CLXVII.—*ω-Mono- and Dibromo-derivatives of Quinaldine and Nitroquinaldines and their Products of Hydrolysis.*

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It has been shown (J., 1923, **123**, 2882) that quinaldine can readily be brominated to ω-tribromoquinaldine, which can be hydrolysed to quinaldinic acid. A similar route to the corresponding α-aldehyde and alcohol has now been investigated. Unfortunately, quinaldine cannot be selectively brominated to the *ω-mono-* and *dibromo*-derivatives; ω-tribromo-quinaldine, however, can be reduced to the two other ω-bromoquinaldines by the action of the calculated quantities of titanous or stannous chloride in alcoholic or acetone solution. ω-Dibromoquinaldine can also be obtained in about 60% yield by the action of excess of sodium arsenite on the tribromo-compound in aqueous-alcoholic solution.

Unlike ω-tribromoquinaldine, the mono- and dibromo-derivatives cannot be hydrolysed by the action of acids; even oleum acting at 50° for 12 hours is ineffective. Alkalis yield coloured and resinous products. Silver nitrate, however, in aqueous alcohol converts these derivatives quantitatively into the alcohol and aldehyde respectively.

The mononitro-compounds obtained by the direct nitration of quinaldine have been directly brominated to the ω-di- and tribromo-derivatives. The latter, on hydrolysis, yield nitrocarboxylic acids which give nitroquinolines on fusion; these have been identified as the 5- and 8-nitro-compounds. The orientation of the products of the direct nitration of quinaldine given by Decker and Remfrey (*Ber.*, 1905, **38**, 2773) is thus confirmed.

EXPERIMENTAL.

ω-Dibromoquinaldine.—A solution of 23·7 g. (2 mols.) of stannous chloride in 100 c.c. of acetone was slowly added, with constant shaking and cooling, to 20 g. (1 mol.) of ω-tribromoquinaldine (*loc. cit.*) in 250 c.c. of acetone. After 1 hour, the acetone was removed, the solution neutralised with chalk and distilled with steam for about 9 hours. The white, crystalline solid in the distillate crystallised from ligroin in colourless needles, m. p. 120° (yield 9·0 g.; 60%) (Found: Br, 52·8. $C_{10}H_7NBr_2$ requires Br, 53·1%).

Quinoline-2-aldehyde.—A mixture of ω-dibromoquinaldine (8 g.) in 50 c.c. of boiling alcohol with 8·6 g. (2 mols.) of silver nitrate in 10 c.c. of hot water was boiled for 10 minutes and, after addition of hydrochloric acid and filtration, distilled with steam to remove the alcohol. The solution was now neutralised with chalk and again distilled with steam; the oil that slowly solidified in the distillate separated from ligroin in colourless crystals, m. p. 71° (yield 4·6 g.; 100%) (Found: N, 8·9. Calc. for $C_9H_6N{\cdot}CHO$: N, 8·0%). The aldehyde gave an oxime, m. p. 184°, and a phenylhydrazone, m. p. 204° (compare Kaufmann and Vallette, *Ber.*, 1913, **46**, 56).

ω-*Monobromoquinaldine* was prepared exactly as ω-dibromoquinaldine, twice the amount of stannous chloride in acetone solution being used. The *monobromoquinaldine* distilled in steam as a readily solidifying oil and crystallised from ligroin in colourless needles, m. p. 83° (Found: Br, 36·1. $C_{10}H_8NBr$ requires Br, 36·0%). The yield was about 50%.

ω-*Hydroxyquinaldine* was obtained in quantitative yield from ω-monobromoquinaldine by the action of the calculated quantity of silver nitrate in alcoholic solution, exactly as in the preparation of quinoline-2-aldehyde (*vide supra*). The *carbinol* is volatile in steam and crystallises from ligroin or alcohol in fine needles, m. p. 64° (Found: N, 8·65. $C_9H_6N{\cdot}CH_2{\cdot}OH$ requires N, 8·8%). It is readily oxidised by chromic acid to quinoline-2-aldehyde.

ω-*Tribromo*-8-*nitroquinaldine.*—A solution of quinaldine in excess of cold concentrated sulphuric acid was shaken with the calculated quantity of potassium nitrate crystals until these had dissolved. After heating for 20 minutes on the water-bath, the mixture was poured into water and nearly neutralised with sodium hydroxide, whereupon 8-nitroquinaldine separated (compare Doebner and Miller, *Ber.*, 1884, **17**, 1700, who added quinaldine nitrate to concentrated sulphuric acid). A solution of 7 g. of the recrystallised nitroquinaldine (m. p. 130°) in 150 c.c. of glacial acetic acid saturated with sodium acetate was slowly treated with 20 g. (3 mols.) of bromine in 50 c.c. of glacial acetic acid. After 20 minutes' heating on the water-bath, the mixture was poured into water; the ω-*tribromo*-8-*nitroquinaldine* that separated crystallised from alcohol in faintly yellow needles, m. p. 132° (yield 100%) (Found: N, 6·5. $C_{10}H_5O_2N_2Br_3$ requires N, 6·6%).

8-*Nitroquinaldinic Acid.*—ω-Tribromo-8-nitroquinaldine (10 g.)

was boiled with 20% sulphuric acid for 10 hours; the 8-nitroquinaldinic acid obtained on pouring the mixture into water and partly neutralising it separated from alcohol in almost colourless crystals, m. p. 182° (Besthorn and Ibele, *Ber.*, 1906, **39**, 2329, give m. p. 177°). The acid on fusion gave 8-nitroquinoline which, recrystallised from ligroin, melted at 89° alone or mixed with a pure specimen.

ω-*Dibromo*-8-*nitroquinaldine* was prepared in the same way as ω-tribromo-8-nitroquinaldine, except that two molecular proportions of bromine were used instead of three. The compound crystallises from alcohol in pale yellow needles, m. p. 183° (Found: N, 7·9. $C_{10}H_5O_2N_2Br_2$ requires N, 8·1%).

8-*Nitroquinoline*-2-*aldehyde*.—Hydrolysis of ω-dibromo-8-nitroquinaldine in the usual way with alcoholic silver nitrate gave about 50% yields of 8-*nitroquinoline*-2-*aldehyde*, which crystallises from alcohol in golden needles, m. p. 152° (Found: N, 13·7. $C_9H_5O_2N_2{\cdot}CHO$ requires N, 13·9%).

ω-*Tribromo*-5-*nitroquinaldine*.—The second nitroquinaldine, m. p. 82°, obtained by the direct nitration of quinaldine is described by Doebner and Miller (*loc. cit.*) as the 7-nitro-compound. The bromination of this substance does not proceed so readily or so smoothly as in the cases already described and the products were obtained in poor yield and mixed with much gummy material. A solution of 11 g. of the above nitroquinaldine in glacial acetic acid saturated with sodium acetate was slowly treated with 28 g. (3 mols.) of bromine in 75 c.c. of acetic acid. After heating for an hour on the water-bath, the mixture was poured into water. The gummy mass that separated was extracted with hot alcohol, from which an oil separated on cooling. The oil solidified on keeping and after recrystallisation from ligroin melted at 93° (yield 4 g.; 17%) (Found: N, 6·5. $C_{10}H_5O_2N_2Br_3$ requires N, 6·6%).

This ω-tribromonitroquinaldine was boiled for 10 hours with 20% sulphuric acid. The solution on neutralisation gave an acid which was not purified but, after drying, was decarboxylated by fusion; the product, crystallised from ligroin, melted at 72° alone or mixed with pure 5-nitroquinoline. Doebner and Miller's "7-nitroquinaldine" is thus shown to be the 5-nitro-derivative, in accordance with the conclusions of Decker and Remfrey (*loc. cit.*).

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