rated. The chloroform layer was evaporated leaving a red solid, which was recrystallized from 95% ethanol. After several recrystallizations 4.45 g. (71%) of *N*-benzylideneamino-5-methylisatin was obtained as a red solid, m.p. 145–145.5°.

*Anal.* Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.71; H, 4.59; N, 10.60. Found: C, 72.53; H, 4.69; H, 10.53.

*3-Phenyl-6-methylcinnoline-4-carboxylic acid* (IVb). One gram (0.0038 mole) of *N*-benzylideneamino-5-methylisatin was suspended in a solution of 20 g. of sodium hydroxide dissolved in 100 ml. of water. The solution was refluxed for 5 hr. The reaction mixture was filtered and acidified with 6*N* hydrochloric acid. The yellow precipitate which formed was recrystallized from ethanol, giving 1 g. (100%) of 3-phenyl-6-methylcinnoline-4-carboxylic acid, m.p. 229–229.5°.

*Anal.* Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.71; H, 4.59; N, 10.60. Found: C, 72.45; H, 4.69; N, 10.67.

*6-Methyl-3-phenyl cinnoline* (Vb). A mixture of 0.5 g. (0.0019 mole) of 3-phenyl-6-methylcinnoline-4-carboxylic acid and 2.5 g. (0.0025 mole) of benzophenone was heated for 60 min. at 260° under an atmosphere of nitrogen. The gas evolved gave a turbidity when bubbled through barium hydroxide, indicating the gas to be carbon dioxide. After being cooled, the mixture was dissolved in 250 ml. of ether and the ethereal solution was extracted with about 300 ml. of 6*N* hydrochloric acid. The yellow acidic solution was cooled in an ice bath, saturated with potassium carbonate, filtered, and extracted with ether. The ethereal solution was concentrated. The yellow solid which separated was recrystallized from Skellysolve B,[12] giving 0.40 g. (95%) of 3-phenyl-6-methylcinnoline, m.p. 138.5–139.5°.

*Anal.* Calcd. for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 82.06; H, 5.48; N, 12.47.

LINCOLN 8, NEB.

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[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

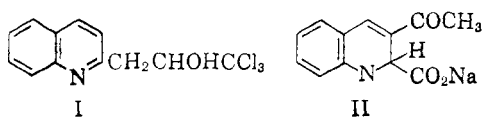
# The Reaction of Chloralquinaldine with Pyridine and Alkali[1,2]

HENRY E. BAUMGARTEN, RICHARD BECKERBAUER, AND MARJORIE R. DEBRUNNER

*Received August 19, 1960*

Chloralquinaldine reacts with pyridine and aqueous potassium hydroxide to yield a purple-black solid, $C_{17}H_{12}N_2O$, which is shown to be 2-(3-hydroxy-5,6-benzo)indolizyl pyridinium betaine (XI). Similar substances are obtained from chloral-2-picoline and chloral-2-methylbenzothiazole. Several reactions of these substances are described and the mechanism of their formation discussed.

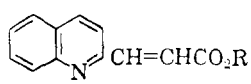
Woodward and Kornfeld[3] have shown that the reaction of chloralquinaldine (I) with aqueous alcoholic sodium hydroxide yields sodium 3-acetyl-1,2-dihydroquinaldate (II) in addition to the expected sodium β-(2-quinolyl)acrylate (IIIa).[4] Mechanisms to explain the formation of II have been suggested by Woodward and Kornfeld,[3]



I



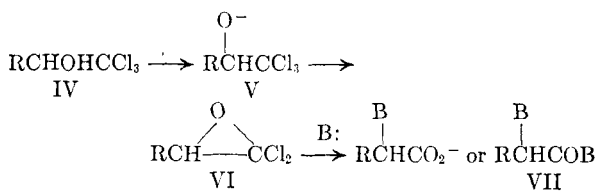
II



IIIa. R = Na
IIIb. R = H

by Brown, Hammick and Robinson,[5] and by Dauben and Vaughan.[6] Although the most recent of these, the mechanism of Dauben and Vaughan,[6] appears to be for the most part quite reasonable, the investigation described in this communication was undertaken to examine an alternative sequence for the *initial phases* of the reaction of I with alkali.

All of the previously reported mechanisms[3,5,6] have been based on the premise that one of the hydrogens on the carbon atom *alpha* to the ring is removed by base in one of the early steps of the reaction. However, it would appear equally if not more likely that the initial proton exchange would involve removal by base of the hydrogen attached to the oxygen of the carbinol group. Thus, there have been a number of reports in the literature describing base-catalysed reactions of trichloromethylcarbinols which take place as shown in the following equation.[7]



IV V VI VII

(1) This work was supported in part by grant CY-3090 of the U. S. Public Health Service.

(2) Abstracted from the M. S. theses of R. B. (February 1960) and M. R. D. (July 1951).

(3) R. B. Woodward and E. C. Kornfeld, *J. Am. Chem. Soc.*, **70**, 2508 (1948).

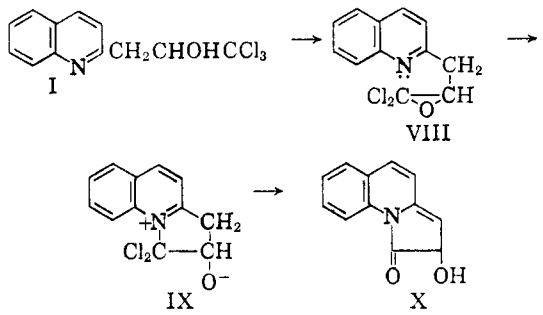
(4) *Cf.* A. Einhorn, *Ber.*, **19**, 904 (1886); A. Einhorn and P. Sherman, *Ann.*, **287**, 26 (1895).

(5) B. R. Brown, D. L. Hammick, and R. Robinson, *J. Chem. Soc.*, 780 (1950).

(6) W. G. Dauben and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 4651 (1953).

(7)(a) K. Garzarolli-Thurnlackh, *Ann.*, **210**, 63 (1881). (b) J. Jocicz, *J. Russ. Phys. Chem. Soc.*, **29**, 97 (1897). (c) A. Wohl and H. Roth, *Ber.*, **40**, 212 (1907). (d) A. Kotz and K. Otto, *J. prakt. Chem.*, [2], **88**, 531 (1913). (e) A. Kotz and C. Diebel, *J. prakt. Chem.*, [2], **90**, 297 (1914). (f) P. Hebert, *Bull. soc. chim. France*, [4], **27**, 45 (1920). (g) G. Banti, *Gazz. chim. ital.*, **59**, I, 819 (1929). (h) C. Weizmann, M. Sulzbacher, and E. Bergmann, *J. Am. Chem. Soc.*, **70**, 1153 (1948). B = Cl: Ref. (a), (b). B = OH: Ref. (b), (d), (e), (f). B = OR: Ref. (a), (e), (f), (h). B: = aniline: Ref. (g).

Using this apparently general reaction as a basis, we suggest the following alternative for the initial steps in the mechanism of Dauben and Vaughan.[6]



In this sequence I is converted by base into the ethylene oxide (VIII) and the three-ring of VIII is cleaved by the nucleophilic attack of the heterocyclic nitrogen to form the betaine (IX), which undergoes hydrolysis to X, an intermediate in the Dauben-Vaughan mechanism,[8] which then reacts further to form II as proposed by Dauben and Vaughan.[6] With respect to the step, IX → X, it may be noted that the reactions of heterocyclic compounds with ethylene oxide derivatives have not been very thoroughly studied; however, it has been recorded that the two classes of compounds do react quite readily to give highly colored products with salt-like character.[9] The hydrolysis of the dihalogen derivative IX may proceed through other ethylene oxide intermediates (and may precede or follow the actual ring opening step).

Inasmuch as the mechanism proposed here involves the interaction of the ethylene oxide moiety of VIII with a tertiary heterocyclic amine, the possibility of altering the ratio or nature of the products in the reaction of I with alkali was explored by running the reaction in the presence of a large excess of a competing amine, pyridine. Under these conditions the usual products, II and III, were not isolated (although they may have been present) but a new substance, not previously reported, was obtained in the form of large, purple-black crystals with a bright metallic luster. For convenience this substance will be called compound A.

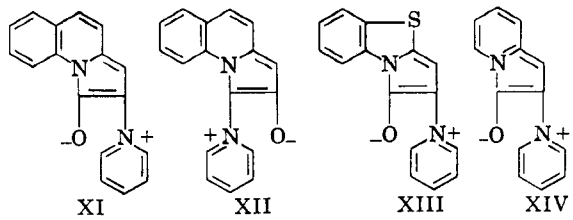
Elementary analyses and ebullioscopic molecular weight data indicated the molecular formula of compound A to be $C_{17}H_{12}N_2O$. Based on this formula the yield obtained of compound A was 35–58%. The compound was fairly stable at room temperature (in the absence of acids), although over a period of several years it slowly decomposed into an intractable black solid and pyridine. *Dilute* mineral acids or acetic acid appeared to accelerate this decomposition. At 165–170° the compound decomposed into pyridine and an amorphous black solid. Further heating of the latter at 330–340° or distillation of compound A with zinc dust yielded quinaldine plus traces of other substances that were not identified.

Chloral-2-methylbenzothiazole reacted with pyridine and alkali to give compound B, $C_{15}H_{10}N_2SO$, which was similar in physical appearance and behavior to compound A. Chloral-2-picoline likewise reacted with pyridine and alkali to give a deep blue crystalline substance, compound C; however, this compound was much less stable than the previous two, completely decomposing at room temperature into pyridine and an amorphous black substance a short time after its preparation and isolation.

The preparations of compounds B and C indicate that the benzo ring and the 3- and 4-positions of the hetero ring probably are not involved in the formation of these substances. If the easy removal of the pyridine moiety is taken as indicating that the pyridine ring is essentially intact in the compounds A, B, and C, then only the fragment $C_4HNO$ remains unaccounted for in compound A (eliminating $C_6H_4$ for the benzo ring, $C_2H_2$ for the 3,4-positions of the quinoline ring, and $C_5H_5N$ for the pyridine ring).

The infrared spectrum of compound A (in chloroform solution) showed no strong absorption in the carbonyl region; therefore, the lone oxygen atom probably was not present in a carbonyl group. In the potassium bromide pellet the spectrum showed absorption characteristic of the C=C stretching vibrations of aromatic and heterocyclic compounds in the 1625–1450 cm.$^{-1}$ region and two bands at 788 and 752 cm.$^{-1}$ characteristic of two, four, and/or five adjacent hydrogen atoms on the heteroaromatic ring.[10]

All of these data taken together strongly suggest that the fragment $C_4HNO$ exists in a cyclic arrangement and that compound A has the structure



XI or XII. Both of these substances are enol betaines of the 5,6-benzoindolizine ring system.

To confirm this tentative identification and to distinguish between XI and XII a series of hydrogenation experiments were carried out. In general indolizines are easily hydrogenated over

(8) Other sequences that appear to be equally plausible for the subsequent changes required to yield II but not involving X *per se* can be written. However, in the absence of experimental evidence, intermediate X is a reasonable compromise.

(9) H. Lohmann, *J. prakt. Chem.*, [2], **153**, 57 (1939); *cf.* M. J. Astle and F. J. Donat, *J. Org. Chem.*, **25**, 507 (1960).

(10) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958, p. 277.

TABLE I

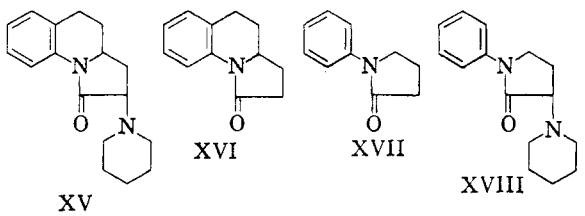
INFRARED SPECTRA[a]

| Compound | Medium[b] | Frequency, Cm.$^{-1}$ |
|---|---|---|
| Compound A (XI) | KBr | 1615m, 1583s, 1500w, 1472s, 1431s, 1392s, 1344w, 1213m, 1012m, 788m, 752s |
| | $CHCl_3$ | 2985m, 1627w, 1615m, 1585s, 1472s, 1393s, 1348w, 1005s |
| XV | KBr | 2940m, 1671s, 1602w, 1498m, 1492w, 1397m, 1315m, 755s |
| | $CHCl_3$ | 3670w, 2910m, 2840w, 1694s, 1608m, 1495w, 1400w, 1371m, 1347w, 1323m |
| XV-HCl | KBr | 2930m, 2600–2400m, 1695s, 1607w, 1587w, 1500s, 1463m, 1400s, 1327s, 760s, 772s |
| XVI | KBr | 2942w, 1682s, 1601m, 1494s, 1458m, 1393s, 1372s, 1325s, 1286m, 1227m, 763s |
| | $CHCl_3$ | 2915w, 1688sh, 1680s, 1586w, 1463w, 1395m, 1374m, 1324m |
| XVII | $CHCl_3$ | 1684s, 1600s, 1485w, 1395s, 1303s |
| XVIII | $CHCl_3$ | 2940m, 1695s, 1605s, 1495s, 1403m, 1308s |
| XIX | KBr | 2960vw, 1730s, 1647s, 1597m, 1576s, 1350m, 1285s, 837s, 762m |
| | $CHCl_3$ | 1728s, 1638s, 1597s–1575s, 1366m, 1300m, 1150m |
| XX | KBr | 3360bw, 1676s, 1607w, 1502m, 1410m, 761m |
| | $CHCl_3$ | 3540bw, 3350w, 2920w, 1702sh, 1688s, 1608w, 1590w, 1495w, 1405m, 1376m, 1313m |
| XXI | KBr | 3400s, 2910m, 1710s–1725s, 1614s, 1590m, 1500s, 1320s, 1289s, 1210s, 747s |
| | $CHCl_3$ | 3510m, 3390m, 2920w, 1729s, 1612s, 1593m, 1482m, 1360m, 1315bs |

[a] Run using Perkin-Elmer Model 21 recording spectrophotometer and a sodium chloride prism. [b] Concentration of chloroform solution was 5 mg./ml.

platinum or palladium catalysts, most effectively in acid solution; however, the acid hydrolysis of compound A (*vide infra*) prevented this reduction in acetic acid (in which three moles of hydrogen were absorbed and piperidine plus amorphous material were formed), and the pyridine moiety appeared to poison these catalysts in neutral or basic media. However, a suspension of compound A in ethanol was rapidly hydrogenated over Raney nickel, five moles of hydrogen being absorbed. To the colorless product, $C_{17}H_{22}N_2O$, which was obtained in 63% yield, has been assigned the structure XV, which was established as follows.

Under similar conditions IIIb took up three moles of hydrogen and gave a 33% yield of 3,3a,-4,5-tetrahydropyrrolo[1,2-a]quinoline-1(2H)one (XVI). The infrared spectra of XV and XVI



XV XVI XVII XVIII

were quite similar, differing only in detail in the potassium bromide pellet. There was no absorption in the $\nu$(N—H) region, indicating that cyclization had occurred. The $\nu$(C=O) absorption for XV appeared at 1694 cm.$^{-1}$ (chloroform) and for XVI at 1680 cm.$^{-1}$ (chloroform). These values were compatible with those expected for *N*-phenyl-substituted, saturated five-membered ring lactams (Table I). Thus, for example, the $\nu$(C=O) frequency of *N*-phenyl-2-pyrrolidone (XVII) was found to be 1684 cm.$^{-1}$ (chloroform). Through comparison of these values with that for *N*-methylacetanilide [$\nu$(C=O) 1646 cm.$^{-1}$ (chloroform)][11] it may be seen that there is a frequency-raising effect in the present series, presumably caused by the five-membered ring. In terms of the observation made earlier,[11] the combined results of frequency raising due to the five-membered ring and of frequency lowering due to alkyl substitution on the nitrogen of the acetanilide moiety [acetanilide, $\nu$(C=O) 1686 cm.$^{-1}$ ($CHCl_3$)] appear to lead to a near cancellation of effects so that only a very slight depression in frequency is observed in comparing XV and XVII with acetanilide. The somewhat higher frequency observed for XVI may be attributed to the electron-withdrawing inductive effect of the $\alpha$-piperidino group. Similar frequency-raising effects were found in the spectra of *N*-phenyl-3-(1-piperidino)-2-pyrrolidone XVIII [$\nu$(C=O) 1695 cm.$^{-1}$ (chloroform)] and of 2-hydroxy-3,3a,4,5-tetrahydropyrrolo[1,2-a]quinoline-1(2H)one (XX) [$\nu$(C=O) 1688 cm.$^{-1}$ (chloroform)], although in the latter instance the effect was small, perhaps because of hydrogen bonding.

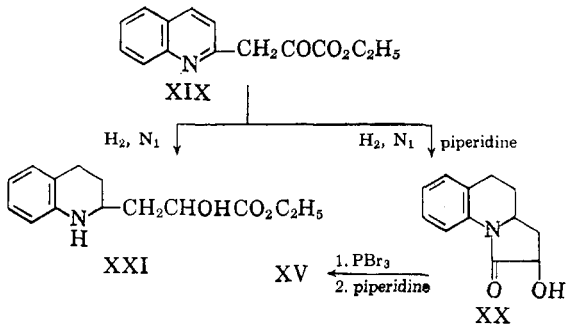
If compound A had had the structure XII, its hydrogenation product would have been a cyclic $\alpha$-amino ketone, a typical example of which, benzo[c]-7-keto-1-azabicyclo[4.3.0]nonane, is reported by Leonard, Swann, and Fuller[12] to show a much higher $\nu$(C=O) absorption at 1754 cm.$^{-1}$ (chloroform).

While these results appear to confirm the position of the carbonyl group in XV (and of the enolate oxygen anion in XI), they do not establish the position of attachment of the piperidine (or pyridine) unit which could be $\alpha$- or $\beta$- to the carbonyl (or enolate) carbon atom. To establish the $\alpha$-attachment XV was synthesized from ethyl $\beta$-(2-quinolyl)-pyruvate (XIX). An attempt was made to synthesize XV in one step by the combined hydrogenation of the pyridine ring, reductive ammination of the keto carbonyl group with piperidine, and closure of the five-membered ring. The actual product in

(11) H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Am. Chem. Soc.*, 82, 3977 (1960).

(12) N. J. Leonard, S. Swann, Jr., and G. Fuller, *J. Am. Chem. Soc.*, 76, 3193 (1954).

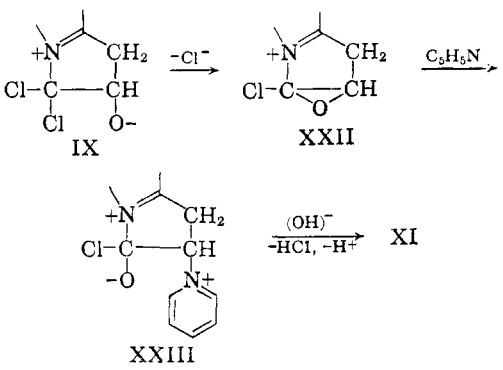
21–37% yield, however, was 2-hydroxy-3,3a,4,5-tetrahydropyrrolo[1,2-a]quinoline-1(2H)one (XX), as established by its analysis and infrared spectrum. Interestingly enough XX was not formed in the absence of piperidine, under which conditions the most readily isolated product (in 25% yield) was ethyl α-hydroxy-β-[2-(1,2,3,4-tetrahydroquinolyl)]-propionate (XXI) (as indicated by analysis and infrared spectrum). Cyclization of XXI gave XX, but in only 17% yield. Reduction of the potassium enolate of XIX gave XX in 10% yield.




Reaction of XX with phosphorus tribromide followed by treatment with piperidine gave XV in 78% yield. Although α-halo esters (and, thereby, presumably, α-halo lactams) are known to react *at elevated temperatures*[13] with amines to give both α- and β-amino amides, usually the reaction at low temperatures gives the α-amino derivative. In the present instance no other product (other than piperidine hydrobromide) was isolated. Thus, although this result is not entirely unambiguous, it appears to be reasonable evidence in favor of structure XV and, hence, of XI. By analogy compounds B and C would have structures XIII and XIV, respectively.

Hydrogenation and desulfurization of compound B gave a compound, $C_{15}H_{20}N_2O$, to which was assigned the structure, *N*-phenyl-3-(1-piperidino)-2-pyrrolidone (XVIII), by analysis, infrared spectrum, and analogy to the foregoing.

From the structure of compound A and the mechanistic premise on which this work was based, a reasonable mechanism for the formation of XI can be offered. Intermediate IX (*vide supra*) forms




(13) *Cf.* Ref. 7h.

TABLE II

ULTRAVIOLET SPECTRA[a]

| Compound | Solvent[b] | Bands, mμ (log ε) Maxima | Minima |
|---|---|---|---|
| Compound A (XI) | $CHCl_3$ | 242 (4.15) | 263 (0.00) |
| | | 289 (3.65) | 314 (2.70) |
| | | 344 (3.65) | 356 (3.55) |
| | | 572 (4.07) | |
| | 6*N* HCl | 242 (4.61) | 224 (3.81) |
| | | 260sh (3.70) | 287 (3.31) |
| | | 320 (3.48) | |
| 5,6-Benzoindolizine[c] | 95% $C_2H_5OH$ | 227 (3.61) | 338 (2.90) |
| | | 243 (2.96) | 246 (2.94) |
| | | 251 (2.97) | 262 (2.65) |
| | | 265 (2.65) | 273 (2.49) |
| | | 278 (2.69) | 290 (2.70) |
| | | 350 (2.48) | |
| | 6*N* HCl | 210 (4.33) | 213 (4.29) |
| | | 215 (4.30) | 230 (3.94) |
| | | 255 (4.26) | 259 (4.23) |
| | | 263 (4.36) | 274 (2.85) |
| | | 341 (3.97) | 349 (4.04) |
| | | 354 (5.02) | |
| IIIb | 6*N* HCl | 264 (3.71) | 230 (2.92) |
| | | 338 (3.40) | 289 (2.30) |
| Quinaldine and pyridine[d] | 6*N* HCl | 239 (4.24) | 254 (3.11) |
| | | 257sh (3.50) | 272 (2.47) |
| | | 318 (2.93) | |
| Pyridine | 6*N* HCl | 254 (3.72) | |

[a] Run using Cary model 11 recording spectrophotometer. [b] Concentrations varied between $10^{-3}$ and $10^{-5}$M. [c] E. M. Roberts, M. Gates, and V. Boekelheide, *J. Org. Chem.*, **20**, 1443 (1955). [d] Equimolar mixture.

the epoxide (XXII) which reacts with pyridine to form XXIII. Dehydrohalogenation and, at some point in the sequence, base-catalyzed removal of the hydrogen at the 4-position of the incipient pyrrole ring[6] complete the required changes.

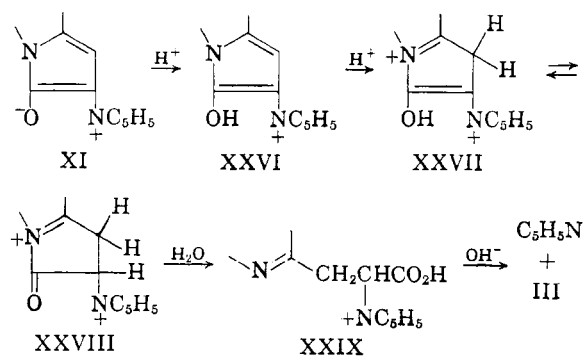
Weizmann, Sulzbacher, and Bergmann[7h] have shown why in the sequence IV→V→VI→VII the intermediacy of the epoxide VI appears to be required. A similar argument can be employed to justify the intermediacy of VII and/or XXII in the reaction of I with pyridine and alkali. It appears feasible that VIII or XXII may also be involved in the reaction of I with alkali that forms II, for, although it is not required that the two reactions of I be related, it would appear to be more reasonable that they are than that they are not. However, for these reactions a number of mechanisms, differing only in detail, can be based on the formation of VII and/or XXII. The sequences cited here (I → VIII → IX → X and IX → XXII → XXIII → XI) represent an arbitrary but reasonable choice from the various possibilities and it is not suggested that the exact details of these sequences are demanded by the available evidence.

The deep colors of the compounds A, B, and C are not unreasonable in view of the long conjugated systems involved. Many of the known enol betaines[14] are highly colored even though they in-

(14) F. Krohnke, *Ber.*, 68B, 1177 (1935).

volve much shorter conjugated systems. Compounds of similar color were formed from the reaction of chloralquinaldine with a variety of tertiary heterocyclic amines, but for the most part these were not readily isolated. The compound from chloral 2-methylcinchoninic acid was prepared and characterized but not examined further. Attempts to prepare similar colored compounds from chloralquinaldine and saturated tertiary amines (such as triethylamine and dimethylaniline) were not successful. Piperidine gave small yields of a mixture of products.

Although compound A reacted with dilute mineral acids and glacial acetic acid to form the black, intractable solid mentioned above (the structure of which is still under study), compound A reacted with concentrated hydrochloric acid in a fairly well defined manner. When solutions of the compound in the concentrated acid were diluted and made alkaline with sodium hydroxide and then just neutralized, IIIb was isolated in 66% yield. However, the ultraviolet spectrum (Table II) of the original strongly acidic solution indicated that IIIb had not yet formed at this stage of the sequence (absence of the strong band at 338 mμ and the presence of the strong band at 242 mμ). Indeed, the ultraviolet spectrum resembled closely the spectrum of an equimolar mixture of pyridine and quinaldine in acid of comparable strength. For this reaction we suggest the following mechanism.




Compound A (XI) first adds a proton to the oxygen atom to form XXVI. As indolizines have been shown by Lowe and King[15] to protonate preferentially at the 1- or 3-position to give carbonium ions which are converted (by a shift of electrons) to a resonance-stabilized pyridinium ion conjugated with an olefinic bond, it appears reasonable that the next step in the present sequence is the protonation at the 3-position of the indolizine moiety to form XXVII, which is in keto-enol equilibrium with XXVIII. Hydrolysis of the lactam ring forms XXIX. During the neutralization with base the pyridinium group is eliminated from XXIX to form III. On the basis of the present evidence it is also possible that the pyridinium group is removed earlier in the sequence through nucleophilic displacement by chloride ion so that the product just before neutralization with base could have a chloro group in place of the pyridinium group. The ultraviolet spectrum of either of these possibilities probably would resemble that of the mixture of pyridine and quinaldine in acid.[16]

(15) O. G. Lowe and L. C. King, *J. Org. Chem.*, **24**, 1200 (1959).

## EXPERIMENTAL[17]

*Compound A* (XI). (a) *Preparation.* Preparation of small amounts of the compound proved to be the most successful. To a solution of 5 g. (0.017 mole) of chloralquinaldine[18] in 20 ml. (0.625 mole) of pyridine, warmed on the steam bath, was added a warm solution of 10 g. (0.179 mole) of potassium hydroxide in 100 ml. of water. The reaction mixture was shaken vigorously, heated until boiling began, allowed to cool slowly to room temperature, and then chilled overnight. Filtration of the solution yielded 2.4–2.6 g. (53–58%) of compound A in the form of dark purple needles, decomposing at 165–170° (Kofler hot stage). This product, with no further purification, gave the following analysis.

*Anal.* Calcd. for $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76. Found: C, 78.46; H, 4.78; N, 10.10.

Extraction of the filtrate from the reaction mixture with chloroform and addition of petroleum ether failed to yield a detectable amount of compound A although the chloroform solution took on a bright purple color. Evaporation of the chloroform yielded only a black, insoluble residue and pyridine.

Other experiments gave yields of 35–54% of compound A with starting quantities of chloralquinaldine varying from 100 mg. to 100 g. No reaction occurred when potassium carbonate was substituted for potassium hydroxide.

Compound A was essentially insoluble in water, 5% sodium hydroxide solution, carbon tetrachloride, ethyl ether, Skellysolves B and C,[19] and petroleum ether (b.p. 30–60°). It was soluble in pyridine but only slightly soluble (less than 5 mg./ml.) in tetrahydrofuran, benzene, acetone, methanol, ethanol, dioxane, ethyl and methyl acetates, and Methyl Cellosolve. It was soluble in chloroform to the extent of 10 mg./ml. and could be purified by dissolution in chloroform and precipitation with petroleum ether.

For most purposes the compound prepared as above was sufficiently pure, and, indeed, further purification tended to cause some decomposition. For analysis the compound was purified by extraction (Soxhlet) with acetone or by recrystallization from benzene. The extraction process gave best results when carried out in the absence of air and as rapidly as possible. The recrystallization from benzene was carried out by heating 1–2 g. of the crude substance to boiling with 200 ml. of *dry* benzene, filtering the hot solution quickly, and immediately chilling the filtrate in ice. About 0.2 g. of small purple-black needles with a metallic luster were obtained.

*Anal.* Calcd. for $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76. Found: C, 78.54, 78.10, 79.04; H, 4.80, 4.67, 4.54; N, 10.85, 10.27, 10.19.

The molecular weight of compound A could not be determined by the Rast method, but with due care ebullioscopic molecular weights were determined by the Menzies-Wright

(16) The data in Table II do not afford as striking a comparison of the similarities in spectra as does comparison of the curves themselves.

(17) Melting points are corrected. Analyses are by Clarke Microanalytical Laboratory, Urbana, Ill., and Micro-Tech Laboratories, Skokie, Ill.

(18) A. A. Alberts and G. B. Bachman, *J. Am. Chem. Soc.*, **57**, 1284 (1935).

(19) Hydrocarbon solvents, b.p. 60–69° and 88–98°, respectively.

procedure with acetone or benzene as solvent. From seven determinations the molecular weight was found to be 262 ± 7, calcd. 260.29.

The compound was fairly stable (in the absence of acids) at room temperature. Samples were kept in covered Petri dishes for several months without noticeable decomposition, *i.e.*, change of the purple-black crystals to a dull black amorphous powder with total loss of luster accompanied by evolution of pyridine. One sample was kept for 2 years with only traces of decomposition (indicated by the odor of pyridine detectable when the container was unstoppered) but had decomposed completely (although in this instance without loss of luster) after nine years. Attempts to dye strips of cotton with solutions of the compound failed, for the color rapidly faded when exposed to the air.

(b) *Reaction with acids.* Dilute mineral and organic acids decomposed the compound into a black, intractable amorphous solid. A 1-g. (0.004-mole) portion of compound A was added to 100 ml. of 10% acetic acid and the suspension was heated for 0.5 hr. on the steam bath. The solution was filtered and a dark, amorphous solid was collected. The solid was washed three times with water, boiled with 50 ml. portions of chloroform, acetone, ethanol, and finally washed three times with hot chloroform. The resulting black solid was air dried.

*Anal.* Found: C, 66.56; H, 3.97; N, 6.75; Ash, 4.95.

The analyst reported that the compound could not be completely oxidized at temperatures up to 850–900°. The infrared spectrum of the solid in potassium bromide showed a band in the $\nu$(C=O) region at 1690 cm.$^{-1}$

Concentrated mineral acids solubilized compound A immediately with the evolution of heat. A 2.6-g. (0.01-mole) portion of compound A was added to 25 ml. of concd. hydrochloric acid; 75 ml. of water was added and the solution was filtered to remove a black tarry residue (0.2 g.). The filtrate was neutralized with 10% sodium hydroxide solution and then made just acidic with 5% hydrochloric acid. Filtration of the acidic mixture gave 1.25 g. (75%) of a gray solid, m.p. 185°. Recrystallization from 50 ml. of methanol and decolorization with 1 g. of Norit yielded 1.11 g. (66%) of β-(2-quinolyl)acrylic acid, m.p. 194.5–196° (lit.[18] m.p. 195–196°), which was identified by its amide, m.p. 175–177° (lit.[18] m.p. 176–177°), mixture melting point and infrared spectrum.

Attempts to acetylate compound A with acetic anhydride or with acetyl chloride in triethylamine resulted in the same decomposition observed with dilute acids.

(c) *Thermal decomposition.* A 5-g. sample of compound A was decomposed by heating in a small distilling flask. In the range 175–180° a volatile liquid was rapidly evolved. This liquid was purified by redistillation (b.p. 114–116°) and converted into the picrate, m.p. 164.5–165.5°, and the chloroplatinate, m.p. 243–246°. The reported melting points for the corresponding derivatives of pyridine are 163–165° and 240–242°.[20] Further heating of the black residue left in the flask resulted in a second decomposition when the temperature of the mass was 330–340° and yielded a small amount of liquid product, which gave a picrate, m.p. 189–191°, mixture m.p. with quinaldine picrate 189–191°.

A 3-g. sample of compound A was mixed and ground with 5 g. of zinc dust and the mixture was heated slowly over a open flame in the usual manner for about 20 min. The oil which distilled into the receiver had a strong odor of pyridine, which was removed by passing air over the solution for 30 min. The oil was dissolved in 10% hydrochloric acid, and the solution was warmed, filtered, made basic with sodium carbonate, and steam distilled. The steam distillate was extracted with ether, giving a solution with a pale blue fluorescence. Evaporation of the dried (magnesium sulfate) solution gave a small amount of dark brown oil. The infrared spectrum of the oil in chloroform showed the same major peaks as an authentic sample of quinaldine; however, the spectrum of the former contained additional bands not found in the quinaldine spectrum, including a strong carbonyl band at 1730 cm.$^{-1}$ Because of the low over-all yield the mixture was not examined further.

(d) *Oxidation.* A 2.6-g. (0.01-mole) portion of compound A was added to 20 ml. of 30% hydrogen peroxide. The solution was heated gently with stirring. At 65° a vigorous reaction took place with the evolution of pyridine. After the reaction subsided, the mixture was filtered to yield a dark brown solid and a light orange solution. Catalytic amounts of lead monooxide (PbO) and 10 ml. of ethanol were added to the filtrate, and the solution was heated on the steam bath until the excess hydrogen peroxide was decomposed. The ethanol was evaporated under reduced pressure and the resulting solid was recrystallized from absolute methanol. The crude solid obtained melted at 170–180°. It was soluble in dilute bases, from which it was precipitated by acids. The infrared spectrum of this compound in potassium bromide indicated it to be largely quinaldinic acid *N*-oxide (lit.[21] m.p. 171°). The dark brown solid obtained from the reaction mixture was soluble in dilute sodium hydroxide from which it was precipitated by acid. The resulting solid was added to 50 ml. of hot methanol and the solution was filtered. A brown residue remained which decomposed at 235–240°. Concentration of the methanolic solution and cooling yielded an orange solid, m.p. 215–220°. The latter two products have not been examined further.

(e) *Hydrogenation.* Attempted hydrogenation using platinum oxide in the presence of hydrogen in chloroform, ethanol, or 10% hydrochloric acid resulted in the decomposition of compound A with no uptake of hydrogen. Hydrogenation in glacial acetic acid solution resulted in decomposition also but with the uptake of 3 moles of hydrogen and the formation of piperidine, identified through it benzenesulfonamide, m.p. and mixture m.p. 92–93°.

Two grams (0.008 mole) of compound A was added to a mixture of 100 ml. of 95% ethanol and 5 teaspoonfuls of W-2 Raney nickel, and the mixture was hydrogenated at 45 p.s.i.g. Approximately 0.046 mole of hydrogen was taken up immediately and shaking for 20 min. did not result in further absorption of hydrogen. The resulting solution had lost the initial purple color and the ethanol solution remaining after removal of the Raney nickel was colorless. Evaporation of the ethanol under reduced pressure left 1.5 g. of white solid, m.p. 121–124°. Recrystallization of the solid from Skellysolve B[19] yielded 1.3 g. (63%) of white needles, m.p. 129.5–131°, of 2-(1-piperidino)-3,3a,4,5-tetrahydropyrrolo[1,2a]quinoline-1(2H)one. The compound failed to give a derivative with 2,4-dinitrophenylhydrazine.

*Anal.* Calcd. for $C_{17}H_{22}N_2O$: C, 75.52; H, 8.20; N, 10.36. Found: C, 75.63; H, 8.35; N, 10.51.

One gram (0.038 mole) of compound A in 200 ml. of ethanol was hydrogenated with 2 teaspoonfuls of W-2 Raney nickel at atmospheric pressure in a quantitative hydrogenation apparatus. The measured hydrogen uptake was 5.1 ± 0.1 moles in 2 hr., after which time no further uptake was noted. Treatment of the reaction mixture as described above gave 0.6 g. (59%) of the same product.

In two experiments the solid residue remaining after the evaporation of the ethanol was dissolved in ether, and the solution was filtered and then saturated with dry hydrogen chloride, giving 1.90–1.95 g. (81–83%) of the hydrochloride of 2-(1-piperidino)-3,3a,4,5-tetrahydropyrrolo[1,2a]-quinoline-1(2H)one, subliming at 210–220°. For analysis a small sample was recrystallized from the minimum amount of ethanol, but for routine purification the product was precipitated from ethanol solution with dry ether.

*Anal.* Calcd. for $C_{17}H_{23}N_2OCl$: C, 66.54; H, 7.57; N, 9.13. Found: C, 66.39; H, 7.57; N, 9.12.

(20) S. P. Mulliken, *Identification of Pure Organic Compounds*, Vol. III, Wiley, New York, 1916, p. 136.

(21) G. Heller and A. Sourlis, *Ber.*, 41, 2692 (1908).

*Compound B.* (a) *Preparation.* The procedure of Ettel, Weichet, and Chyba[22] for the preparation of chloral-2-methylbenzothiazole was modified to improve on the reported yield of 31%. A mixture of 45 g. (0.30 mole) of 2-methylbenzothiazole and 45 g. (0.30 mole) of chloral was heated under reflux with stirring at 110–115° (bath temperature) for 4 hr. To the cooled mixture was added 60 ml. of ethanol, 30 ml. of concd. hydrochloric acid, and 120 ml. of water. The resultant mass was shaken vigorously until the product solidified. The crude product was dissolved in 500 ml. of absolute ethanol and decolorized with three 5-g. portions of activated charcoal. The ethanolic solution was heated on the steam bath and hot water was added slowly to the point at which precipitation began. On cooling 85.5 g. (95%) of pale straw-colored crystals were obtained, m.p. 110–112°, which were pure enough for most purposes. Recrystallization of this product from dilute ethanol gave white leaflets, m.p. 125.5–126° (lit.[22] m.p. 126–127°). In other experiments the yields were 60–95%.

To a warm solution of 29.6 g. (0.1 mole) of chloral-2-methylbenzothiazole in 25 ml. of pyridine was added a solution of 39 g. (0.6 mole) of potassium hydroxide in 200 ml. of water. The resultant mixture was heated on the steam bath and shaken vigorously until boiling began. The flask was removed from the steam bath and, as soon as boiling had subsided, was cooled, then chilled in ice. The product was collected by suction filtration as fine purple-black crystals with a bright metallic luster. The yield varied from 6.0 to 9.5 g. (23–36%) of crude compound B. Variation in the amount of pyridine used from 25 to 75 ml. made no difference in the yield. The conditions for this reaction were more critical than for the similar reaction with chloralquinaldine, for compound B appeared to decompose when heated for long periods with aqueous alkali. The crude compound was purified by extraction with acetone.

*Anal.* Calcd. for $C_{15}H_{16}N_2OS$: C, 67.65; H, 3.79; N, 10.52. Found: C, 67.35; H, 4.09; N, 10.39.

Compound B showed the same solubility characteristics as compound A and the same sensitivity to acids. Attempts to melt this compound also resulted in decomposition at about 175–180° with the liberation of pyridine and the formation of an amorphous, brown to black solid.

(b) *Hydrogenation and desulfurization.* Two grams (0.007 mole) of compound B was suspended in 100 ml. of 20% sodium hydroxide solution and 20 g. of Raney nickel alloy was added slowly over a period of 2 hr. with constant stirring. The temperature was maintained below 10° during this period. The solution was allowed to come to room temperature with stirring. The reaction mixture was then heated on the steam bath until hydrogen evolution ceased (*ca.* 1.5 hr.). The mixture was cooled and washed three times with 300-ml. portions of water. The mixture of Raney nickel and organic product was added to 250 ml. of 95% ethanol and the resultant slurry was heated and stirred under reflux for 3 hr., during which time the color of the solution changed from deep purple to colorless. The reaction mixture was allowed to stand for 2 days and the Raney nickel was filtered off. The alcohol was removed under reduced pressure and the resultant, two-phase liquid system was extracted with an ether-water (1:1) mixture, the bulk of the organic material going into the ether layer. Evaporation of the ether left a nearly colorless oil, which was dissolved in the minimum amount (25 ml.) of Skellysolve B.[19] Cooling of this solution and filtration yielded 0.53 g. (31%) of a white solid, m.p. 55–62°. Recrystallization of this solid from 20 ml. of Skellysolve B[19] gave 0.44 g. (26%) of *N*-phenyl-3-(1-piperidino)-2-pyrrolidone, m.p. 78–80°.

*Anal.* Calcd. for $C_{15}H_{20}N_2O$: C, 73.73; H, 8.25; N, 11.47. Found: C, 73.59; H, 8.08; N, 11.35.

*Reactions of chloralquinaldine with other nitrogenous bases in alkali.* Two-gram portions of chloralquinaldine were added to 20 ml. each of quinaldine, quinoline and 2-picoline and the mixtures were warmed on the steam bath. To each mixture was added 100 ml. of 10% potassium hydroxide solution. A dark purple color formed immediately, but no solid products were obtained from these reaction mixtures, only dark, intractable oils.

To warmed solutions of 5 g. of nicotinic acid and of nicotinamide in 20 ml. of ethanol were added 2-g. portions of chloralquinaldine. To each mixture was added 100 ml. of 10% potassium hydroxide solution. A dark purple color formed immediately but only small amounts of solid materials could be separated from these mixtures and these solids were black, insoluble materials which were not examined further.

A solution of 5 g. of chloralquinaldine in 20 ml. of dimethylaniline was warmed and 100 ml. of 10% potassium hydroxide solution was added. Vigorous boiling occurred with no dark coloration. From the reaction mixture 4.4 g. of the starting material was recovered and no other solid product was obtained. Similar results were obtained with triethylamine. With piperidine a small amount of blue-green solid was formed in some experiments and little visible reaction occurred in others.

Chloral-2,3-dimethylquinoline[5] gave a purple-black solid similar to compound A when heated with pyridine and alkali and the crude addition product from 2,3-dimethylquinoline-4-carboxylic acid gave a dark purple solution, but these materials were not examined further. Chloral-2-aminopyridine[23] reacted with pyridine and alkaline to give a red solution but no solid product was obtained.

*Reduction of ethyl β-(2-quinolyl)pyruvate.* (a) *In the presence of piperidine.* To a suspension of 5 teaspoonfuls of W-2 Raney nickel in 100 ml. of absolute ethanol was added 1 g. (0.004 mole) of ethyl β-(2-quinolyl)pyruvate[24] and 0.69 g. (0.008 mole) of piperidine, and the mixture was hydrogenated at 45 p.s.i.g. for 2 hr. The solution was filtered and the solvent was removed from the filtrate under reduced pressure. The dark yellow oil remaining was heated under reflux with 200 ml. of Skellysolve B[19] for 20 min. The solvent was decanted from the insoluble oil, cooled, and filtered, giving a white solid, m.p. 138–140°. Recrystallization of this solid from Skellysolve B[19] yielded 0.16 g. (21%) of 2-hydroxy-3,3a,4,5-tetrahydropyrrolo-[1,2-a]quinoline-1(2H)-one as white needles, m.p. 140–141°.

*Anal.* Calcd. for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89. Found: C, 71.08; H, 6.56; N, 6.50.

Hydrogenation in the presence of an equimolar amount of piperidine gave a 37% yield of the product, but hydrogenation in the presence of small amounts of ethanolic sodium hydroxide gave only traces of the desired product plus a yellow oil that did not crystallize.

(b) *In the absence of added base.* A suspension of 2 teaspoonfuls of W-2 Raney nickel in a solution of 5 g of ethyl β-(2-quinolyl)pyruvate in 100 ml of absolute ethanol was hydrogenated at 45 p.s.i.g. for 2 hr. The hydrogen uptake was *ca.* 0.058 mole. The solution was filtered and the solvent removed from the filtrate by evaporation. The yellow oil remaining was not soluble in hot Skellysolve B.[19] Addition of cold ether to the oil initiated solidification of a waxy material. Several treatments of this solid with cold ether yielded 1.3 g. (25%) of white crystals, m.p. 67–69°. Two recrystallizations from anhydrous ether gave an analytical sample of ethyl α-hydroxy-β-[2-(1,2,3,4-tetrahydroquinolyl)]propionate, m.p. 68.5–69°.

*Anal.* Calcd. for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.05; H, 7.41; N, 5.56.

A suspension of 0.7 g. (0.0028 mole) of the ester in 30 ml. of 10% sodium hydroxide solution was warmed on the steam bath for 15 min, during which time the ester dissolved. The solution was cooled and neutralized with 25%

(22) V. Ettel, J. Weichet, and O. Chyba, *Collection Czechoslov. Chem. Communs.*, **15**, 528 (1950).

(23) L. Schmid and B. Becker, *Monatsh.*, **46**, 675 (1925).

(24) N. J. Leonard and J. H. Boyer, *J. Am. Chem. Soc.*, **72**, 2980 (1950).

acetic acid solution. Extraction of the solution with 50 ml. of warm Skellysolve B[19] and evaporation of the solvent gave 0.1 g. (17%) of 2-hydroxy-3,3a,4,5-tetrahydropyrrolo[1,2-a]quinoline-1(2H)one, m.p. 137–139°, whose infrared spectrum was essentially identical with that of the compound described in part (a) of this section.

(c) *Reduction of the potassium enolate.* Following a procedure similar to that described in (b) 3 g. of the potassium enolate of the ester[23] was hydrogenated in absolute ethanol. The yellow oil that remained after removal of the solvent was taken up in a small amount of ethanol and acidified with dilute acetic acid. Evaporation of the solvent left a brown solid, from which extraction with Skellysolve B[19] (Soxhlet) gave 0.5 g. (10%) of 2-hydroxy-3,3a,4,5-tetrahydropyrrolo[1,2-a]quinoline-1(2H)one, m.p. 139–140°.

*3,3a,4,5-Tetrahydropyrrolo[1,2-a]quinoline-1(2H)one* (XIX). A mixture of 0.64 g. (0.003 mole) of β-(2-quinolyl)-acrylic acid and 5 teaspoons of W-2 Raney nickel in 125 ml. of ethanol was hydrogenated at atmospheric pressure in a quantitative hydrogenation apparatus. The total uptake was 2.8 moles ± 0.3 mole of hydrogen and required 3.5 hr. The resulting solution was filtered and the ethanol was removed under reduced pressure. The resulting yellow oil was taken up in 50 ml. of hot Skellysolve B.[19] The solution was decanted from a dark yellow insoluble oil and cooled. Filtration of the chilled solution gave *ca.* 0.3 g. of white crystals, m.p. 105–107°. Recrystallization of this solid from 25 ml. of Skellysolve B[19] gave 0.2 g. (33%) of white crystals, m.p. 109–111° (lit.[25] m.p. 115–116°) of 3,3a,4,5-tetrahydropyrrolo[1,2-a]quinoline-1(2H)one. Further recrystallization gave no change in melting point.

*2-Piperidino-3,3a,4,5-tetrahydropyrrolo[1,2-a]quinoline-1(2H)one* (XVII). To a chilled solution of 0.35 g. (1.67 mmoles) of 2-hydroxy-3,3a,4,5-tetrahydropyrrolo[1,2-a]-quinoline-1(2H)one in 10 ml. of anhydrous benzene was added 0.224 g. (0.826 mmole) of phosphorus tribromide in 5 ml. of anhydrous benzene. The mixture was stirred at 0–5° for 2 hr. (protected from moisture), was allowed to come to room temperature and was stirred for 1 hr. at 60 mm. pressure and for 1 hr. at 20 mm. pressure to remove most of the excess phosphorus tribromide. The benzene layer was decanted from the white and yellow solids adhering to the walls of the flask. (These solids were taken up in water and extracted with ether, from which 10–20 mg. of a yellow solid appearing to be unchanged starting material was obtained. The aqueous layer contained no organic material.) The benzene solution was added to a solution of 0.349 g. (4.1 mmoles) of piperidine in 5 ml. of anhydrous benzene. The solution was heated under reflux for 2 hr., cooled, and filtered, giving 0.17 g. (85%) of piperidine hydrobromide, m.p. 236°. The benzene solution was treated with dry hydrogen chloride, forming a white solid. (Excess hydrogen chloride caused redissolution of the solid, but boiling the benzene solution to drive off the excess hydrogen chloride caused it to reprecipitate.) The solution was cooled and filtered, yielding 0.385 g. of white solid, m.p. 196–201°, whose infrared spectrum indicated it to be a mixture of piperidine hydrobromide and the expected product. Chilling the mother liquor overnight followed by concentration produced additional crops of 0.09 and 0.11 g. of product which sublimed at 210–220° and whose infrared spectrum was identical with that of the hydrochloride of the hydrogenation product of compound A. Recrystallization of the product from benzene gave 0.35 g. (78%) of the hydrochloride of 2-piperidino-3,4a,4,5-tetrahydropyrrolo[1,2-a]quinoline-1(2H)-one, subliming at 220°, and having an infrared spectrum identical with that of the hydrochloride of the hydrogenation product of compound A.

A 0.185-g. sample of the crude hydrochloride (before removal of the piperidine hydrochloride) was dissolved in 3 ml. of water, and the solution was filtered and made slightly alkaline with dilute sodium hydroxide solution. The white precipitate that formed was washed twice with 5 ml. of water and dried, m.p. 126–127°. Recrystallization of this solid from Skellysolve B gave 10 mg. of product, m.p. 129–131°, whose infrared spectrum was identical with that of 2-piperidino-3,3a,4,5-tetrahydropyrrolo[1,2-a]quinoline-1(2H)-one prepared from the hydrogenation of compound A.

*Compound C (XVI).* Chloral-2-picoline was prepared in 68% yield by the procedure of Tullock and McElvain.[26] To a solution of 24.0 g. (0.10 mole) of chloral-2-picoline in 30 ml. of pyridine was added a solution of 39 g. (0.6 mole) of potassium hydroxide in 200 ml. of water. The mixture was heated on the steam bath and shaken vigorously until boiling began, the flask was removed and, as soon as boiling subsided, was cooled then chilled in ice. Filtration of the product gave 5.5–11.2 g. (26–52%) of compound C as deep blue needles.

Compound C was much less stable than compounds A and B. Attempts to purify the crystals for analysis resulted only in decomposition. This compound, while showing the general solubility characteristics of the others, was more soluble in water. Crude compound C which became slightly moist decomposed within an hour after preparation, but attempts to dry the compound in the vacuum desiccator (over phosphorus pentoxide or in the absence of a desiccant) resulted in the rapid removal of pyridine.

*Chloral-2-methylcinchoninic acid.* A mixture of 70 g. (0.375 mole) of 2-methylcinchoninic acid, 60 g. (0.41 mole) of chloral, and 120 ml. of pyridine was heated on the steam bath for 2 hr. and poured into 500 ml. of cold water with vigorous stirring. The crude solid product, 70 g., was filtered off and washed with 1:1 ethanol-water. Acidification of the filtrate yielded an additional 10 g. of crude product. The crude product was nearly insoluble in acetone, ethanol, Cellosolve, chloroform, ethyl acetate, and benzene. An analytical sample was prepared by dissolving the crude material in pyridine (charcoal) and diluting the solution with an equal volume of water, giving colorless crystals of chloral-2-methylcinchonic acid, m.p. 204–204.5° dec.

*Anal.* Calcd. for $C_{13}H_{10}NO_3Cl_3$: C, 46.66; H, 3.01; N, 4.25; Cl, 31.79. Found: C, 47.08; H, 3.12; N, 4.44; Cl, 31.79.

This procedure did not work well for large quantities. Thus, the remainder of the crude product was dissolved in 100 ml. of pyridine, diluted with an equal volume of water, and neutralized with hydrochloric acid in a stepwise fashion removing the precipitated product after each incremental addition of acid. The yield of nearly white crystals was 50 g. (40%), m.p. 203–205° dec.

*Reaction of chloral-2-methylcinchoninic acid with pyridine and alkali.* To a solution of 6.6 g. (0.02 mole) of chloral-2-methylcinchoninic acid in 10 ml. of pyridine was added a solution of 6 g. of potassium hydroxide in 20 ml. of water. The solution was warmed gently on the steam bath until a vigorous reaction began. After the boiling had subsided, the purple solution was chilled in ice and neutralized with 6 ml. of glacial acetic acid. A deep purple-black solid separated which was collected and washed with water, giving 3.0–4.2 g. (50–70%) of crude product.

To 200 ml. of boiling absolute ethanol 1 g. of crude product was added and the mixture was heated for 2 min. The solution was rapidly filtered and immediately chilled in ice. The product formed fine, lustrous purple-black crystals of the enol betaine, which were soluble in dilute potassium hydroxide solution, slightly soluble in ethanol, less so than compound A in acetone, acetic acid, and hydrochloric acid and insoluble in ether, dioxane, and petroleum ether. The analytical sample was found to contain one molecule of ethanol of crystallization.

*Anal.* Calcd. for $C_{18}H_{12}N_2O_3 \cdot C_2H_6O$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.71; H, 5.15; N, 8.23.

LINCOLN 8, NEB.

(25) W. Koenigs, *Ber.*, **33**, 218 (1900).

(26) C. V. Tullock and S. M. McElvain, *J. Am. Chem. Soc.*, **61**, 961 (1939).