = 2$).

Aminocamphanodihydroquinoxaline (II).—The dinitrophenylaminocamphor (20 g.) was finely powdered and heated with stannous chloride (86 g.), hydrochloric acid (90 c.c.), and water (50 c.c.) until a clear, dark red solution was obtained. The liquid was cooled and diluted, and concentrated caustic soda solution added until the tin hydroxides were redissolved. The bulk of the *base* was separated by decantation, and the remainder by extraction with ether. The washed and dried product crystallised from acetone in small yellow prisms, m. p. 189°, $[\alpha]_D$ + 41·9° in alcohol ($c = 1{\cdot}61$; $l = 2$)

(Found : C, 74·8; H, 8·0; *M*, cryoscopic in benzene, 251. $C_{16}H_{21}N_3$ requires C, 75·3; H, 8·2%; *M*, 255).

With acetic anhydride the base gave a *diacetyl* derivative, m. p. 220° (Found : C, 70·9; H, 7·4. $C_{20}H_{25}O_2N_3$ requires C, 70·8; H, 7·4%), and with benzoyl chloride a *benzoyl* derivative, m. p. 227° (Found : C, 76·9; H, 6·8. $C_{23}H_{25}ON_3$ requires C, 76·9; H, 6·9%), both of which crystallised from acetone in colourless prisms.

Action of methyl iodide. The base was heated with slightly more than 1 mol. of methyl iodide in a sealed tube at 100° for a few minutes and the product was warmed with chloroform. The red hydriodide readily dissolved, and the solution was filtered from the yellow methiodide. After addition of benzene the chloroform solution slowly deposited small, deep red crystals. The yellow substance, *aminocamphanodihydroquinoxaline methiodide* (III), crystallised from acetone–alcohol in small yellow needles which dissolved readily in water and gave no precipitate on the addition of caustic soda (Found : I, 31·7. $C_{17}H_{24}N_3I$ requires I, 32·0%). The red substance *methylaminocamphanodihydroquinoxaline hydriodide*, dissolved in water with partial hydrolysis, and a yellow fluorescent base was precipitated with alkali (Found : I, 31·3. $C_{17}H_{23}N_3$,HI requires I, 32·0%). The base gave a red solution in dilute acids, and with nitrous acid a colourless *nitrosoamine* was precipitated which crystallised in small prisms from acetone (Found : C, 68·6; H, 7·2. $C_{17}H_{22}ON_4$ requires C, 68·4; H, 7·3%).

Both the acetyl and the benzoyl derivative of the base, when heated with methyl iodide at 100° for a few minutes, readily gave methiodides, which crystallised from alcohol in small yellow needles and, like the methiodide of the base, decomposed when heated.

A dinitrophenyl derivative of aminocamphanodihydroquinoxaline separated in golden-yellow needles, m. p. 237°, when 2 mols. of the base were heated with 1 mol. of 2 : 4-dinitrochlorobenzene in alcoholic solution for ½ hour. It dissolved in concentrated hydrochloric acid and was partly precipitated on dilution. There was no primary amino-group in the molecule, so the dinitrophenyl group must have displaced a hydrogen atom from the primary amino-group of the base.

Bornylamine, like aminocamphor, readily reacts with 2 : 4-dinitrochlorobenzene in hot alcoholic solution, depositing small flat orange needles, m. p. 159°, of dinitrophenylbornylamine.

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