Conductivity experiments made some time ago in their laboratory by the authors has shown that vapor-phase gasoline which had undergone oxidation possessed to a very appreciable degree the ability to conduct the electric current. Hence, it is apparent that ions actually are present in such a medium. This information has been of value to the authors in explaining the results of their investigation on the autoxidation of the amylenes,[4] assuming that the atmospheric oxidation of amylenes also produces ions, or maintains ionization.

(E) Summary

1. Cobalt soaps of oleic acid have been prepared, and their catalytic effects studied.

2. It has been shown that the cobalt*ic* soap is responsible for the great catalytic activity of cobalt soaps in promoting autoxidation.

3. It has further been shown that bases exert a negative whereas fatty acids exert a positive catalytic effect on autoxidation in the presence of a cobalt soap.

4. The activity of cobalt soaps has been explained on the assumption of the formation of a complex cobaltic acid.

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SALTS OF THE AMMONO-ENOLIC MODIFICATION OF QUINALDINE[1]

BY F. W. BERGSTROM

Introduction

Since the group —CH=N— is related to ammonia as —CH=O is related to water,[2] it follows that the heterocyclic nitrogen compounds, pyridine, quinoline, isoquinoline and quinoxaline are aldehyde-acetals of an ammonia system. The aldehydic properties of pyridine, quinoline and isoquinoline are not marked, because of the stability of the six-membered ring they contain. Nevertheless, Mr. McAllister and the author have shown that all three of these compounds react with the Grignard reagent in ether at 150°.[3] Ziegler and his co-workers have quite recently

[1] Presented at the Berkeley, California, meeting of the National Academy of Sciences, September, 1930, and at the Eugene, Oregon, meeting of the A. A. A. S., June, 1930. Abstract in *Science*, **72**, 402 (1930).

[2] This is not strictly true, since nitrogen is trivalent, while oxygen is divalent. The third valence of the nitrogen in the —CH=N— group may be attached to an alkyl or aryl radical, giving all of the ammono aldehydes the dual character of aldehyde-acetals [Strain, THIS JOURNAL, **49**, 1559 (1927)].

[3] Bergstrom and McAllister, *ibid.*, **52**, 2845 (1930).

shown that the lithium alkyls and aryls, in ethereal solution, add very readily to the —CH=N— bond of these cyclic aldehyde acetals at ordinary temperatures.[4] Quinoxaline, in distinction from pyridine, quinoline and isoquinoline, reacts with ethereal solutions of the Grignard reagent under ordinary conditions.[5] Quinoxaline therefore more closely resembles the familiar aquo aldehydes in its behavior.

If quinoline be regarded as a cyclic ammono aldehyde (-acetal) it follows that 2-methylquinoline (quinaldine) is a cyclic ammono ketone (-acetal) because it contains the grouping —N=C(CH₃)—.[6] In harmony with this view, quinaldine has been found to condense readily with benzaldehyde in the presence of zinc chloride to form benzylidene-quinaldine[7] in accordance with the equation
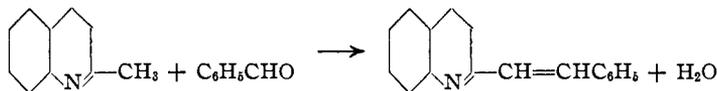
Clearly this type of reaction, which is by no means restricted to benzaldehyde and quinaldine, can be compared to the union of benzaldehyde with acetone to form dibenzalacetone. Reactions of this nature have led Mills and Smith[8] to compare quinaldine with the ketones of the water system.

The oxidation of quinaldine with potassium permanganate[9] yields N-acetylanthranilic acid, perhaps in accordance with the equation
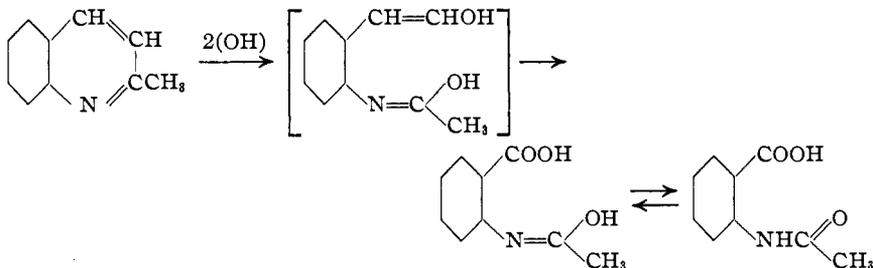
The rupture of the carbon chain has occurred between the carbon of the ammono carbonyl group, =C=N—, and an adjacent carbon of the ring. The aliphatic aquo ketones on oxidation are similarly broken apart on one side or the other of the carbonyl group.

Many ketones of the water system are tautomeric, in that they exist

⁴ Ziegler, Ber., 63, 1847 (1930); Ziegler and Zeiser, Ann., 485, 174 (1931).

⁵ Bergstrom and Ogg, THIS JOURNAL, 53, 245 (1931).

⁶ Compare the O=C(CH₃)— group of the aquo ketones.

⁷ Wallach and Wüsten, Ber., 16, 2008, 2832 (1883); Jacobsen and Reimer, ibid., 2606.

⁸ Mills and Smith, J. Chem. Soc., 121, 2724 (1922).

⁹ Doebner and v. Miller, Ber., 15, 3077 (1882); Drewsen, ibid., 16, 1955 (1883).

in a ketonic and an enolic modification, both of which are often capable of independent existence. In cases where both modifications cannot be isolated as such, derivatives of both forms may be known. This is true of quinaldine, since the ammono-keto form is the only one that has been obtained, although many reactions are best explained by the ammono-enolic formula, No. B below, in which Na is replaced by H.[8,10] The N-alkyl derivatives of this form (B) represent a rather reactive but definitely known class of compounds, the N-alkyl-2-methylene-1,2-dihydroquinolines.[11] The replacement of the N-hydrogen atom of formula B by potassium, sodium or other metals should likewise give fairly stable derivatives of the ammono-enol (enamic)[12] modification. It was for the purpose of preparing some of these compounds that the present investigation was undertaken. Ziegler and Zeiser[13] have already announced the preparation of the N-lithium salt of quinaldine ammono-enol (compare formula B) which was effected by the action of lithium phenyl upon quinaldine in ethereal solution. In the present work it is desired to bring to completion the study of the action of the alkali amides upon quinaldine in liquid ammonia, as reported in part last year by the author.[1]

Preparation of Salts of the Ammono-enolic Modification of Quinaldine.—In a preliminary fashion, it was found that the amides of potassium, sodium and lithium reacted readily with a solution of quinaldine in liquid ammonia at $+20$ or $-33°$ to form opaque rich red solutions of the ammono-enolic (enamic) modification of quinaldine. Thus sodium amide and quinaldine react in accordance with the equation
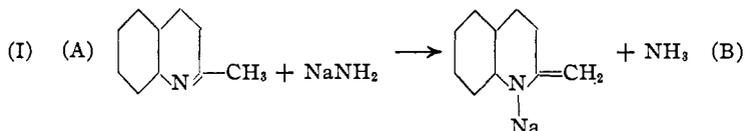
The isolation of the sodium salt in a state of fair purity is illustrated by the following typical experiment.

In one limb of a two-legged reaction tube[14] was placed 0.36 g. of metallic sodium, together with a coil of iron wire to serve as a catalyst for the reaction of sodium with the solvent to form sodium amide. The other leg contained 1.0 cc. of quinaldine, that is, approximately half the amount required by the above equation. After the disappearance of the blue color of the sodium solution, the quinaldine was washed into the leg containing the resultant sodium amide, whereupon an opaque red solution formed at once with a slight evolution of heat. To insure the completeness of reaction, the solu-

10 Chichibabin, *Ber.*, **60**, 1607 (1927).

11 Rosenhauer, Hoffmann and Unger, *ibid.*, **59**, 946 (1926); *cf.* Mumm and co-workers, *Ann.*, **443**, 272 (1925); Königs, Köhler and Blindow, *Ber.*, **58B**, 933–940 (1925).

12 Short and Watt, *J. Chem. Soc.*, 2293 (1930).

13 Ziegler and Zeiser, *Ann.*, **485**, 179 (1931).

14 Franklin and co-workers, THIS JOURNAL, **27**, 831 (1905); **29**, 1694 (1907); **35**, 1460 (1913); *J. Phys. Chem.*, **15**, 510 (1911); **16**, 694 (1912).

tion above the remaining sodium amide was concentrated to a small volume and the tube set aside for a day. The concentrated red solution was carefully decanted into the clean leg of the reaction tube and evaporated to dryness by permitting the liquid ammonia to evaporate from the tube, since it proved impossible to induce crystallization of the salt even at $-78°$. The ammono-enol salt so prepared unavoidably contained the sodium amide that was simultaneously transferred in solution. Since the solubility of sodium amide in ammonia is of the order of a gram a liter at $20°$, this error is not serious. The reaction tube, prepared in the customary manner for analysis, was evacuated at $20°$ and at $100-150°$. The reddish-brown ammono-enolate solidified to a voluminous froth at the lower temperature. The loss of ammonia at the higher temperature is evidently attended with a slight ammonolysis of the salt, since a few very small droplets of liquid (quinaldine) condensed on the cooler portions of the tube. The specimen, after heating, was hydrolyzed overnight with water vapor, a yellowish very viscous liquid of somewhat sharp odor being formed. This was dissolved in dilute hydrochloric acid and analyzed for sodium.[15] A second aliquot was made alkaline with sodium hydroxide, the liberated base extracted with ether, the ether evaporated and the residue taken up in alcohol. From this alcoholic solution a picrate was prepared which could not be obtained in a pure state. Obviously quinaldine was not formed in any quantity by the hydrolysis of its heated potassium salt. This was not unexpected, since the heated salt was insoluble in ether, while the unheated material was readily soluble.

Quinaldine could be isolated when unheated specimens of the potassium and sodium salts of the ammono-enol were hydrolyzed. Apparently, the free ammono-enol first liberated in the hydrolysis is only partially converted to the ammono-keto form (ordinary quinaldine), the rest perhaps being polymerized to products of indefinite nature.

The lithium and barium salts of quinaldine ammono-enol were prepared in the same manner from quinaldine and the amides of lithium and barium, which were made by the catalytic action of iron wire upon liquid ammonia solutions of these metals. In neither of these cases does the reaction appear to be quite complete, since small amounts of quinaldine were always unattacked. Calcium amide reacts only to a very slight extent with quinaldine.

The potassium salt of the ammono-enol, prepared by the action of potassium amide upon quinaldine, could not be crystallized from ammonia solution at $-78°$.[16] Therefore, in order to accomplish its isolation, the product of the action of an excess of potassium amide solution upon quinaldine was freed from solvent ammonia (the liquid ammonia was evaporated from the tube and the latter evacuated) and extracted in the reaction tube with anhydrous ether.[17] The salt remaining after evapora-

[15] One aliquot portion ($^1/_4$) was evaporated dry and gently ignited to carbonize the organic matter. Then sulfuric acid was added and after ignition the precipitate was weighed as sodium sulfate.

[16] Potassium amide is soluble in liquid ammonia to about the same extent.

[17] The stopcock of the evacuated reaction tube was immersed in ether and opened to allow the introduction of the required amount of ether. The stopcock was then closed. The ether in the tube, under its own vapor pressure, could be evaporated from one leg to the other in the same manner as liquid ammonia (procedure of E. C. Franklin, unpublished work).

tion of the ether retained a small amount of both ether and ammonia at 20° in a vacuum.   This was given off at 100°, but the salt simultaneously suffered some decomposition.

In duplicate experiments, in which the loss of weight occasioned (cf. Equation I) by the reaction of weighed quantities of potassium amide and quinaldine was determined,[18] it was found that the potassium salt of the ammono enol retained less than 0.1 mole of ammonia in a vacuum at 20°. Conversely, it was found that the sodium salt of quinaldine retained 0.561 mole of ammonia after intermittent evacuation at room temperatures for a period of two days.   Ammonia in excess of half a molecule, at least, cannot be held by the salt as true solvent of "Crystallization."

TABLE I

ANALYSES OF QUINALDINE SALTS

	Metal, %		Calculated for		
Salt	At 20°	At 100-50°	Anammonous salt	Salt xNH$_3$	x
K	20.3, 20.2[b]	22.4, 21.5	21.6		
Na	12.3	13.9	13.9	12.6	0.5
Li[a]	3.74	3.80	4.66	3.80	2
Ba[a]	27.2	27.9	32.6	28.1	4
Ca	Reaction very slow and incomplete				

[a] These figures merely represent the maximum amount of lithium amide or barium amide dissolved by quinaldine, and do not quite correspond to definite compounds, since a little quinaldine was unattacked.

[b] Both ammonia and ether retained by salt.   Two specimens analyzed.

An attempt to prepare the zinc and silver salts of the ammono-enol of quinaldine by metathesis in liquid ammonia resulted in failure.   The precipitates obtained by adding a solution of the sodium salt of the ammono-enol to a solution of zinc cyanide or to silver iodide when washed proved to be, respectively, an impure zinc amide and a slightly impure metallic silver.   Evidently the ammono-enolic modification of quinaldine is a very weak acid, since its zinc and silver salts are so completely ammonolyzed.   The appearance of metallic silver instead of silver amide in the above reaction is probably due to a reduction of the latter to metal and the equivalent nitridation of the ammono-enol.

Preparation of Salts of Quinaldine in Other Solvents

Since the use of liquid ammonia is inconvenient for many laboratories, attempts were made to prepare the potassium and sodium salts of quinaldine in other solvents.   It was found that quinaldine was unaffected by a solution of sodium ethylate in absolute alcohol at 20°, since the characteristic red color of the enolate failed to develop.   The potassium and sodium salts of quinaldine were very slightly soluble in benzene and toluene but readily soluble in anhydrous ethyl ether and in quinaldine

[18] Cf. Kraus and Greer, THIS JOURNAL, **45**, 3079 (1923).

itself. Preliminary experiments indicated the feasibility of preparing these salts from sodium or potassium amide and quinaldine in absolute ether, but not in benzene or in toluene. The products must necessarily contain ammonia since a molecule of ammonia is liberated in the reaction. (Equation I.)

The Action of Alkyl and Aryl Halides upon Ether and Liquid Ammonia Solutions of the Salts of Quinaldine Ammono-Enol.—Since the sodium salt of the enolic modification of acetoacetic ester reacts with alkyl halides to form alkylated homologs of the keto form, it seemed probable that the related potassium and sodium salts of the ammono-enolic modification of quinaldine would behave similarly—and yield homologs of quinaldine with a lengthened side chain, in accordance with the type equation[19]

(II)
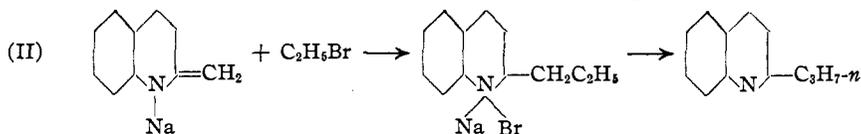
2-Ethyl, 2-n-propyl, 2-n-butyl and 2-ω-phenylethylquinolines were thus prepared by the action of methyl iodide, ethyl bromide, n-propyl bromide or benzyl bromide, respectively, on liquid ammonia or absolute ethereal solutions of the potassium salt of quinaldine. These reactions were conveniently carried out in a preliminary fashion in liquid ammonia reaction tubes. For the preparation of larger quantities of these homologs of quinaldine, it was necessary to adopt a different procedure, which may be illustrated by describing the preparation of 2-n-propylquinoline.

A Pyrex tube, 32 cm. long, 4.5 cm. in diameter and closed at one end was placed inside of a Dewar vessel of slightly larger internal dimensions. The top of the Dewar tube vessel was closed by a rubber stopper through which passed (1) a tube reaching to the bottom of the Pyrex tube lining the Dewar, (2) a short tube bent at right angles for introducing liquid from a tank of commercial anhydrous ammonia, (3) a similar bent tube for venting the ammonia that evaporates within the Dewar to the waste and (4) the tip of a 20-cc. buret, the latter passing through a hole in the center of the stopper. This arrangement is similar to that described by Wooster and Mitchell,[20] but differs from it in the use of a removable Pyrex tube to line the Dewar and in the use of a current of ammonia, introduced through tube (1), for stirring the reaction mixture. The use of a mechanical stirrer in these reactions was found to be unnecessary.

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[19] Since Rosenhauer, Hoffmann and Unger[11] have found that ethyl iodide and N-methyl-2-methylene-1,2-dihydroquinoline react to form 2-n-propylquinoline methiodide, the addition represented by the above equation has been assumed to proceed in a like manner. (A primary 1,3-addition to the enonium conjugated system of Decker, $CH_2{=}C{-}N{-}$ [*Helv. Chim. Acta*, **13**, 666 (1930).] Ziegler and Zeiser (Ref. 13) have

discussed reactions of this type, and have prepared, among other compounds, 2-n-butyl- and 2-ω-phenylethylquinoline by the action of n-propyl bromide and benzyl chloride, respectively, on the lithium salt of quinaldine.

[20] Wooster and Mitchell, THIS JOURNAL, **52**, 691 (1930).

The Pyrex inner tube fitting the Dewar having been filled approximately half full of liquid ammonia from the tank, the stopper was removed for a short while and 6.2 g. of metallic potassium introduced together with 0.1 g. of ignited ferric oxide to serve as a catalyst for the conversion of the liquid ammonia solution of potassium to potassium amide. When the conversion of the potassium to potassium amide was complete—as shown by the disappearance of the blue color of the metal solution—19.5 cc. (21.5) g. of quinaldine (0.9 equivalent) was slowly introduced from the buret, while ammonia gas was passed through tube (1) to stir the solution.[21]   After standing for two or three hours to make sure that all of the quinaldine had been converted to the potassium salt, ethyl bromide was slowly run into the solution from the buret with stirring until the deep red color of the solution had disappeared. The reaction was fairly vigorous. The reaction product, 2-n-propylquinoline, partly separated as a liquid phase denser than the solvent. The Pyrex tube lining the Dewar was now removed, the mouth loosely plugged with cotton, and the ammonia allowed to evaporate off under the hood (tube wrapped with toweling to prevent too rapid volatilization of the ammonia). The residue was treated with water to dissolve the potassium bromide and extracted twice with ether to remove the n-propylquinoline. The liquid remaining after evaporation of the ether was distilled in a vacuum, the fraction boiling at 124.5–126° (uncorr.) at 6 mm. being saved as the product; yield, 19.3 g. or 75% of the theoretical.[22]

Picrate, yellow crystals from alcohol, m. p. 162–163° (corr.);[23] mixed melting point with the picrate of 2-n-propylquinoline, prepared by the method of Meisenheimer and Schütze (m. p. 162–163°) is 162–163°, proving their identity.[24]

Methiodide, m. p. 181.7–182.7° (corr.):[24]   Analysis of the dried picrate (Dumas): 0.1223 g. gave 13.70 cc. of nitrogen under standard conditions. Calcd. for $C_{18}H_{16}N_4O_7$: N, 14.0. Found: N, 14.0. Analysis of the free base: 0.2823 and 0.2580 g. gave 18.78 and 16.78 cc. of nitrogen under standard conditions. 0.1654 g. gave 0.5111 g. CO_2 and 0.1174 g. H_2O. Calcd. for $C_{12}H_{13}N$: C, 84.16; H, 7.66; N, 8.19. Found: C, 84.28; H, 7.94; N, 8.30, 8.13.

The results of the reactions of other alkyl and aryl halides with the potassium salt of quinaldine are summarized in Table II.

Experiments 1–6, inclusive, and 9 and 12 were carried out in the manner described under the larger scale preparation of 2-n-propylquinoline. About 10 g. of quinaldine

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[21] In order that the quinaldine may flow into the reaction cell, it was necessary to connect the top of the buret with the waste ammonia line, which, of course, was directly attached to one of the tubes (3) leading into the cell.

[22] It appears that 2-ethyl-, 2-n-propyl- and 2-n-amylquinolines undergo a slow change (absorption of small amounts of oxygen from the air?) over long periods of time, since analyses of old preparations of these substances (after redistillation in a vacuum) are invariably low in carbon (cf. analysis of 2-ethylquinoline). Therefore freshly prepared specimens of 2-n-propyl- and 2-n-amylquinolines were analyzed with the result that the percentages of carbon rose almost to the theoretical. (These analyses are included in the present article.)

The purity of all of the alkylated quinolines prepared in the present article was markedly lowered by using potassium amide much in excess of the amount required by Equation I. The excess of potassium amide appears to react with some of the alkylated quinoline produced in the reaction to form a potassium salt, which in turn is alkylated by treatment with an alkyl halide (cf. Ziegler and Zeiser, Ref. 13).

[23] 163–164° according to Meisenheimer and Schütze, Ber., **56B**, 1356 (1923).

[24] M. p. 180°, Meisenheimer;[23]   184° Freund and Kessler, J. prakt. Chem., **98**, 243 (1918).

TABLE II
RESULTS WITH OTHER COMPOUNDS

	Halide	Chief organic product identified	B. p. (uncorr.), °C.	P, mm.	Solvent used	Yield, %
1	CH_3I	2-Ethylquinoline	123–126	5	NH_3, ether	46
2	C_2H_5Br	2-n-Propylquinoline	128–130	9	NH_3, ether	75
3	$n\text{-}C_3H_7Br$	Mixture, chiefly butyl- quinolines	146–165	10	Ether[a]	26
4	$n\text{-}C_3H_7Br$	n-Butylquinoline	139–143	5	NH_3	71
5	$n\text{-}C_4H_9Br$	n-Amylquinoline	140–142.5	4	Ether[a]	32
6	$n\text{-}C_5H_{11}Br$	Mixture of bases chiefly hexylquinolines	165–170	12	NH_3	38
7	C_6H_5Br	No reaction, even at 100°				
8	C_6H_5I	No reaction at 100° in toluene				
9	$C_6H_5CH_2Br$	2-Phenylethylquinoline	205–210	9	NH_3	34
10	$CHCl_3$	Quinaldine			NH_3	
11	CH_2Cl_2	Quinaldine			NH_3	
12	$Br(CH_2)_2Br$	Quinaldine			NH_3, ether[a]	
13	CH_2I_2	Quinaldine			NH_3	
14	$C_6H_5CH_2CH_2Br$	Reaction very slow, even at 50°			Ether[a]	
15	$Br(CH_2)_3Br$	Quinaldine			NH_3	
16	$C_6H_{11}Br$	Quinaldine + a little cyclohexyl- methylquinoline(?)			Ether[a]	

[a] Some gaseous NH_3 always remained dissolved in the ether.

was used in each experiment, together with 1.1 equivalents of potassium. All other experiments were performed on a smaller scale in ammonia tubes. Where ether was used as a solvent, the potassium salt of quinaldine was first prepared in liquid ammonia, the latter evaporated and absolute ether added. The desired alkyl halide was introduced into this solution.

Notes on Identification

(1) **2-Ethylquinoline.**—Picrate, yellow needles from alcohol, m. p. 149–151°, (corr.).[25] Analysis of free base: 0.2537 g. gave 18.02 cc. of nitrogen under standard conditions. 0.1697 g. gave 0.5203 g. CO_2 and 0.1082 g. H_2O. Calcd. for $C_{11}H_{11}N$: C, 84.02; H, 7.06; N, 8.92. Found: C, 83.62; H, 7.13; N, 8.89.

(4) **n-Butylquinoline.**—Picrate, separating slowly from alc. soln., m. p. 163–165°, (corr.). The picrate of 2-n-butylquinoline melts at 162–163°.[26] Analysis of base: 0.3132 g. gave 19.62 cc. of nitrogen under standard conditions. 0.1692 g. gave 0.5224 CO_2 and 0.1266 H_2O. Calcd. for $C_{13}H_{15}N$: C, 84.26; H, 8.17; N, 7.57. Found: C, 84.25; H, 8.37; N, 7.84.

(5) **n-Amylquinoline.**—Picrate, yellow needles separating slowly from alcohol, m. p. 108.5–109.5° (corr.). Analysis of this picrate: 0.1240 g. gave 13.18 cc. of nitrogen under standard conditions. Calcd. for $C_{20}H_{21}N_4O_7$: N, 13.1. Found: N, 13.30. Analysis of the free base: 0.2935 and 0.3105 g. gave 16.18 and 17.53 cc. of nitrogen under standard conditions. 0.1536 g. gave 0.4748 g. CO_2 and 0.1201 g. H_2O. Calcd. for $C_{14}H_{17}N$: C, 84.36; H, 8.61; N, 7.04. Found: C, 84.31; H, 8.76; N, 6.89, 7.06.

For purposes of comparison, an independent synthesis of 2-n-amylquinoline was carried out by Mr. P. S. Winnek, who followed the method of Späth and Pikl[27] with a slight

[25] Mulliken, Vol. II, p. 155, gives 146–147° (148°) as the melting point.

[26] Ziegler and Zeiser, *Ann.*, **485**, 184 (1931).

[27] Späth and Pikl, *Ber.*, **62B**, 2249 (1929).

modification. Butylidene quinaldine was prepared, in accordance with the directions of these authors, by condensing n-butyraldehyde with quinaldine; b. p. 162–165° at 5 mm.; 11.5 g. of this product was dissolved in absolute alcohol and reduced with gaseous hydrogen in the presence of platinum oxide according to the directions of Adams.[28] The calculated amount of hydrogen (one mole per mole of butylidene quinaldine) was absorbed in half an hour; b. p. of product saved, 150–151° at 5–7 mm.; yield, 5 g. or 43% of the theoretical. Analysis showed this fraction to have the composition of a slightly impure amylquinoline; picrate, m. p. 107.5–109.0° (corr.); mixed melting point with the picrate of n-amylquinoline prepared in liquid ammonia (m. p. 108.5–109.5°) is 108.2–109.0°, showing their identity. The cause of the difference between the preparation of Späth and Pikl and the two specimens of amylquinoline prepared in the present work has not been determined.

(9) **2-ω-Phenylethylquinoline.**—Pale yellow liquid as first distilled, almost all boiling at 210° (uncorr.) (9 mm.). Most of the liquid solidified on standing. The crystals were freed from mother liquor by pressing on a porous plate, m. p. 28.5–29.5°, corr.[29] *Anal.* 0.1408 and 0.1652 g. gave 7.13 and 7.84 cc. of nitrogen under standard conditions. 0.1098 g. gave 0.3520 g. CO_2 and 0.0663 g. H_2O. Calcd. for $C_{17}H_{16}N$: C, 87.50; H, 6.49; N, 6.01. Found: C, 87.43; H, 6.69; N, 6.33, 5.93. Picrate, yellow needles, m. p. 131–132°, (corr.).[30] Analysis of this picrate: 0.1684 g. gave 16.41 cc. of nitrogen under standard conditions. Calcd. for $C_{23}H_{19}N_4O_7$: N, 12.1. Found: N, 12.2. In addition to this picrate there was obtained another picrate in smaller amount, melting at 120.5–121.5°. Analysis of this picrate: 0.0538 g. gave 5.30 cc. of nitrogen under standard conditions. Calcd. for $C_{23}H_{19}N_4O_7$: N, 12.1. Found: N, 12.3. Therefore the two picrates have the same composition.

(10)–(16) Quinaldine, if reported as a product of the reactions summarized in the above table, was always identified as the picrate (m. p. 194–195°) and the identification confirmed by determining the mixed melting point of this with some known quinaldine picrate, m. p. 194–195°. The mixed melting points in no cases were changed. Quinaldine in these experiments did not appear to be formed quantitatively.

(16) **Cyclohexylmethylquinoline (?).**—The chief basic product of the action of cyclohexyl bromide on the potassium salt of quinaldine in liquid ammonia was quinaldine itself. A picrate, prepared from the higher boiling fraction (above 140° at 10 mm.) melted at 146.5–147.8° (corr.) after several crystallizations. *Anal.* 0.2679 g. gave 27.36 cc. of nitrogen under standard conditions. Calcd. for $C_{22}H_{23}N_4O_7$: N, 12.3. Found: N, 12.8. Perhaps this was the picrate of the expected 2-ω-cyclohexylmethylquinoline. It was obtained in very poor yield.

Discussion

The reactions enumerated in Table II are evidently complicated to some extent by the ammonia retained by the potassium salt of quinaldine, this perhaps accounting for the partial regeneration of quinaldine in experiments (10) to (15) inclusive. If we assume that the potassium salt of quinaldine is slightly ammonolyzed in solution to potassium amide and quinaldine, the observed reactions may be due to the combination of potassium amide with the paraffin polyhalide. The alkyl mono halides

[28] Adams and others, "Organic Syntheses," John Wiley and Sons, New York, 1928, Vol. VIII, p. 92. Späth and Pikl used a slower-acting palladium catalyst.

[29] M. p. according to Ziegler and Zeiser,[26] 28°.

[30] M. p. of the picrate of 2-ω-phenylethylquinoline according to Ziegler and Zeiser,[26] is 132°.

on the other hand must preferentially add to the enonium conjugated system, $CH_2=C-NK-$[19] in the manner of Equation II.

In this connection it is of interest to find that the potassium salt of the enol of acetophenone, prepared in liquid ammonia according to the directions of Strain,[31] reacts with ethyl bromide (the ammonia tube was cooled to $-40°$ to permit the introduction of the ethyl bromide)[32] to form some acetophenone, but none of the expected butyrophenone. In the absence of liquid ammonia, alkylated acetophenones are formed in excellent yield.[33]

The Action of Heat upon the Salts of Quinaldine.—It has been previously recorded in this article that quinaldine may be recovered in fair yield from the products of hydrolysis of the unheated sodium and potassium salts of quinaldine. The failure to find quinaldine (except in two cases) in the mixture resulting from the hydrolysis of the heated potassium, sodium and lithium salts of the ammono-enol strongly suggests that these salts are thermally unstable.

In order to test this supposition, 5.2 g. of quinaldine was heated in a bomb tube with the potassium amide from 1.5 g. of potassium (1.0 equivalent) for six hours at 150°.[34]

At the end of this time, the ammonia in the bomb was distilled off and the Pyrex tube containing the heated potassium salt immersed in a bath of liquid ammonia. Fresh ammonia was distilled into the tube, but the enolate was not completely soluble. Furthermore, ethyl bromide in excess of the calculated amount did not react vigorously with the opaque red solution, nor did it cause the complete decolorization of some reddish mud in the bottom of the reaction tube. The material remaining after evaporation of the ammonia was extracted with ether and the extract distilled. No picrate of 2-n-propylquinoline could be isolated in a pure state from any of the fractions. It is clear then that heating destroyed most of the potassium salt.

Attempt to Prepare the Ammono-enolic Form of Quinaldine.— A solution of the potassium salt of quinaldine ammono-enol, prepared in an ammonia reaction tube at ordinary temperatures, was decanted into a solution of an excess of ammonium bromide. The red color of the enolate did not completely disappear for a few seconds. This would indicate that the ammono-enol form of quinaldine or its ammonium salt has a transitory existence in ammonia solution at room temperatures. Ordinary quinaldine was recovered after evaporation of the solvent am-

[31] Strain, THIS JOURNAL, **52**, 3383 (1930).

[32] Compare Schurman and Fernelius, *ibid.*, **52**, 2428 (1930).

[33] Haller, *Bull. soc. chim.*, [4] **31**, 1973 (1922).

[34] Blair, THIS JOURNAL, **48**, 91 (1926). The interior of the bomb was lined with a Pyrex tube closed at one end only. The formation of potassium amide and of the potassium salt of quinaldine in this tube was accomplished in the same manner as in the larger scale preparation of 2-n-propylquinoline, described above. The ammonia was evaporated from this reaction tube, which was allowed to warm up to room temperature before introduction into the bomb. Then, with the head of the bomb tightened, the desired amount of ammonia was distilled in and the bomb heated in an upright electric furnace.

monia and identified as the picrate, m. p. 194–195°, mixed melting point with authentic quinaldine picrate (m. p. 194–195°), 194–195°.

Nitridation of the Potassium Salt.—It was hoped that the addition of iodine to a liquid ammonia or absolute ethereal solution of the potassium salt of quinaldine would produce either 1,4-diquinolylbutane, or 2-ω-iodoquinaldine. Neither of these compounds could be isolated as a product of the reaction. Large quantities of a reddish-black tar were formed, together with smaller amounts of quinaldine, irrespective of whether the reaction was carried out in ammonia or in ether. Bromine reacted in a similar fashion with a solution of potassium quinaldine ammono-enolate in ether with the formation of the same products.

Attempted Preparation of Quinaldine-2-acetic Acid.—It was hoped that this compound would be formed by passing dry carbon dioxide through a solution of the potassium salt of quinaldine in absolute ether.[35] The only organic product isolated in any quantity was quinaldine, while the potassium appeared to be converted to potassium aquocarbonate. No cyanamide (ammonocarbonic acid) or cyanate (mixed aquo-ammono-carbonic acid) was formed in the reaction. Ziegler and Zeiser[4b] obtained only quinaldine by the action of carbon dioxide on the lithium salt.

The Action of Acetophenone on the Potassium Salt of Quinaldine.—Acetophenone reacts with a liquid ammonia solution of potassium quinaldine ammono-enolate to form a precipitate of the sparingly soluble potassium acetophenone enolate[31] and quinaldine (the latter identified as picrate). The solution becomes colorless, indicating the complete disappearance of the quinaldine salt.

Notes on the Use of Iron and Cobalt Oxides as Catalysts in the Reaction between Potassium and Ammonia.—In one of the preceding experiments, a liquid ammonia solution of several grams of potassium was converted within a few minutes to potassium amide by the catalytic action of 0.1 g. ignited ferric oxide.[36] The latter is therefore a much more effective catalyst for this reaction than either metallic iron or platinum. The use of oxide catalysts in small quantity for the preparation of potassium amide at −33° is perfectly justified, provided the reaction is not influenced by the iron oxide or by traces of potassium oxide in solution. As a catalyst in ammonia tube experiments where one desires a potassium amide of highest purity, ferric oxide is not to be recommended. The following experiments illustrate the point in mind.

Three-tenths gram of freshly ignited ferric oxide was brought into contact with the potassium amide from 0.44 g. of potassium in an ammonia reaction tube at room temperatures. At the end of a day, the oxide, originally red, was coated with a thin black

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[35] The potassium salt still retained a small amount of ammonia.

[36] C. A. Kraus and students have long used ferric oxide as a catalyst for this reaction.

layer which slowly increased in depth during the next three and a half months. After this time had elapsed, the mixture of unchanged ferric oxide and the iron–nitrogen–potassium compound was washed with ammonia dried in a vacuum and dissolved in dilute sulfuric acid. *Anal.* Fe (in solution), 35.9; N, 9.1; K, 28.7; Fe_2O_3 (not dissolved by the dilute acid), 17.0. The precipitate reacted vigorously with water, and therefore resembled the iron–nitrogen–potassium compounds previously described.[37] Nearly all of the potassium oxide (or hydroxide) formed in this reaction was transferred to the other leg as a result of washing the black precipitate. This is to be expected only if the action of potassium amide on ferric oxide yields potassium monoxide, which Kraus and Whyte[38] have shown to be slightly soluble in ammonia.

Potassium hydroxide, if formed, would be slightly soluble in potassium amide solution, as the following experiment indicates: a strong solution of potassium amide, which had been in contact with a stick of potassium hydroxide in one leg of an ammonia reaction tube at room temperatures, was decanted into a much larger volume of pure ammonia in the other leg of the tube. There resulted immediately a precipitate of fine white needles. These were washed with ammonia and analyzed. Calcd. for KOH: K, 69.7. Found: K, 69.6; N, a trace. Apparently the reaction of Kraus and Whyte, expressed by the top arrow in the following equation, is reversible

$$K_2O + NH_3 \rightleftharpoons KNH_2 + KOH$$
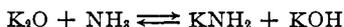
Ignited cobalt oxide (Co_3O_4) also proved to be an excellent catalyst for the potassium–ammonia reaction. Like ferric oxide, the oxide of cobalt was very slowly attacked by the potassium amide solution that resulted.

Summary

1. Quinaldine reacts readily with the amides of sodium, potassium and lithium and more slowly with barium amide to form salts of the ammono-enolic form. In this respect quinaldine behaves as a cyclic ammono ketone (ketone-acetal).

2. The potassium salt of quinaldine reacts with methyl iodide, ethyl bromide, *n*-propyl bromide and benzyl bromide to form, respectively, 2-ethyl-, 2-*n*-propyl-, 2-*n*-butyl- and 2-ω-phenylethylquinoline. With *n*-butyl bromide, a base having the composition of an amylquinoline is formed in poor yield. Polyhalides of methane and ethane, in so far as investigated, react with the potassium salt in the presence of ammonia to regenerate quinaldine. Iodine and bromine convert the potassium salt largely to a tar.

3. The potassium salt of quinaldine has been shown to decompose in liquid ammonia solution at 150°. Decomposition likewise takes place in the absence of solvent at 100–150°.

4. Potassium amide in liquid ammonia solution reacts slowly with ferric and cobalto-cobaltic oxide to form potassium oxide or hydroxide and iron- or cobalt–potassium–nitrogen compounds. Potassium amide dissolves potassium hydroxide in small quantities, probably to form potassium oxide.

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[37] Bergstrom, THIS JOURNAL, **46**, 2635 (1924).
[38] Kraus and Whyte, *ibid.*, **48**, 1781 (1926).