412. *Quinolizines. Part V.*[1] *The Synthesis and Properties of Some Hydroxyquinolizinium Salts.*

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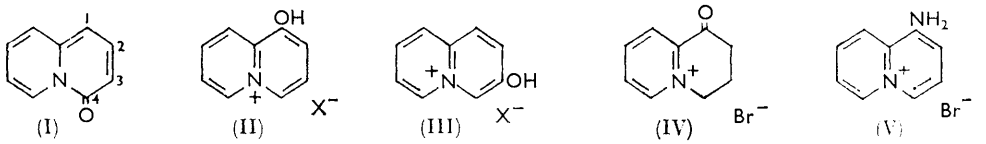
Some 1-hydroxy- and 1,2-dihydroxy-quinolizinium salts have been synthesised and shown to be typically phenolic.

Of the possible hydroxyquinolizinium salts, the 1- and the 3-hydroxy-compounds (II and III) should be typical phenols (like 3-hydroxypyridines), while the 2- and the 4-hydroxy-compounds should behave more as cyclic amides or vinylogous amides (like 2- and 4-hydroxypyridines). The only monohydroxyquinolizinium compound of which the properties are reported [2] is the 4-substituted derivative, 4-quinolizone (I), and this is weakly basic, forming salts which are hydrolysed by water. We report here the synthesis of 1-hydroxy- (II) and 1,2-dihydroxy-quinolizinium salts (VIII) and an account of some of their properties.

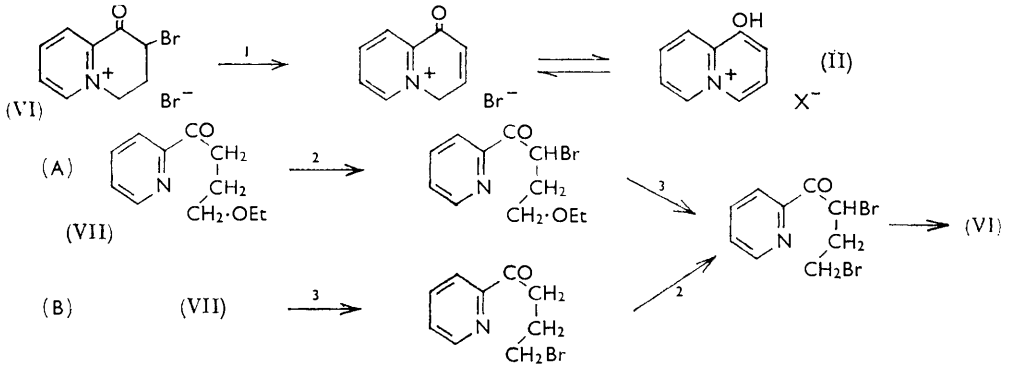


1-Hydroxyquinolizinium picrate (II; X = picrate) has previously been prepared by dehydrogenating the ketone (IV),[3] and by diazotising 1-aminoquinolizinium bromide (V) and heating the aqueous diazotisation mixture. In both cases the yield was poor and the only crystalline salt obtained was the picrate. Other methods were sought which would give greater yields of the picrate or preferably the bromide (II; X = Br) of the 1-hydroxyquinolizinium system. An attractive route appeared to be from the 2-bromo-1,2,3,4-tetrahydro-1-oxoquinolizinium bromide (VI) by elimination of hydrogen bromide, as in the chart.

Bromination of the cyclic ketone (IV) in concentrated hydrobromic acid gave a high yield of the monobromo-ketone bromide (VI), whose infrared spectrum showed a carbonyl stretching frequency little removed from that of the parent ketone (IV); to confirm the 2-position of the bromine (and hence presumably its quasi-axial nature [4]) the reaction

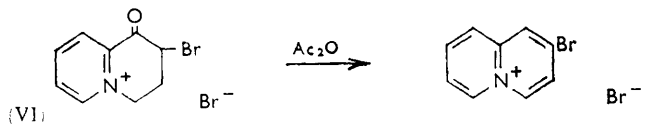
[1] Part IV, Collicut and Jones, *J.*, 1960, 4101.
[2] Boekelheide and Lodge, *J. Amer. Chem. Soc.*, 1951, **73**, 3681.
[3] E. E. Glover, Ph.D. Thesis, Keele, 1959.
[4] Jones *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 2828; Corey, *ibid.*, 1953, **75**, 2301.

sequences illustrated were performed. The uncyclised ether (VII) was brominated before (A), and after (B), cleavage with hydrobromic acid. In both cases, after cyclisation in chloroform, compound (VI) was obtained; since these compounds possess only one activated site for bromination (adjacent to the carbonyl group) the cyclic bromo-ketone is correctly formulated as (VI). Treatment of the bromo-ketone (VI) with boiling acetic

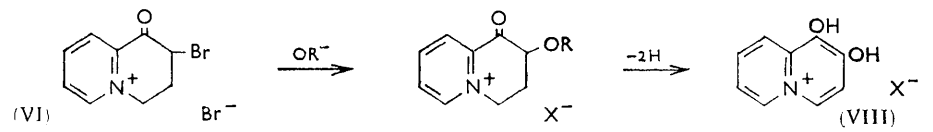


anhydride gave 2-bromoquinolizinium bromide, aromatisation occurring as with the previously reported [4,5] alkyl- and aryl-quinolizinium compounds.

Attempts were made to dehydrobrominate the bromo-ketone (VI) by the strongly basic resin Amberlite IRA-400 (OH) in boiling methanol, and also by concentrated aqueous ammonia. Both reactions gave the same major product, isolated as a picrate, and believed at first to be 1-hydroxyquinolizinium picrate (II; X = picrate). However, the picrate



could not be converted into the bromide by passage through an anion-exchange column. Analyses were consistent with a formula $C_9H_8NO_2$ for the cation and this compound has been shown to be 1,2-dihydroxyquinolizinium picrate (VIII; X = picrate). Treatment of the bromo-ketone (VI) with hot aqueous silver acetate gave a good yield of 1,2-dihydroxyquinolizinium bromide (VIII; X = Br) which formed a lead salt—a characteristic of pyrocatechols. The reaction between the bromo-ketone (VI) and basic reagents does not proceed through the 1-hydroxyquinolizinium salt (with subsequent nucleophilic attack by hydroxide ion) since 1-hydroxyquinolizinium bromide (II; X = Br), prepared as described below, was unchanged by treatment with strongly basic anion-exchange resin,



under the conditions of formation of 1,2-dihydroxyquinolizinium salts. In the reaction between the bromo-ketone (VI) and aqueous silver acetate the initial 2-acetoxy-1-hydroxyquinolizinium salt would be hydrolysed in water, as are 2-acetoxypyridine [6] and certain 1-acetoxyisoquinolines.[7]

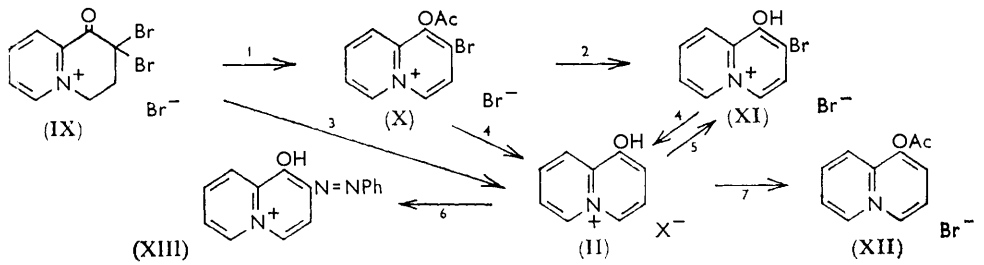
[5] Glover and Jones, *J.*, 1958, 3021.
[6] Chichibabin and Szakow, *Ber.*, 1925, **58**, 2651.
[7] Jones, *J.*, 1960, 1896.

A minor product in the bromination of the ketone (IV) was a dibromo-ketone (IX), and this could be made the principal product by increasing the amount of bromine used. Its carbonyl stretching frequency showed the expected considerable shift (20 cm.$^{-1}$) from those of the parent ketone (IV) and of the monobromo-ketone (VI). The structure (IX) was confirmed when the nuclear magnetic resonance of the ketones (VI) and (IX) was found to include a triplet centred at 5·1 τ (relative to tetramethylsilane) assigned to the two protons at position 4; the monobromo-ketone (VI) showed a broad quartet centred at 7·1 τ assigned to the two protons at position 3. With the dibromo-ketone (IX) the last pair appear as a triplet centred at 6·65 τ, the additional chemical shift being due to the extra bromine atom on the adjacent position 2.

When the ketone (IX) was boiled in acetic anhydride a high yield of an acetoxy-bromo-quinolizinium bromide (X) was formed. This was hydrolysed to a bromo-hydroxy-quinolizinium bromide (XI) by aqueous hydrobromic acid. This bromo-hydroxy-quinolizinium bromide was also obtained by heating the dibromo-ketone (IX) in concentrated hydrobromic acid, or in very high yield by heating the dry dibromo-ketone (IX) to 160°, copious evolution of hydrogen bromide being observed.

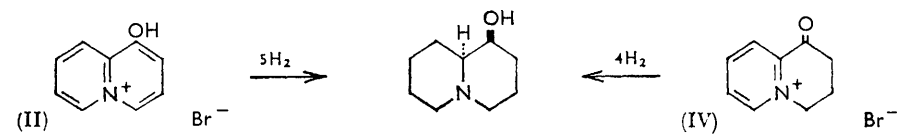
Hydrogenolysis of the bromo-hydroxyquinolizinium salt (XI) or of the acetoxy-bromo-compound (X) gave good yields of a hydroxyquinolizinium bromide, which from its mode of formation must be the 1-hydroxyquinolizinium salt (II; X = Br). This was confirmed by comparison of the picrate (II; X = picrate) with that obtained previously.[1,3] Finally, this picrate was obtained directly from the dibromo-ketone by treatment with hot dimethylaniline (a similar reaction is reported [8] with 2,2-dibromo-1-tetralone, giving 1-naphthol [9]).

1-Hydroxyquinolizinium bromide gives a violet ferric chloride colour, and has pK_a ~5. Catalytic reduction gave a 1-hydroxyquinolizidine, obtained by Swan [9] from the ketone (IV), and formulated as the *trans*-compound. Acetylation gave 1-acetoxyquinolizinium bromide (XII), and bromination occurred readily in concentrated hydrobromic acid to



Reagents: 1, Ac_2O. 2, H^+–H_2O. 3, $NPhMe_2$. 4, H_2. 5, Br_2. 6, $Ph{\cdot}N_2^+$. 7, Ac_2O–H_2SO_4.

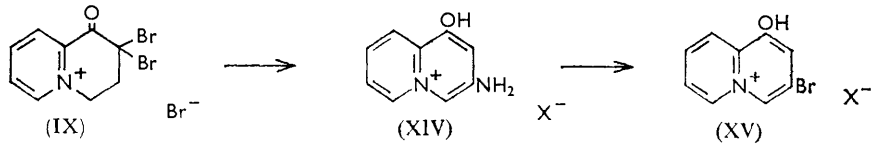
give 2-bromo-1-hydroxyquinolizinium bromide (XI). The ease of bromination is surprising in view of the positive charge carried by the ring system. Treatment of the hydroxy-quinolizinium bromide (II; X = Br) with diazotised aniline gave a very insoluble red precipitate which could not be crystallised but is assumed to be the azo-compound (XIII). Nitration of the hydroxyquinolizinium bromide (II; X = Br) proceeded readily, giving



complex products which will be described in a subsequent publication. 1,2-Dihydroxy-quinolizinium bromide (VIII; X = Br) failed to react with bromine in hydrobromic acid solution.

[8] Krollpfeiffer and Muller, *Ber.*, 1935, **68**, 1169.
[9] Swan, *J.*, 1958, 2051.

When the dibromo-ketone (IX) was treated with concentrated aqueous ammonia, an amino-hydroxyquinolizinium salt was isolated. This compound gave a green colour with ferric chloride but failed to form a complex with aqueous cupric acetate, suggesting that the amino- and hydroxy-groups are not adjacent. Diazotisation of the amino-hydroxy-compound gave a solution which coupled with alkaline 2-naphthol, and from which, on heating in aqueous hydrobromic acid, a bromohydroxyquinolizinium salt could be



(IX) (XIV) (XV)

obtained. This compound was not identical with the previously described 2-bromo-1-hydroxyquinolizinium salt (XI) and is tentatively assigned the 3-bromo-1-hydroxy-structure (XV); the amino-hydroxy-compound would then have structure (XIV). It is assumed that the initially formed 2-bromo-1-hydroxyquinolizinium bromide reacts with the aqueous ammonia through a compound of pyridyne type to give the 3-amino-1-hydroxyquinolizinium salt.

Experimental

M. p.s were determined on a Kofler block. Ultraviolet absorption spectra were determined for aqueous solution unless otherwise stated.

2-*Bromo*-1,2,3,4-*tetrahydro*-1-*oxoquinolizinium Bromide* (VI).—(*a*) To a vigorously stirred solution of 1,2,3,4-tetrahydro-1-oxoquinolizinium bromide [10] (IV) (8·0 g.) in 50% aqueous hydrobromic acid (50 ml.) was added bromine (5·8 g.) in hydrobromic acid (20 ml.). A yellow solid was precipitated. Stirring was continued for a further 5 min., and the mixture was heated until the solid had redissolved. Evaporation under reduced pressure gave the *bromo-ketone bromide* which recrystallised from absolute ethanol as pale yellow needles, m. p. 159—160° (9·52 g., 89%) (Found: C, 35·7; H, 3·15; N, 4·4; Br, 51·7. $C_9H_9Br_2NO$ requires C, 35·25; H, 2·95; N, 4·55; Br, 52·1%), $\lambda_{max.}$ 2440, 2730, and 3450 Å (log ε 3·64, 3·83, and 3·21). The *picrate* crystallised from methanol as yellow rhombs, m. p. 153° (Found: C, 39·9; H, 2·5; N, 11·9. $C_{15}H_{11}BrN_4O_8$ requires C, 39·6; H, 2·4; N, 12·5%).

(*b*) A solution of 2-γ-ethoxybutyrylpyridine (VII) (1·9 g.) in chloroform (25 ml.) was treated with bromine (1·7 g.) in chloroform (25 ml.), kept for 3 hr., then heated on a boiling-water bath. After the chloroform had distilled off the residue was boiled under reflux in concentrated aqueous hydrobromic acid for 1 hr. Cyclisation as described previously [10] gave the bromo-ketone bromide (VI).

(*c*) A solution of the pyridine (VII) (4·5 g.) in concentrated hydrobromic acid (50 ml.) was boiled under reflux for 0·5 hr. The solution was cooled and bromine (4 g.) in concentrated hydrobromic acid (10 ml.) was added with stirring. The mixture was heated, evaporated to dryness, and subsequently cyclised as described previously,[10] to give the ketone (VI).

Specimens obtained by methods (*a*—*c*) were identical.

2-*Bromoquinolizinium Bromide*.—The bromo-ketone bromide (VI) (5 g.) was boiled in acetic anhydride (150 ml.) for 2 hr. Evaporation under reduced pressure gave a *bromide* that recrystallised from absolute ethanol as colourless needles, m. p. 260—261° (3·4 g., 74%) (Found: C, 37·6; H, 2·5; N, 4·7. $C_9H_7Br_2N$ requires C, 37·4; H, 2·4; N, 4·85%), $\lambda_{max.}$ 2800, 2905, 3050, 3170, 3240, and 3310 Å (log ε 3·50, 3·56, 3·79, 4·19, 4·09, and 4·38). The *picrate*, from ethanol, had m. p. 186—187° (Found: C, 41·3; H, 2·4. $C_{15}H_9BrN_4O_7$ requires C, 41·2; H, 2·1%).

1,2-*Dihydroxyquinolizinium Salts* (VIII).—(*a*) A solution of the bromo-ketone bromide (VI) (1·0 g.) in methanol (50 ml.) was stirred and boiled under reflux with Amberlite IRA-400 (OH) (15 ml.) for 1·5 hr. The cooled mixture was filtered and evaporated and picric acid (0·75 g.) in methanol (5 ml.) was added to the residue. Concentration of the resulting solution to 2·5 ml., followed by addition of ether, gave a sticky solid, which was washed with ether by decantation, heated in methanol with charcoal, and recovered. It then crystallised from water as orange prisms, m. p. 180°. Recrystallisation from acetone gave 1,2-*dihydroxyquinolizinium*

[10] Glover and Jones, *J.*, 1958, 1750.

picrate (VIII; X = picrate), m. p. 223—226° (decomp.) (0·35 g., 20%) (Found: C, 46·2; H, 2·8; N, 13·9. $C_{15}H_{10}N_4O_9$ requires C, 46·25; H, 2·55; N, 14·15%), $\lambda_{max.}$ 2130, 2340, 3330, and 3500 Å (log ε 4·49, 4·45, 4·2, 4·23). Attempts to exchange the picrate for other anions on Amberlite IRA-400 were unsuccessful.

(*b*) A solution of the bromide (VI) (0·5 g.) in water (10 ml.) was treated with aqueous ammonia (*d* 0·880) (10 ml.). A slightly exothermic reaction occurred, giving a deep red solution. The mixture was heated on a water-bath for 0·5 hr., then boiled to remove the ammonia. The aqueous solution was passed through a column of Amberlite IRA-400 (OH) and again boiled to remove liberated ammonia. Evaporation to dryness with added hydrobromic acid gave a solid residue from which the picrate (VIII; X = picrate) was obtained.

(*c*) The bromo-ketone bromide (VI) (1·0 g.) in water (20 ml.) was stirred and boiled with silver acetate (2·0 g.) in water (130 ml.), under reflux for 2 hr., cooled, filtered, and evaporated under reduced pressure. The residue was dissolved in water and passed through a column of Amberlite IRA-400 (Br) and again evaporated (A). The picrate (VIII; X = picrate) prepared from the residue (A) by treatment with aqueous sodium picrate crystallised from absolute ethanol as yellow needles, m. p. 223—227°.

The residue (A) above did not crystallise, but after treatment with boiling acetic anhydride (2·5 hr.) a solid *bromide* (VIII; X = Br) was isolated, and recrystallised (charcoal) from absolute ethanol–ethyl acetate as flesh-coloured cubes (0·20 g., 25%), m. p. 225—227° (Found: C, 44·7; H, 3·7; N, 5·3. $C_9H_8BrNO_2$ requires C, 44·65; H, 3·3; N, 5·8%), $\lambda_{max.}$ 2120, 2335, and 3250 Å (log ε 4·41, 4·35, and 4·01). This bromide gave a deep jade-green colour with aqueous ferric chloride. The *lead salt*, prepared from it by addition of aqueous lead acetate, recrystallised from water as yellow prisms, m. p. 339—342° (Found: C, 24·7; H, 1·4; N, 3·25. $C_9H_6BrNO_2Pb$ requires C, 24·2; H, 1·35; N, 3·15%), $\lambda_{max.}$ 2140, 2340, 3410, and 3700 Å (log ε 4·27, 4·17, 3·75, and 3·53).

2,2-*Dibromo*-1,2,3,4-*tetrahydro*-1-*oxoquinolizinium Bromide* (IX).—The ketone (IV) (5·0 g.) in 50% hydrobromic acid (75 ml.) was treated with bromine (10 g.) in hydrobromic acid (20 ml.), with stirring that was continued for 15 min. subsequently. The mixture was warmed until the precipitate dissolved and then evaporated under reduced pressure. A solution of the residue in water was evaporated to dryness. The residue crystallised from absolute ethanol, to give the *dibromo-ketone bromide* (IX), as yellow needles, m. p. 236—237° (7·63 g., 91%) (Found: C, 28·1; H, 2·1; N, 3·55; Br, 61·8. $C_9H_8Br_3NO$ requires C, 28·0; H, 2·1; N, 3·6; Br, 62·1%), $\lambda_{max.}$ 2680 Å (log ε 3·78). The *picrate* crystallised from methanol as yellow rhombs, m. p. 133° (Found: C, 34·3; H, 2·0; N, 11·0. $C_{15}H_{10}Br_2N_4O_8$ requires C, 33·7; H, 1·9; N, 10·5%).

1-*Acetoxy*-2-*bromoquinolizinium Bromide* (X).—A solution of the dibromo-ketone bromide (IX) (10·0 g.) in acetic anhydride (150 ml.) was boiled under reflux for 1·5 hr. Evaporation under reduced pressure gave a solid, which was washed with ethyl acetate and then recrystallised from absolute ethanol–ethyl acetate, to give 1-*acetoxy*-2-*bromoquinolizinium bromide* (X) as buff rhombs, m. p. 193·5—194° (7·71 g., 86%) (Found: C, 38·2; H, 2·35; N, 3·8. $C_{11}H_9Br_2NO_2$ requires C, 38·1; H, 2·6; N, 4·0%), $\lambda_{max.}$ 2130, 2330, 2930, 3210, and 3360 Å (log ε 4·67, 4·62, 3·76, 4·32, and 4·45).

2-*Bromo*-1-*hydroxyquinolizinium Bromide* (XI).—(*a*) A solution of the dibromo-ketone bromide (IX) (0·5 g.) in 50% hydrobromic acid (15 ml.) was boiled under reflux for 4 hr. The solution was evaporated under reduced pressure, and the residual solid was treated in absolute ethanol with ethyl acetate. 2-*Bromo*-1-*hydroxyquinolizinium bromide* (XI), m. p. 226—228° (0·271 g., 70%), crystallised from absolute ethanol as buff needles, m. p. 227·5° (Found: C, 35·4; H, 2·25; N, 4·1. $C_9H_7Br_2NO$ requires C, 35·4; H, 2·3; N, 4·6%), $\lambda_{max.}$ 2160 and 3830 Å (log ε 4·49, 4·09). An aqueous solution gave a purple colour with neutral ferric chloride.

(*b*) A solution of 1-acetoxy-2-bromoquinolizinium bromide (X) (0·3 g.) in 50% aqueous hydrobromic acid (10 ml.) was boiled under reflux for 1·5 hr. Evaporation to dryness was followed by dissolution of the residue in water, and the solution was again evaporated. The residue, on recrystallisation from ethyl acetate–ethanol, gave the bromide (XI), m. p. 225—227° (0·15 g., 57%).

(*c*) The dibromo-ketone bromide (0·3 g.) was heated at 150—160° (oil bath) for 0·5 hr., hydrogen bromide being evolved. The residue (0·227 g.) was pure 1-bromo-2-hydroxyquinolizinium bromide (XI), identical in infrared absorption with specimens prepared by methods (*a*) and (*b*).

1-*Hydroxyquinolizinium Salts* (II).—(*a*) 1-Acetoxy-2-bromoquinolizinium bromide (X)

(7·0 g.) in 95% ethanol (100 ml.) with 10% palladium–charcoal (1 g.) was hydrogenated at atmospheric temperature and pressure, one mol. of hydrogen being absorbed. The mixture was filtered and concentrated; cooling gave 1-*hydroxyquinolizinium bromide* (II; X = Br) *monohydrate*, m. p. 184—185° (4·2 g., 86%) (Found: C, 44·3; H, 4·1; N, 5·4. C_9H_8BrNO,H_2O requires C, 44·3; H, 4·1; N, 5·7%), $\lambda_{max.}$ 2370 and 3450 Å (log ε 4·15 and 4·17). An aqueous solution gave a deep purple colour with neutral aqueous ferric chloride. The *picrate* crystallised from ethanol as yellow needles, m. p. 218—219° (Found: C, 48·3; H, 2·9; N, 14·85. $C_{15}H_{10}N_4O_8$ requires C, 48·15; H, 2·7; N, 14·95%), $\lambda_{max.}$ 2370 and 3460 Å (log ε 4·39 and 4·40).

(*b*) A solution of 2-bromo-1-hydroxyquinolizinium bromide (XI) was similarly hydrogenated, the hydrogenation being stopped when one mol. of hydrogen had been absorbed. Isolation as described above gave 1-hydroxyquinolizinium bromide in 86% yield.

(*c*) The dibromo-ketone bromide (IX) (2·0 g.) in dimethylaniline (30 ml.) was boiled under reflux for 4·5 hr., giving a deep red solution. The amine was removed under reduced pressure and the residue dissolved in water and again evaporated (three times in all). The residue was shaken with water and ether, the aqueous layer evaporated and the residue dissolved in 50% hydrobromic acid (20 ml.). The solution was boiled under reflux for 1·5 hr. and evaporated to dryness; the evaporation was repeated with water to remove all acid. The residue was dissolved in methanol (charcoal) and recovered; it then gave 1-hydroxyquinolizinium picrate (1·4 g., 78%) on treatment with aqueous sodium picrate, m. p. 221—223° (decomp.) (from acetone).

1-*Hydroxyquinolizidine*.—A solution of 1-hydroxyquinolizinium bromide (II; X = Br) (2·3 g.) in 95% ethanol (100 ml.) was hydrogenated at atmospheric temperature and pressure on Adams catalyst (75 mg.). Two mol. were rapidly absorbed, and a further 3 mol. more slowly. The mixture was filtered and evaporated to dryness. The residue was treated with saturated aqueous sodium carbonate solution and extracted with chloroform. The dried (K_2CO_3) chloroform extracts were concentrated under a stream of nitrogen and the residue sublimed, giving 1-hydroxyquinolizidine (0·47 g.), m. p. 76—78°, identical with that obtained by the hydrogenation of the ketone (IV).[9]

1-*Acetoxyquinolizinium Bromide*.—A solution of compound (II; X = Br) (0·300 g.) in acetic anhydride (10 ml.) with one drop of concentrated sulphuric acid was heated under reflux for 2·5 hr. The anhydride was distilled off under reduced pressure and the residue dissolved in absolute alcohol (charcoal). Precipitation with ethyl acetate gave 1-*acetoxyquinolizinium bromide* (0·12 g., 36%) that recrystallised from ethyl alcohol–ethyl acetate as colourless needles, m. p. 185—187° (Found: C, 49·0; H, 3·9; N, 5·4. $C_{11}HBrNO$ requires C, 49·25; H, 3·75; N, 5·2%), $\lambda_{max.}$ 2090, 2300, 2900, 3160, and 3290 Å (log ε 4·54, 4·26, 3·56, 4·00, and 4·20).

Bromination of 1-*Hydroxyquinolizinium Bromide*.—A solution of bromine (0·2 g.) in 50% hydrobromic acid (35 ml.) was added to a stirred solution of 1-hydroxyquinolizinium bromide (II; X = Br) (0·24 g.) in 50% hydrobromic acid (5 ml.). A yellow solid separated, which dissolved when the mixture was heated on a boiling-water bath. The solution was evaporated, water was added, and the solution again evaporated to give a solid. This solid was dissolved in absolute ethanol and precipitated with ethyl acetate, giving 2-bromo-1-hydroxyquinolizinium bromide (XI), m. p. 225—228° (0·245 g., 80%), identical with that obtained by the methods described above.

3-*Amino*-1-*hydroxyquinolizinium Salts* (XIV).—The dibromo-ketone (IX) (1·0 g.) reacted exothermally with aqueous ammonia (*d* 0·880) (15 ml.), to give a deep brown solution. After the initial violent reaction the solution was heated on a boiling-water bath for 0·5 hr., and finally boiled to remove the excess of ammonia. The aqueous solution was passed down a column of Amberlite IRA-400 (OH) and again boiled to remove ammonia, then evaporated to dryness under reduced pressure. The residue was dissolved in absolute ethanol (charcoal) and concentrated, giving 3-*amino*-1-*hydroxyquinolizinium hydroxide* (XIV; X = OH) (0·215 g., 48%), recrystallising from acetone as yellow needles, m. p. 179—182° (Found: C, 60·8; H, 5·82; N, 15·7. $C_9H_{10}N_2O_2$ requires C, 60·7; H, 5·8; N, 15·7%), $\lambda_{max.}$ 2160 and 3330 Å (log ε 4·43 and 4·03). The amino-hydroxy-compound gave a green colour with aqueous ferric chloride, and after treatment with pentyl nitrite and hydrochloric acid gave a deep red insoluble precipitate with alkaline 2-naphthol. No change in colour was observed with cupric acetate solution. The *picrate* crystallised from methanol as yellow needles, m. p. 215—217° (Found: C, 45·4; H, 3·1. $C_{15}H_{11}N_5O_8,CH_3{\cdot}OH$ requires C, 45·6; H, 3·6%).

3-*Bromo*-1-*hydroxyquinolizinium Bromide* (XV).—The amino-hydroxy-compound (XIV;

X = OH) (0·17 g.) in ethanol (10 ml.) with concentrated hydrobromic acid (5 drops) was treated with pentyl nitrite until an excess was present. The solution was concentrated, aqueous hydrobromic acid was added, and the solution was boiled under reflux for 2·5 hr. Evaporation to dryness several times with water gave a solid, which was dissolved in absolute ethanol (charcoal) and treated with ethyl acetate. The precipitated *3-bromo-1-hydroxyquinolizinium bromide* (XV) (0·075 g., 25%) crystallised from absolute ethanol as rhombs, m. p. 266° (decomp.) (Found: C, 36·1; H, 2·75; N, 5·0. $C_9H_8Br_2NO$ requires C, 35·4; H, 2·3; N, 4·6%), $\lambda_{max.}$ 2280 and 3050 Å (log ε 4·54 and 4·13). It gave a deep red colour with aqueous ferric chloride.

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