712. *The Structures of Some Monoquaternary Salts of 5-Substituted 4 : 7-Phenanthrolines.*

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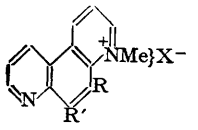
The methiodide prepared directly from 5-chloro-4 : 7-phenanthroline is shown to be the 7-methiodide, isomeric with the 5-chloro-4-methyl-4 : 7-phenanthrolinium iodide synthesised from a quaternary salt of 6-acetamido-8-chloroquinoline by means of a Skraup reaction. The methiodides of 5-acetamido-, 5-bromo-, and 5-chloro-4 : 7-phenanthroline, prepared directly, are converted in simple steps into the same compound, 5-amino-7 : 8-dihydro-7-methyl-8-oxo-4 : 7-phenanthroline; therefore the reaction of methyl iodide with either 5-acetamido- or 5-bromo-phenanthroline, as with the 5-chloro-compound, produces a 5-substituted 7-methiodide.

The main object of the present work was to identify the products of direct quaternisation of certain 5-substituted 4 : 7-phenanthrolines. Both 5-acetamido- and 5-bromo-4 : 7-phenanthroline give good yields of monomethiodides when heated with excess of methyl iodide in sealed tubes at 100° for 30 min. (Haworth and Sykes, *J.*, 1944, 311). In each case the product is a single compound, not a mixture of the 4- and the 7-methiodide (I; X = I, R′ = H; X = I, R = H, respectively; Ring Index numbering). A methiodide (*A*) of 5-chloro-4 : 7-phenanthroline was prepared by a method parallel to that described for the bromo-analogue; a Skraup reaction with 2-chloro-4-nitroaniline gave 8-chloro-6-nitroquinoline which was reduced with stannous chloride, and the resulting 6-amino-8-chloroquinoline in a second Skraup reaction gave 5-chloro-4 : 7-phenanthroline, which was quaternised in 80% yield with an excess of methyl iodide. The 5-chloro-4 : 7-phenanthroline was identified by oxidation with potassium permanganate in alkaline solution to 3 : 3′-dipyridyl-2 : 2′-dicarboxylic acid with the liberation of chloride ions, and by conversion into the known 5-amino-4 : 7-phenanthroline (Haworth and Sykes, *loc. cit.*).

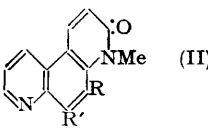
A second methiodide (*B*) of 5-chloro-4 : 7-phenanthroline was obtained in 35% yield by precipitation with potassium iodide from the neutralised products of Skraup reactions

performed on the methiodide or, more conveniently, the methotoluene-*p*-sulphonate of 6-acetamido-8-chloroquinoline.

The methiodide (*B*) must be 5-chloro-4-methyl-4 : 7-phenanthrolinium iodide (I; X = I, R = Cl, R′ = H), and (*A*) must therefore be the 7-methiodide (I; X = I, R = H, R′ = Cl). Two lines of evidence showed that isomerisation did not take place during the Skraup reaction used to prepare the 4-methiodide: first, a 30% recovery of unchanged



(I)



(II)

7-methiodide alone was made after its subjection to the conditions of the Skraup reaction; secondly, a Skraup reaction performed on the crude product of alkaline ferricyanide oxidation of 6-acetamido-8-chloroquinoline methotoluene-*p*-sulphonate gave, although in very poor overall yield, the same dihydro-*N*-methyl-oxo-compound (II; R = Cl, R′ = H) as was obtained by oxidation of the methiodide (*A*). The two methiodides of chlorophenanthroline were oxidised by alkaline potassium ferricyanide to the corresponding dihydro-*N*-methyl-oxo-derivatives in about 70% yield, and these were shown to be isomeric by conversion into the same 5-chloro-3 : 4 : 7 : 8-tetrahydro-4 : 7-dimethyl-3 : 8-dioxo-4 : 7-phenanthroline by alkaline ferricyanide oxidation of their methiodides. 5-Chloro-7 : 8-dihydro-7-methyl-8-oxo-4 : 7-phenanthroline (II; R = H, R′ = Cl) was unaffected when heated for as long as 2 hr. with excess of methyl iodide at 100° but was quaternised by treatment with hot methyl toluene-*p*-sulphonate, whilst the 3 : 4-dihydro-4-methyl-3-oxo-compound (II; R = Cl, R′ = H) reacted readily with methyl iodide at 100°.

Unlike 8-chloroquinoline (Claus and Schöller, *J. pr. Chem.*, 1893, **48**, 144), 6-acetamido-8-chloroquinoline reacted very little, if at all, with methyl iodide at 100° (1 hr.). A quaternary salt was obtained in 70% yield by the action of methyl toluene-*p*-sulphonate at about 200°. The product was easily hydrolysed by hot mineral acid to the 6-amino-derivative. Alkaline ferricyanide oxidation of the quaternary salts of both 6-acetamido- and 6-amino-8-chloroquinoline gave very poor yields, and it was to avoid losses in working up that the crude product obtained from the 6-acetamido-salt was used in the above Skraup reaction.

The amino-dihydro-*N*-methyl-oxo-compounds (II; R = NH_2, R′ = H; and R = H, R′ = NH_2) were prepared by heating the corresponding chloro-bases with concentrated ammonia solution, phenol, and a trace of copper salt for 3 days at about 180° (B.P. 454,525). 5-Amino-7 : 8-dihydro-7-methyl-8-oxo-4 : 7-phenanthroline was also obtained when these conditions were applied to the dihydro-*N*-methyl-oxo-compound prepared from 5-bromo-4 : 7-phenanthroline methiodide, which was thus shown to be a 5-substituted 7-methiodide. Further, this amino-derivative was identical with the product obtained, although in very small yield, by alkaline ferricyanide oxidation of the directly prepared methiodide of 5-acetamido-4 : 7-phenanthroline and subsequent hydrolysis of the crude product; the acetamidophenanthroline methiodide is, therefore, yet another 5-substituted 7-methiodide.

5-Acetamido-4 : 7-phenanthroline was prepared from the amino-derivative obtained by replacement of the halogen atom in 5-bromo-4 : 7-phenanthroline (B.P. 454,525; Haworth and Sykes, *loc. cit.*) or, similarly but in rather smaller yield (about 30%), from 5-chloro-4 : 7-phenanthroline; the overall yields in the somewhat tedious preparations from the benzenoid precursors were in neither case good. Renewed attempts to prepare 5-nitro-4 : 7-phenanthroline and 4 : 7-phenanthroline-5-sulphonic acid in the hope of providing easier access to the aminophenanthroline were unsuccessful; further Skraup reactions (cf. Haworth and Sykes, *loc. cit.*) with 2 : 5-diaminonitrobenzene and 2 : 5-diaminobenzenesulphonic acid failed. The intention to prepare 4 : 7-phenanthrolinesulphonic acid in two stages was not accomplished; a Skraup reaction with 2-amino-5-nitrobenzenesulphonic acid yielded, not the expected 6-nitroquinoline-8-sulphonic acid, but 6-nitroquinoline, identical with the product of a Skraup reaction on *p*-nitroaniline. A similar desulphonation is reported to occur in the attempted preparations of two hydroxy-

quinolinesulphonic acids (Claus and Posselt, *J. pr. Chem.*, 1890, **41**, 32). From attempts at direct sulphonation of 4 : 7-phenanthroline in fuming sulphuric acid (50% w/w SO_3) for 35 hr. at 90° or 2 hr. at about 150° good recoveries of the unchanged base only were made : the latter conditions are similar to those stated to be effective for the sulphonation of 3-phenyl-4 : 7-phenanthroline (Willgerodt and Jablonski, *Ber.*, 1900, **33**, 2918).

There exists a long-standing claim for the preparation of 5-amino-3 : 4-dihydro-4-methyl-3-oxo-4 : 7-phenanthroline. Kaufmann and Radošević (*Ber.*, 1909, **42**, 2612) found that, unlike the parent base, 3 : 4-dihydro-4-methyl-3-oxo-4 : 7-phenanthroline was readily nitrated by mixed concentrated sulphuric and fuming nitric acids at 100° to a mononitro-derivative, and they assigned position 5 to the substituent without substantiating evidence ; they reduced this compound to the amino-compound. A specimen of Kaufmann and Radošević's amino-derivative, prepared by their method with small modifications, was not identical with either of our 5-amino-dihydro-*N*-methyl-oxo-4 : 7-phenanthrolines, and the nitro-group cannot, therefore, have been introduced at either of the *Bz*-positions.

Experimental

8-Chloro-6-nitroquinoline.—A mixture of 2-chloro-4-nitroaniline (25 g.), water (70 c.c.), concentrated sulphuric acid (90 c.c.), glycerol (35 c.c.), and arsenic acid (40 c.c.; *d* 1·8) was boiled gently under reflux for 3 hr. The product was cooled, diluted to 1 l., filtered, and made alkaline with 40% sodium hydroxide solution, the mixture being kept cool by addition of ice. The precipitate was filtered off, washed, dried, and extracted with boiling benzene (300 c.c.) ; *8-chloro-6-nitroquinoline* (15 g.) crystallised from the extract when it was allowed to cool. Recrystallisation from benzene or alcohol (charcoal) gave yellow prisms or needles respectively, m. p. 154° (Found : Cl, 16·8. $C_9H_5O_2N_2Cl$ requires Cl, 17·0%).

6-Amino-8-chloroquinoline.—A solution of stannous chloride dihydrate (70 g.) in concentrated hydrochloric acid (50 c.c.) was added in small portions with stirring to a cooled solution of 8-chloro-6-nitroquinoline (20 g.) in concentrated hydrochloric acid (60 c.c.). The mixture was cooled thoroughly and the precipitated stannichloride was filtered off, dissolved in boiling water (600 c.c.), and poured with vigorous stirring into 20% sodium hydroxide solution (1—2 l.). After cooling, the precipitate was filtered off, washed, dried, and extracted with boiling dibutyl ether (600 c.c.) from which, when it was cooled, 6-amino-8-chloroquinoline (12 g.) separated. Recrystallisation of the product from dibutyl ether or benzene gave pale yellow leaflets, m. p. 153° [Hutchinson and Kermack (*J.*, 1947, 678), who used West's method, give m. p. 154° and quote Curd's product (unpublished method), m. p. 156—157°] (Found : Cl, 19·7. Calc. for $C_9H_7N_2Cl$: Cl, 19·9%). The *acetyl* derivative, prepared in almost quantitative yield by acetic anhydride–acetic acid on the water-bath (10—15 min.), crystallised from 10% acetic acid in clusters of threads, m. p. 196—197° (Found : C, 59·4; H, 4·2; N, 12·5; Cl, 15·8. $C_{11}H_9ON_2Cl$ requires C, 59·9; H, 4·1; N, 12·7; Cl, 16·1%).

6-Acetamido-8-chloro-1-methylquinolinium Toluene-p-sulphonate.—6-Acetamido-8-chloroquinoline (10 g.) was dissolved by stirring it into methyl toluene-*p*-sulphonate (100 g.) at about 120°. The mixture was heated during 10 min. to about 200°, and the dark red product, while still hot, was poured on to an equal weight of crushed ice. Unchanged ester was removed by extraction with ether (2 × 150 c.c.). The aqueous solution was mixed with cold, saturated ammonium sulphate solution (300 c.c.), and the precipitated solidifying oil was filtered off, washed with methanol, and dried (13 g.). The product crystallised from methanol in yellow prisms, m. p. about 227° with previous darkening and softening. That this product was the *methotoluene-p-sulphonate* and not a methosulphate was shown by its freedom from sulphate and ammonium ions, by the preparation from it of a specimen of toluene-*p*-sulphonamide after removal of the cation as its sparingly soluble iodide and then of excess of iodide with silver nitrate, and by its composition (Found : S, 8·2; Cl, 8·6. $C_{19}H_{19}O_4N_2SCl$ requires S, 7·9; Cl, 8·7%). The *methiodide* (4 g.) was deposited when potassium iodide (5 g.) in a little water was added to the methotoluene-*p*-sulphonate (5 g.) in water (50 c.c.) ; recrystallised from water it formed yellow prismatic needles, m. p. about 200° (decomp.) depending on the rate of heating, with previous softening (Found : I, 34·6. $C_{12}H_{12}ON_2ClI$ requires I, 35·0%).

6-Amino-8-chloro-1-methylquinolinium Iodide.—A solution of 6-acetamido-8-chloroquinoline methotoluene-*p*-sulphonate (3 g.) in 2N-hydrochloric acid (30 c.c.) was boiled under reflux for 1 hr., cooled, and neutralised to pH 6—7. Addition of potassium iodide (10 g.) in a little water gave an immediate yellow precipitate of *6-amino-8-chloroquinoline methiodide* (2·2 g.), golden-

yellow needles (from methanol), m. p. about 198° (decomp.) (Found: I, 39·2. $C_{10}H_{10}N_2ClI$ requires I, 39·6%).

6-*Acetamido*-8-*chloro*-1 : 2-*dihydro*-1-*methyl*-2-*oxoquinoline*.—To a cold solution of 6-acetamido-8-chloroquinoline methotoluene-*p*-sulphonate (4 g.) in water (100 c.c.), or an equivalent solution of the methiodide, was added 10% sodium hydroxide solution (15 c.c.), followed immediately by 10% potassium ferricyanide solution (80 c.c.), with stirring. After 30 min. the dark, turbid mixture was made strongly alkaline with 40% sodium hydroxide solution, and the sticky, solidifying precipitate was separated, air-dried (about 1 g.), and extracted with a small volume of chlorobenzene in a continuous extractor. The brown material which crystallised on cooling was recrystallised from methanol (charcoal), to produce pale yellow needles (0·1 g.) of the *oxo*-compound, m. p. 258—259° (Found: Cl, 14·4. $C_{12}H_{11}O_2N_2Cl$ requires Cl, 14·2%).

5-*Chloro*-4 : 7-*phenanthroline*.—6-Amino-8-chloroquinoline (10 g.), water (25 c.c.), concentrated sulphuric acid (25 c.c.), glycerol (15 c.c.), and crude sulphonated nitrobenzene (15 g.) were refluxed gently for 6 hr., then cooled, diluted to 250 c.c., and filtered. The filtrate was made strongly alkaline with ammonia solution (*d* 0·88) (ice-cooling) and kept overnight. The separated product was purified by conversion into the nitrate, which crystallised on cooling of a hot solution of the base in 2N-nitric acid (100 c.c.). The crude *chlorophenanthroline*, liberated by gradually basifying a paste of the nitrate with water, was dried (7 g.) and purified by distillation at 20 mm. and crystallisation from chlorobenzene–ligroin from which it formed colourless needles, m. p. 155° (Found: Cl, 16·3. $C_{12}H_7N_2Cl$ requires Cl, 16·5%). Oxidation of the chlorophenanthroline (2·1 g.) with alkaline potassium permanganate in alkaline solution, by Smith's procedure (*J. Amer. Chem. Soc.*, 1930, **52**, 397) for the unsubstituted base, gave 3 : 3′-dipyridyl-2 : 2′-dicarboxylic acid (0·5 g.), m. p. 210° (decomp.) alone or mixed with a specimen prepared from 4 : 7-phenanthroline. The *nitrate* of chlorophenanthroline on crystallisation from dilute nitric acid (charcoal) and then from water formed colourless threads, m. p. 256° (decomp.) (Found: equiv., 276. $C_{12}H_7N_2Cl,HNO_3$ requires equiv., 277·7).

5-*Chloro*-7-*methyl*-4 : 7-*phenanthrolinium iodide* (I; X = I, R = H, R′ = Cl) was obtained by heating the base (3 g.) with an excess of methyl iodide in a sealed tube in a boiling-water bath for 30 min. The orange product (4 g.), when washed with ether and crystallised from water, formed red prisms, m. p. 278° (decomp.) with previous darkening and softening (Found: I, 35·3. $C_{13}H_{10}N_2ClI$ requires I, 35·6%).

5-*Chloro*-4-*methyl*-4 : 7-*phenanthrolinium Iodide* (I; X = I, R = Cl, R′ = H).—6-Acetamido-8-chloroquinoline methotoluene-*p*-sulphonate (10 g.), water (12 c.c.), concentrated sulphuric acid (12 c.c.), glycerol (7 c.c.), and crude sulphonated nitrobenzene (7 g.) were boiled gently under reflux for 3 hr. and the product was cooled, diluted to 150 c.c., and neutralised to pH *ca.* 6 (ice-cooling). After separation from the precipitated tar and treatment with charcoal, the supernatant liquid was mixed with a solution of potassium iodide (50 g.) in a little water.

Deposition of the chlorophenanthroline *methiodide* was complete in about 30 min. The product (3 g.) crystallised from water as yellow prismatic needles, m. p. 272° (decomp.) with previous darkening and softening, sharp decomp. on rapid heating to > *ca.* 230° (Found: I, 35·4%). The methotoluene-*p*-sulphonate could be replaced by the methiodide, but iodine liberated immediately on mixing caused bumping; there was no nuclear iodination.

5-*Chloro*-7 : 8-*dihydro*-7-*methyl*-8-*oxo*-4 : 7-*phenanthroline* (II; R = H, R′ = Cl).—5-Chloro-4 : 7-phenanthroline 7-methiodide (4 g.) was oxidised with alkaline potassium ferricyanide (cf. Douglas, Jacomb, and Kermack, *J.*, 1947, 1659). The product precipitated by the final addition of alkali was dried and extracted with boiling chlorobenzene from which the *chloro-base* (2 g.) crystallised on cooling. Recrystallisation from benzene or chlorobenzene gave very pale yellow needles, m. p. 251° (Found: Cl, 14·4. $C_{13}H_9ON_2Cl$ requires Cl, 14·5%). The *methiodide* was prepared by heating the chloro-base (1 g.) briefly in methyl toluene-*p*-sulphonate (10 g.) solution, partitioning the cooled product between ether and water, and adding potassium iodide to the aqueous solution. The product (0·6 g.) crystallised from methanol in flocculent yellow threads, decomp. > *ca.* 200° leaving a residue of the original base (Found: I, 32·9. $C_{14}H_{12}ON_2ClI$ requires I, 32·8%).

5-*Chloro*-3 : 4-*dihydro*-4-*methyl*-3-*oxo*-4 : 7-*phenanthroline* (II; R = Cl, R′ = H).—5-Chloro-4 : 7-phenanthroline 4-methiodide (4 g.) was similarly oxidised with alkaline potassium ferricyanide. The *chloro-base* separated from the reaction mixture without the final addition of strong alkali, and was dried (2 g.) and crystallised from chlorobenzene or benzene in very pale yellow needles, m. p. 209° (Found: Cl, 14·3%). The same compound (0·05 g.) was obtained by a Skraup reaction from the crude oxidation product of 6-acetamido-8-chloroquinoline methiodide (2 g.), the proportions of reactants prescribed for the Skraup reaction on the methiod-

ide itself being used. The ***methiodide*** of (II; R = Cl, R′ = H) was obtained (1·4 g.) by heating the chloro-base (1 g.) with excess of methyl iodide at 100° for 30 min., and crystallised from water or methanol in orange needles, m. p. about 253° (decomp.) with previous darkening and softening (Found: I, 32·4%).

5-Bromo-7 : 8-dihydro-7-methyl-8-oxo-4 : 7-phenanthroline (II; R = H, R′ = Br).—The 7-methiodide (5 g.) prepared directly from 5-bromo-4 : 7-phenanthroline (Haworth and Sykes, *loc. cit.*) was oxidised with alkaline potassium ferricyanide by the procedure given above for the oxidation of the chloro-analogue. The *product*, which separated practically completely without the reaction mixture being made strongly alkaline, was washed with water and dried (3 g.); it crystallised from chlorobenzene or xylene in yellow needles, m. p. 278° (Found: Br, 27·8. $C_{13}H_9ON_2Br$ requires Br, 27·6%).

5-Chloro-3 : 4 : 7 : 8-tetrahydro-4 : 7-dimethyl-3 : 8-dioxo-4 : 7-phenanthroline was obtained by oxidation of the methiodides of both 5-chloro-dihydro-*N*-methyl-oxo-4 : 7-phenanthrolines with alkaline potassium ferricyanide. Much of it separated from the reaction mixtures without the final addition of strong alkali, was dried, and crystallised from formamide in thread-like needles, m. p. 326° with previous darkening and softening (Found: Cl, 12·5. $C_{14}H_{11}O_2N_2Cl$ requires Cl, 12·9%).

5-Amino-7 : 8-dihydro-7-methyl-8-oxo-4 : 7-phenanthroline (II; R = H, R′ = NH_2).—The chloro-base (II; R = H, R′ = Cl) (1 g.), phenol (1 g.), concentrated ammonia solution (3 c.c.), and a trace of copper acetate were heated for 3 days at about 180°. The product was washed from the tube with an excess of dilute sulphuric acid and the mixture was treated, while hot, with charcoal. The material precipitated from the cooled solution by basification with 40% sodium hydroxide solution was purified by conversion into the hydrochloride, sparingly soluble in cold dilute hydrochloric acid, and the re-liberated base was dried and extracted in a continuous extractor with a small volume of chlorobenzene. The *amino*-compound, which separated from the chlorobenzene during the extraction and on cooling the extract, was filtered off (0·3 g.) and crystallised from chlorobenzene in yellow needles, m. p. 296° with previous darkening and softening (Found: C, 69·2; H, 4·9; N, 18·5. $C_{13}H_{11}ON_3$ requires C, 69·3; H, 4·9; N, 18·7%). The same product was obtained in similar yield when the bromo-analogue (II; R = H, R′ = Br) was used in place of the chloro-base.

5-Acetamido-4 : 7-phenanthroline methiodide (0·5 g.) (Haworth and Sykes, *loc. cit.*) was oxidised in water (25 c.c.) with 10% sodium hydroxide solution (2 c.c.) and 10% potassium ferricyanide solution (10 c.c.). The dark tar, which separated from the turbid mixture on basificationafter 30 min., was heated in dilute hydrochloric acid solution for 30 min. at 100°. This solution was cooled and made strongly alkaline, and the brown precipitate was dried and extracted with a small volume of chlorobenzene, to yield a few mg. of crystalline material, m. p. 296° with previous darkening and softening. This, on admixture, did not depress the m. p. of the above amino-compound.

5-Amino-3 : 4-dihydro-4-methyl-3-oxo-4 : 7-phenanthroline (II; R = NH_2, R′ = H) was obtained by treatment of the chloro-base (II; R = Cl, R′ = H) (1 g.) as described above for the isomeric chloro-compound except that purification of the product by way of its hydrochloride was omitted. The *amino*-compound (0·2 g.), which was extracted by benzene from the crude product, crystallised from chlorobenzene (charcoal) in yellow prismatic needles, m. p. 257° with previous darkening and softening (Found: C, 69·2; H, 4·9; N, 18·8%).

4 : 7-Phenanthroline Methiodide (I; X = I, R = R′ = H).—4 : 7-Phenanthroline (5·4 g.), prepared by a double Skraup reaction on *NN′*-diacetyl-*p*-phenylenediamine in conditions similar to those of B.P. 394,416, ex. 11, was heated with excess of methanolic methyl iodide (20 c.c. of 40% w/v) in a sealed flask at 100° for 30 min. The solid product, after being washed with ether, was crystallised from water (75 c.c.), to yield as first crop 6—7 g. of the yellow monomethiodide monohydrate (Skraup and Vortmann, *Monatsh.*, 1883, **4**, 570; Kaufmann and Radošević, *loc. cit.*) which was recrystallised from water and dried at 100° to the orange anhydrous salt, m. p. 268° (decomp.) with previous darkening and softening (Douglas, Jacomb, and Kermack, *loc. cit.*, give m. p. 270—271°) (Found, for anhyd. material: I, 39·4. Calc. for $C_{13}H_{10}N_2ClI$: I, 39·4%). The original mother-liquor, after concentration, deposited a mixture of the monomethiodide and dichromate-orange prisms of the dimethiodide.

Pyr- *or* Pyr′-*Amino-3 : 4-dihydro-4-methyl-3-oxo-4 : 7-phenanthroline*.—The nitro-compound (5 g.), prepared (Kaufmann and Radošević, *loc. cit.*) by nitrating the nitrate of the oxidation product (Douglas, Jacomb, and Kermack, *loc. cit.*) of 4 : 7-phenanthroline methiodide, was boiled under reflux for 30 min. with yellow ammonium sulphide solution (40 c.c. of 12% w/v H_2S) and water (60 c.c.). The product was acidified with dilute sulphuric acid, boiled, and

filtered while hot. The filtrate, made alkaline with ammonia and cooled, deposited the crude amino-derivative (3·5 g.) which crystallised from chlorobenzene in yellow plates, m. p. 246° (Kaufmann and Radošević, *loc. cit.*, give m. p. 250°). Like the *Bz*-substituted isomers, this compound had a nitrate and a hydrochloride which were sparingly soluble in the respective dilute acids. Its m. p. was obviously distinct from that of the 5-amino-7 : 8-dihydro-compound and somewhat removed from that of the 5-amino-3 : 4-dihydro-compound; on admixture, it depressed the m. p. of the latter.

6-*Nitroquinoline*.—A mixture of the sodium salt of 2-amino-5-nitrobenzenesulphonic acid (180 g.), water (540 c.c.), concentrated sulphuric acid (540 c.c.), glycerol (270 c.c.), and arsenic acid (270 c.c.; *d* 1·8) was boiled under reflux for 3—4 hr. The product was cooled, diluted, and neutralised, yielding a precipitate (85 g.) which crystallised from dilute acetic acid or alcohol (charcoal) in colourless needles; the purified material was free from sulphur, and its m. p. 151° was not depressed on admixture with authentic 6-nitroquinoline prepared by a Skraup reaction on *p*-nitroaniline in the conditions of B.P. 394,416, ex. 8.

The quaternary salts described herein were dried at 100°, and none lost any significant further proportion of water at 100° *in vacuo* over phosphoric oxide.

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