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# *N*-Quaternary Compounds

## Part XXII.[1] Quinoline Derivatives

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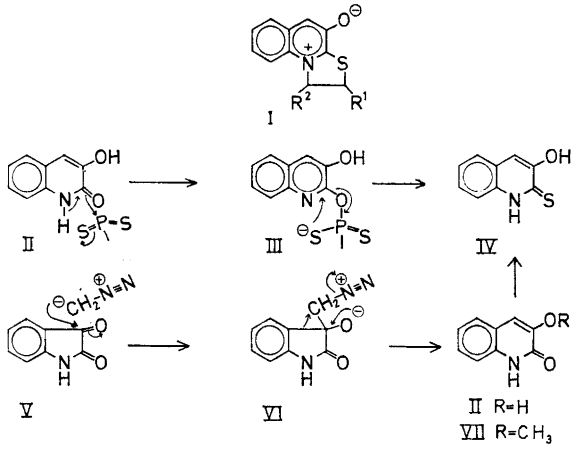
Dihydrothiazolo[3,2-a]quinolinium-10-oxide derivatives are formed when 1,2-dibromoethanes or α-bromo-α,β-unsaturated acids are reacted with 3-hydroxyquinoline-2-thione. The 3-carboxy derivatives readily suffer decarboxylation. Electrophilic substitution in this new ring system first takes place in the *ortho* position to the phenolic oxygen. UV and NMR data are recorded and compared with the data for the corresponding pyridinium series.

Our studies of the dihydrothiazolo[3,2-a]pyridinium system [2–4] have now been extended to derivatives with a phenyl group, fused to the 5,6-positions of the pyridine ring.

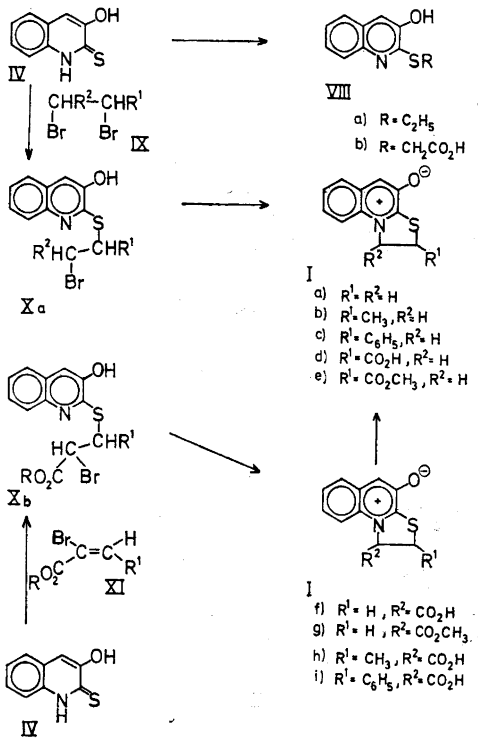
The quinoline-2-thione (IV) was chosen as an intermediate for the preparation of I, in analogy with the reaction sequence in the corresponding pyridine series.[2,3] The thiolactam was made from 2,3-dihydroxyquinoline. The latter was expected to exist largely in its tautomeric lactam form (II). This allows



phosphorus pentasulphide to attack selectively the lactam carbon, as we have previously established for 4,5-dihydroxypyrimidines.[5] Under the reaction conditions for the thiation of the dihydroxy derivative (II) the methyl ether (VII) was largely dealkylated to IV. Mechanistically, the thiation is understood by assuming the formation of an intermediate phosphorus ester over the lactam oxygen (III). The phosphorus ester is then displaced by a sulphur nucleophile. By analogy with halogenation with phosphorus halides the displacement of the phosphorus ester can be an intermolecular or intramolecular process.

2,3-Dihydroxyquinoline can be synthesized by several methods.[6-9] We have found diazomethane ring expansion of isatin (V) most convenient.[6-7] A mixture of II and the 3-methoxy derivative (VII) is obtained. The latter is readily dealkylated with HBr in acetic acid. The $\beta$-carbonyl group in isatin has a lower electron density than the $\alpha$-carbonyl group, which is part of a lactam structure. Therefore, the diazomethane attacks selectively the $\beta$-carbon. The phenolic hydroxyl group in II competes successfully with isatin for diazomethane, as shown by the formation of the 3-methoxy derivative (VII). A slight excess of diazomethane is therefore required. A large excess leads to VII. The selective alkylation of the phenolic 3-hydroxy group in 2,3-dihydroxyquinoline again illustrates the difference in chemical properties of the two hydroxy groups.

The thiolactam is *S*-alkylated by alkyl halides (VIII) and is cyclised over the nitrogen with 1,2-dibromoethanes (IX) in the same way as the corre-



sponding pyridines.[2] The sulphur nucleophile also adds to α-bromo-α,β- unsaturated acid derivatives (XI) and the adducts (Xb) are cyclised to the corresponding quaternary derivatives (I). The reaction is slow. Therefore, the bromoacrylates can be generated *in situ* from corresponding dibromopropionates in the presence of a strong base.

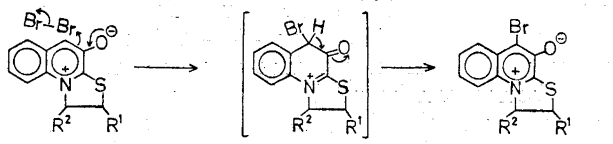
The overall reaction rate for the adduct – cyclisation reaction must depend on the electron density on the sulphur for the adduct forming step, and again on the electron density on the annular nitrogen for the cyclisation step. Thus pyrimid-2-thiones react more slowly than the corresponding pyridines. The electronegativity of the extra phenyl ring in quinoline as compared to the pyridine, also leads to deactivation. This is seen by greatly reduced reaction rates. The cyclisation step (X→I) will be subject to steric interaction as found in the case of the corresponding 6-substituted pyridines. The interaction with the condensed phenyl group is perhaps not so great, but could be of some importance if the formation of the adduct (IV→Xb) is readily reversible. Reversibility of this step seems a reasonable assumption since the methine proton on the α-carbon to the carboxyl group Xb is highly activated by both the bromine atom and the carboxyl group, and since the thiolactam (IV) is a good leaving group.

Introduction of a β-substituent, such as a methyl or a phenyl group into α-bromoacrylic acid, reduces the overall reaction rate further in agreement with the normal observation for the Michael type reaction.[10]

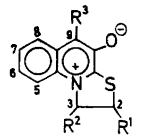
Vigorous reaction conditions were necessary to effect the addition – cyclisation reaction, so that the quaternary products formed from β-methyl- or phenyl-acrylic acid (I h, i) were decarboxylated. In the pyridine series it has been shown that it is not the acrylic acid reagent but the cyclic quaternary acid which is decarboxylated.[3] The great tendency to decarboxylation is due to the activating effect of the quaternary nitrogen.

The behaviour of quinolinium oxides towards electrophilic substitution with bromine was studied. The quinolinium cation itself is attacked in the phenyl ring in the 5- and 8-positions.[11] *N*-Quaternary pyridines resist electrophilic substitution by a reagent such as bromine unless the pyridine nucleus contains strongly electron donating substituents such as found in dihydrothiazolo[3,2-a]pyridinium-8-oxides.[4] In the quinolinium-oxides prepared, it was found that bromine in acetic acid furnished a monosubstituted product. Mass spectrometry also showed the presence of minor amounts of dibrominated products. The mild reaction conditions clearly point to the introduction of the bromine into the *ortho* position to the phenolic hydroxyl group (XIII).

The NMR spectra of the quinolinium oxides in TFA (Table 1) show unresolved four-proton signals around 2 τ and a one-proton singlet at 1.7 – 1.8 τ.




I XII XIII a) $R^1 = R^2 = H$ b) $R^1 = H, R^2 = CO_2H$ c) $R^1 = CO_2H, R^2 = H$

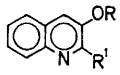
*Table 1.* NMR spectra in TFA of 

| Comp. | Substituents | | | Chemical shifts in τ values[a] | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | $H_2$ | $R^1$ | $H_3$ | $R^2$ | $R^3$ | $H_{5-8}$ |
| I a | H | H | H | | 5.90(6.12) | 4.42(4.90) | | 1.83 | 1.9–2.3 |
| XIII a | H | H | Br | | 5.88(6.07) | 4.44(4.87) | | – | 1.5–2.1 |
| I b | $CH_3$ | H | H | 5.30(5.6) | 8.18(8.30) | 4.2–5.1(4.6) | | 1.82 | 1.9–2.2 |
| I c | $C_6H_5$ | H | H | 4.01(5.0) | 2.5(2.5) | 4.1–4.6(4.2) | | 1.71 | 1.8–2.2 |
| I d | $CO_2H$ | H | H | | 3.7–4.8 (4.2–4.9) | | | 1.76 | 1.8–2.2 |
| XIII c | $CO_2H$ | H | Br | | 3.7–4.8 | | | – | 1.4–2.0 |
| I e | $CO_2H_3$ | H | H | 3.8–4.8(4.2–5.1) 6.95(6.00) | | 3.8–4.8(4.2–5.1) | | 1.84 | 1.9–2.3 |
| I f | H | $CO_2H$ | H | 5.2–5.8 (5.5–5.9) | | 3.22(3.67) | – | 1.78 | 1.9–2.3 |
| XIII b | H | $CO_2H$ | Br | 5.2–5.7(5.5–5.9) | | 3.13(3.73) | – | – | 1.3–2.1 |
| I g | H | $CO_2H_3$ | H | 5.3–5.9 | | 3.26 | 6.00 | 1.82 | 1.9–2.2 |

[a] The chemical shifts for available pyridinium analogues are given in brackets.[2–4]

The latter was shown to be due to the C-9 hydrogen by zinc-deuterioacetic acid reduction of the bromo compound since the deuterio compound did not give this NMR signal. The protons in the dihydrothiozolo ring have suffered a downfield shift in comparison with the pyridine analogues (Table 1).

The quinolines have low water solubility so their UV spectra have been recorded in acidic and alkaline methanolic solution. The condensed phenyl group in quinoline leads to a bathochromic displacement of the absorption bands in comparison with the corresponding pyridines, and also makes accessible bands which are hidden in the lower range of the pyridine spectra (Tables 2 and 3). A comparison of data can be made for the quaternary derivatives with corresponding data for pyridinium derivatives. Thus the pyridinium derivatives in acid solution have a band around 340 mμ, while the quinolinium derivatives have two bands at 380 and 365 mμ (Table 3). In alkaline solution the respective bands are at 360 and at 405–410 mμ. On the basis of the observed UV shifts on going from pyridine to quinoline tentative assignments of the absorption bands can be made. Thus the shift of the $L_b$ band of 50 units from pyridine to quinoline[12] agrees with the shift between the hydroxy pyridine and quinoline analogues of 45 units in alkaline solution and 40 units in acid solution. The 330–340 mμ bands of the quinolines in alkaline solution, and the 240 mμ bands of the analogous pyridinium derivatives are

*Table 2.* UV absorption of 

| Comp. | Substituents | | N HCl in MeOH | | | | | | N KOH in MeOH | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | R | λ | logε | λ | logε | λ | logε | λ | logε | λ | logε | λ | logε |
| II | OH | H | 333 | 4.03 | 319 | 4.08 | 245<br>250[a] | 4.03<br>3.97 | 340 | 4.26 | 327 | 4.23 | 245 | 4.20 |
| VII | OH | $CH_3$ | 331 | 4.03 | 317 | 4.08 | 245<br>250[a] | 4.05<br>4.01 | 335 | 3.96 | 322 | 3.98 | 236 | 4.31 |
| IV | SH | H | 378 | 4.18 | 365[a] | 4.10 | 269 | 3.98 | 382 | 3.85 | 370 | 3.84 | 259 | 4.01 |
| VIII a | $SCH_3$ | H | 374 | 4.04 | 360[a] | 3.92 | 263<br>270 | 3.75<br>3.77 | 363 | 3.70 | 349[a] | 3.64 | 259 | 3.74 |
| VIII b | $SCH_2COOH$ | H | 372 | 3.95 | 360[a] | 3.85 | 267 | 3.68 | 361 | 3.80 | 350[a] | 3.73 | 259 | 4.17 |

[a] Shoulder.

ascribed to $L_a$ transitions. These shifts correspond well to the recorded pyridine-quinoline shift of 80 – 100 units. In acid solution these bands in the quinoline appear to be missing or perhaps hidden under other prominent transitions, as suggested for similar observations for the quinolinium ion.[13] The bands at 275 – 285 mμ and at 265 – 275 mμ in alkaline and acid solution, respectively, could be interpreted as being the $B_b$ band not seen in the pyridines.

## EXPERIMENTAL

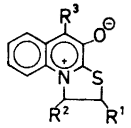
The NMR spectra were recorded on a Varian A-60 A spectrophotometer, and the UV spectra on a Perkin-Elmer model 137-UV spectrophotometer. For chromatography, the systems BuOH:EtOH:$NH_3$:$H_2O$ (4:1:2:1) and BuOH:HOAc:$H_2O$ (100:22:50) were used.

*3-Hydroxyquinolin-2-one (II).* Isatin (50 g, 0.34 mol) in ice-cold ether (400 ml) was suspended by vigorous stirring, while an ice-cold solution of diazomethane (0.6 mol) in ether (1200 ml) was added dropwise. The red colour of isatin had faded away after stirring in the cold for 1.5 h. Instead, a yellowish white precipitate had been formed. After stirring overnight the solid precipitate was collected and found to be an equal mixture of the title compound and 3-methoxyquinolin-2-one; yield 38 g.

This product was added to a solution from 48 % aqueous HBr (100 ml) and acetic anhydride (100 ml), and the resultant solution was heated under reflux for 2 days. Mixed with its hydrobromide the title compound was precipitated from the solution on cooling; yield 41 g. The free base could be liberated by dissolution in hot N NaOH and neutralisation with HCl; m.p. 266 – 268°. (Found: C 67.01; H 4.40; N 8.58. Calc. for $C_9H_7NO_2$: C 67.10; H 4.34; N 8.80.)

*3-Methoxyquinolin-2-one (VII).* This product was prepared as above by the use of three equivalents of diazomethane, m.p. 191 – 192°. (Found: C 68.72; H 5.10; N 8.05. Calc. for $C_{10}H_9NO_2$: C 68.55; H 5.14; N 8.00.)

*3-Hydroxyquinoline-2-thione (IV).* 3-Hydroxyquinolin-2-one hydrobromide (50 g, 0.21 mol) and phosphorus pentasulphide (66 g, 0.30 mol) in pyridine (350 ml) was heated

*Table 3.* UV absorption of 

| Comp. | Substituents | | | N HCl in MeOH | | | | | | | | N KOH in MeOH | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | λ | log ε | λ | log ε | λ | log ε | λ | log ε | λ | log ε | λ | log ε | λ | log ε | λ | log ε | λ | log ε |
| I a | H | H | H | 380 | 4.15 | 365 | 4.09 | 273 | 3.77 | 265 | 3.84 | 406 | 4.02 | 342 | 3.55 | 328 | 3.51 | 282 | 4.06 | 275 | 4.05 |
| I b | $CH_3$ | H | H | 380 | 4.10 | 364 | 4.09 | 273 | 3.78 | 265 | 3.86 | 406 | 4.06 | 343 | 3.51 | 330 | 3.45 | 280 | 4.11 | 274 | 4.11 |
| I c | $C_6H_5$ | H | H | 382 | 4.14 | 367 | 4.20 | 272[a] | 3.89 | 265 | 3.98 | 410 | 3.82 | 342 | 3.89 | 330 | 3.87 | 282 | 4.04 | 275 | 4.02 |
| I d | $CO_2H$ | H | H | 379 | 4.07 | 366 | 4.00 | 273 | 3.89 | 265 | 3.92 | 406 | 3.67 | 343 | 3.73 | 330 | 3.67 | 282[a] | 3.78 | 275[a] | 3.78 |
| I e | $CO_2CH_3$ | H | H | 383 | 4.10 | 367 | 4.05 | 272[a] | 3.80 | 265 | 3.82 | 405 | 3.76 | 342 | 3.66 | 330 | 3.63 | 282[a] | 3.76 | 277[a] | 3.77 |
| I f | H | $CO_2H$ | H | 383 | 4.28 | 367 | 4.23 | 273[a] | 3.85 | 265 | 3.93 | 409 | 4.18 | 345 | 3.53 | 330 | 3.48 | 283 | 4.13 | 276 | 4.15 |
| I g | H | $CO_2CH_3$ | H | 384 | 4.30 | 367 | 4.24 | 274 | 3.85 | 266 | 3.92 | 408 | 4.17 | 345 | 3.64 | 330 | 3.60 | 283 | 4.12 | 276 | 4.12 |
| XIII c | $CO_2H$ | H | Br | 383 | 4.00 | 368 | 3.98 | 279[a] | 3.68 | 270[a] | 3.86 | 410 | 3.90 | 346 | 3.85 | 333 | 3.80 | 287[a] | 3.95 | 280[a] | 3.98 |
| XIII b | H | $CO_2H$ | Br | 384 | 4.27 | 367 | 4.22 | 278[a] | 3.83 | 270 | 4.00 | 411 | 4.24 | 345 | 3.69 | 330 | 3.65 | 286 | 4.12 | 280 | 4.12 |
| XIII a | H | H | Br | 384 | 4.01 | 370 | 4.00 | 276[a] | 3.45 | 267[a] | 3.61 | 412 | 3.49 | 347 | 3.94 | 336[a] | 3.89 | 288 | 3.92 | 278 | 3.91 |

[a] Shoulder.

under reflux overnight. The solution was concentrated to about 200 ml, water (1.5 l) was added with stirring, and the solution allowed to stand in the cold for 3 days. A yellow solid was precipitated; yield 35 g (95 %). The product had m.p. 239 – 240° after one recrystallisation from ethyl acetate. (Found: C 61.13; H 3.97; N 7.85. Calc. for $C_9H_7NOS$: C 61.00; H 3.96; N 7.92.)

*2-Ethio-3-hydroxyquinoline (VIIIa).* To 3-hydroxyquinoline-2-thione (1.77 g, 0.01 mol) in N NaOH (15 ml) ethyl iodide (2.34 g, 0.015 mol) was added and the solution kept at 60° for 3 days. The cold reaction mixture was neutralized with a little HCl, the solid filtered off, washed well with water and dried; yield 1.6 g (78 %), m.p. 151 – 153°. (Found: C 64.07; H 5.32; N 6.83. Calc. for $C_{11}H_{11}NOS$: C 64.35; H 5.32; N 6.83.)

*2-Carboxymethio-3-hydroxyquinoline (VIIIb).* 3-Hydroxyquinoline-2-thione (1.77 g, 0.01 mol) and bromoacetic acid (2.80 g, 0.02 mol) in dry chlorobenzene was stirred at 135° for 30 min. The precipitate was filtered off from the hot solution, dissolved in N NaOH (25 ml), reprecipitated with 6 N HCl at pH 2 and recrystallized from ethanol; yield 2.2 g (93 %), m.p. 190 – 192°. (Found: C 56.05; H 3.72; N 5.85. Calc. for $C_{11}H_9NO_3S$: C 56.20; H 3.83; N 5.96.)

*Dihydrothiazolo[3,2-a]quinolinium-10-oxide (Ia).* 3-Hydroxyquinoline-2-thione (1.77 g, 0.01 mol) and dibromoethane (3.90 g, 0.02 mol) were added to methanolic sodium methoxide (0.02 mol Na, 100 ml), and the solution was heated at 60° for 6 days. The solution was then evaporated, the residue dissolved in N NaOH, the pH of the solution brought to 3 with N HCl, and the solution left in the cold. The title compound crystallized out from the solution; yield 1.55 g (76 %) m.p. > 300°. (Found: C 64.68; H 4.23, N 6.60. Calc. for $C_{11}H_9NOS$: C 65.00; H 4.43; N 6.89.)

*10-Hydroxydihydrothiazolo[3,2-a]quinolinium-3-carboxylate (If).* 2,3-Dibromopropionic acid (3.48 g, 0.015 mol) was added to sodium methoxide (from 0.35 g of sodium, 0.015 mol) in methanol (100 ml). 3-Hydroxyquinoline-2-thione (1.77 g, 0.01 mol) was then added and the solution was heated at 70° for 2 days. The solid formed, 0.5 g of the title compound, was filtered off from the warm reaction mixture. The filtrate was heated for another 2 days at 70°, evaporated, triturated with water and the solid residue (1.5 g) was dried. Chromatography showed this to be about 50 % of the title compound, the other major part being unreacted thiolactam.

The desired product was purified by dissolution in aq. NaOH, and reprecipitation by neutralisation with aq. HCl, followed by recrystallisation from methanol; m.p. 180 – 182°. (Found: C 58.06; H 3.78; N 5.45. Calc. for $C_{12}H_9NO_3S$: C 58.30; H 3.65 N 5.66.)

Reactions with pregenerated α-bromoacrylic acid gave similar results.

*3-Carbomethoxydihydrothiazolo[3,2-a]quinolinium-10-oxide (Ig).* 3-Hydroxyquinoline-2-thione (1.77 g, 0.01 mol) and methyl 2,3-dibromopropionate (2.86 g, 0.012 mol) were added to methanolic (50 ml) sodium methoxide (from 0.55 g of sodium, 0.022 mol) and the solution was heated at 60° for 3 days. The solution was evaporated, and the residue triturated with warm methylene chloride (50 ml). The filtrate was concentrated to about half volume and left in the cold when 1.6 g of a solid precipitate was formed. This product was further purified by recrystallisations from methanol – acetone; m.p. 187 – 188°. (Found: C 59.81; H 4.28, N 5.38. Calc. for $C_{13}H_{11}O_3NS$: C 59.75; H 4.22; N 5.37.)

*10-Hydroxydihydrothiazolo[3,2-a]quinolinium-2-carboxylate(Id).* A solution of 3-hydroxyquinoline-2-thione (1.77 g, 0.01 mol) and methyl 2,3-dibromopropionate (3.8 g, 0.015 ml) in moist chlorobenzene (100 ml) was heated under reflux overnight, the solid precipitate was filtered from the warm reaction mixture, washed with acetone and recrystallized from methanol. The hydrolyzed ester was further purified by dissolution in N NaOH and pH adjustment to 2 – 3 with HCl; yield 1.8 g (73 %), m.p. 261 – 262°. (Found: C 58.01; H 3.62; N 5.39. Calc. for $C_{12}H_9NO_3S$: C 58.30; H 3.65; N 5.66.)

*2-Carbomethoxy-10-hydroxydihydrothiazolo[3,2-a]quinolinium bromide (Ie).* The methyl ester was prepared as the acid above by use of dried chlorobenzene and was recrystallized from a small volume of methanol, m.p. 213 – 217°. (Found: C 45.30; H 3.58; N 4.36. Calc. for $C_{13}H_{11}NO_3S.HBr$: C 45.60; H 3.51; N 4.09.)

*10-Hydroxy-2-phenyldihydrothiazolo[3,2-a]quinolinium bromide (Ic).* A solution of 3-hydroxyquinoline-2-thione (2.7 g, 0.015 mol) and α-bromocinnamic acid (4.6 g, 0.02 mol) in chlorobenzene (100 ml) was heated under reflux for 3 days. The semisolid precipitate formed was isolated by filtration. This material was triturated with warm acetone (100 ml) to give a solid (2.3 g) which NMR showed to be the title compound. The latter has arisen by decarboxylation of the first formed cyclisation product. For further purifica-

tion, the product was dissolved in formic acid (20 ml), treated with charcoal, and reprecipitated by addition of water (80 ml). After two recrystallisations from ethanol the product had m.p. 226–229°. (Found: C 56.30; H 4.16; N 3.63. Calc. for $C_{17}H_{13}NOS.HBr$: C 56.65; H 3.89; N 3.89.)

*2-Methyldihydrothiazolo[3,2-a]quinolinium-10-oxide (Ib).* A solution of 3-hydroxyquinoline-2-thione (0.9 g, 0.005 mol) and α-bromoisocrotonic acid (4.0 g, 0.024 mol) in chlorobenzene (50 ml) was heated under reflux for 4 days. The semisolid precipitate (1.1 g) was collected by filtration. NMR showed this to be the title compound arisen by decarboxylation of the cyclic acid first formed. The material was purified by dissolution in 0.1 N NaOH and reprecipitation by bringing the pH to 3 with HCl. The product was treated with charcoal on recrystallisation from ethanol; m.p. 267–269°. (Found: C 62.05; H 4.81; N 6.18. Calc. for $C_{12}H_{11}NOS$: C 62.40; H 5.08; N 6.46.)

*9-Bromodihydrothiazolo[3,2-a]quinolinium-10-oxide (XIIIa).* To a solution of dihydrothiazolo[3,2-a]quinolinium-10-oxide (0.20 g, 0.001 mol) and potassium acetate (0.35 g, 0.002 mol) in acetic acid (100 ml) at 60° was added dropwise a solution of bromine (0.20 g, 0.001 mol) in acetic acid (20 ml) over 30 min. The solution was stirred at 60° for 12 h, water (50 ml) was added, and the solution concentrated to 70 ml. The bromo compound which precipitated overnight (0.21 g, 75 %) had m.p. > 300°. (Found: C 46.60; H 2.71; N 4.73. Calc. for $C_{11}H_8BrNOS$: C 46.80; H 2.84; N 4.96.)

*9-Bromo-10-hydroxydihydrothiazolo[3,2-a]quinolinium-3-carboxylate (XIIIb).* To a solution of 10-hydroxydihydrothiazolo[3,2-a]quinolinium-3-carboxylate (0.25 g, 0.001 mol) and potassium acetate (0.20 g, 0.002 mol) in acetic acid (50 ml) at 50° was added dropwise a solution of bromine (0.18 g, 0.001 mol) in acetic acid (5 ml) over 30 min. The heating was continued for 15 h. Some precipitated material was filtered off and water (25 ml) was added to the filtrate which was then concentrated to 25 ml and left overnight. The yellow crystalline precipitate was collected and recrystallized from ethanol (0.24 g, 74 %), m.p. 207–208°. (Found: C 43.92; H 2.40; N 4.08. Calc. for $C_{12}H_8BrNO_3S$: C 44.15; H 2.45; N 4.29.)

*9-Bromo-10-hydroxydihydrothiazolo[3,2-a]quinolinium-2-carboxylate (XIIIc).* To a solution of 10-hydroxydihydrothiazolo[3,2-a]quinolinium-2-carboxylate (0.50 g, 0.002 mol) and potassium acetate (0.40 g, 0.004 mol) in acetic acid (50 ml) at 50° was added a solution of bromine (0.35 g, 0.002 mol) in acetic acid (20 ml) over 1 h. The heating was continued overnight. The solution was evaporated and the residue treated with hot water (25 ml). After filtering the hot solution, the pH of the filtrate was adjusted to 2 with N HCl and the solution was left overnight. The yellow-white precipitate was collected, 0.39 g (60 %), m.p. 185–187°. (Found: C 44.01; H 2.36; N 4.15. Calc. for $C_{12}H_8BrNO_3S$: C 44.15; H 2.45; N 4.29.)

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