which ionization, velocities, etc., cannot be expected to be the same as in a pure solvent, as is well known to be the case for solutions in water, alcohol and a mixture of the two solvents.

CHICAGO, August 28, 1912.

THE SALTS OF ACRIDINE, PYRIDINE AND QUINOLINE.[1]

[PRELIMINARY PAPER.]

BY L. H. CONE.

Received October 7, 1912.

The salts of acridine, pyridine and quinoline are universally classified as ammonium salts, *i. e.*, as salts in which the acid radical is held in the molecule by one of the valences of a nitrogen atom. This classification is based on the resemblances of the salts of these three bases to those of the open chain amines. The resemblances are chiefly as follows: the solubility of the salts in water with more or less dissociation into ions, the formation of bases when the salts are treated with strong alkalies and, finally, theirsbitter taste. All except the last of these resemblances are based upon properties which are more or less common to all salts, and cannot therefore be used as arguments for classifying any two sets of salts under the same head. Yet a critical examination of the literature shows surprisingly little evidence, other than these resemblances, for the classification of the salts of acridine, pyridine and quinoline as ammonium salts.

Within recent years a large number of nitrogen-free organic salts have been prepared and studied. Most of them contain oxygen and sulfur, and to these have been ascribed constitutions similar to the ammonium salts, with oxygen or sulfur as the center of basicity instead of nitrogen, so that they have been called oxonium and thionium salts. Salts having only carbon and hydrogen in the cation have also been made, and as every member of this class of salts thus far prepared has a benzene ring in the quinoid state, they have become known as quino-carbonium salts (II). After the existence of the quino-carbonium salts was established, it became a logical question to ask whether many organic salts in which the center of basicity had been assumed to be either nitrogen, oxygen or sulfur might not after all be carbonium salts. The position of carbon in the periodic system leads one to expect that it may be the center of greater basicity than that of nitrogen in any of its compounds.

The first inquiries in this direction by Gomberg and Cone[2] resulted in proving that a large number of so called oxonium and thionium salts were not such at all, but were true quinocarbonium salts (V). The

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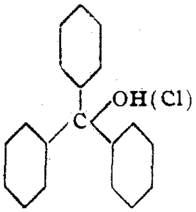
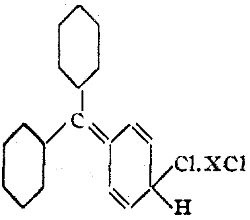
[1] Presented at the International Congress of Applied Chemistry, Organic Section, New York, Sept. 9, 1912.

[2] *Ann.*, **370**, 142 (1909); **376**, 183 (1910).

evidence brought out can be summed up by saying that complete analogy was proven to exist between the oxygen and sulfur-free derivatives of the triphenylmethane series on the one hand (I) and the respective derivatives of the xanthenols and thioxanthenols on the other hand (IV). Previous to that time the salt-like derivatives of the xanthenols and thioxanthenols had been considered oxonium and thionium salts (III), but the close analogy between them and the quinocarbonium salts of the triphenylcarbinols (II) was evidence that oxygen or sulfur is not the center of the basicity of these xanthenol salts.

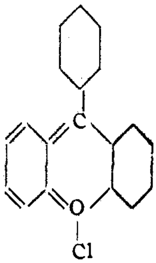


I.



(X = metal)

II.



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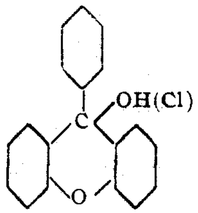
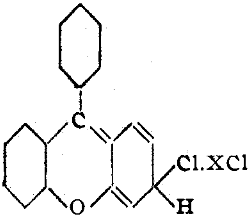


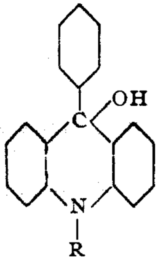
IV.

It was a natural development of the investigation that the studies of the salts of the xanthenols and the thioxanthenols should be followed by a study of the salts of the acridines and especially of phenylacridol (VI), which is so similar in constitution to the triphenylcarbinols and the xanthenols (I and IV).

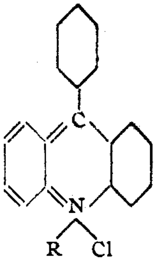


(X = H or metal)

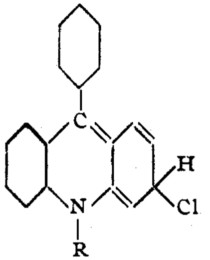
V.



VI.



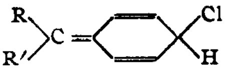
VII.



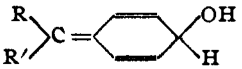
VIII.

Looking at the constitution of phenylacridol (VI) it is apparent that the compound may be considered as a derivative of either diphenylamine, pyridine or quinoline, or triphenylcarbinol. But the salts of diphenylamine are so unstable that there is little similarity between them and the very stable salts of phenylacridol. There is considerable similarity, however, between the salts of pyridine and quinoline on the one hand and of the acridols on the other hand, and if the salts of the former bases are really of the ammonium type there would be reason for considering those of phenylacridol as ammonium salts also (VII). That the center of basicity of pyridine and quinoline is nitrogen is, however, at best a mere assumption which was made at the time when all known organic bases were of the ammonium type. Now that the carbonium salts are known, this assumption should no longer be allowed to stand without experimental testing. If phenylacridol retains essentially the character of triphenylcarbinol, then its salts, like those of the latter, should be considered and formulated as quinocarbonium salts (VIII).

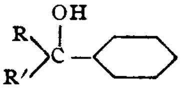
Hantzsch[1] has claimed that the salts of the acridols cannot be of the carbonium type because when treated with strong alkalies they give colored, water-soluble, ionizable bases, which bases quickly tautomerize over into colorless, water-insoluble, non-ionizable pseudo-bases or acridols. He claims that this change from an ionizable, colored base over to a non-ionizable, colorless base is characteristic of the bases of ammonium salts only. This is however a mere assumption. There is no reason why some quinocarbonium salts of the type (IX) should not give colored, water-soluble, ionizable bases of the type (X) which would then rapidly tautomerize to the colorless benzoid form (XI). Investigations are now being carried on in this laboratory with the object of finding nitrogen-free carbonium salts which will react in this manner. In a later paper Hantzsch[2] is not so clear in his objections to the carbonium formulation of the salts of acridine. In this paper he assumes that the carbonium hypothesis recognizes the pseudo-base or carbinol form (XI) as the true base of the carbonium salts. This is not the case, as the papers of Gomberg and Cone on this subject have always emphasized the quinoid nature of the carbonium salts and obviously also then the quinoid form of their true bases (X).



IX.

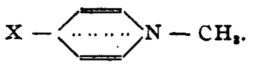


X.



XI.

In this same paper Hantzsch has shown that the salts of acridine, pyridine, quinoline and isoquinoline have an optical variability which he cannot explain without modifying the accepted ammonium formulation of their salts. He introduces Werner's "Nebenvalenz" formulation of the ammonium salts and assumes that salts of pyridine, *e. g.*, can exist under certain circumstances in a form represented by the following structure:



(X = anion.)

The similarity of this formula, with its characteristic quinoid ring, to the structure of the quinocarbonium salts is at once apparent. Hantzsch, however, claims that he wishes to indicate that the anion is still intimately

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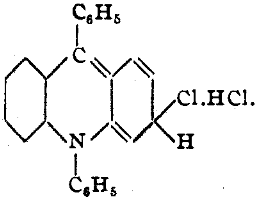
[1] *Ber.*, **43**, 339 (1910).

[2] *Ibid.*, **44**, 1801 (1911).

dependent upon the nitrogen atom through the "Nebenvalenz," which idea is not conveyed in a carbonium formulation. He admits, however, that by the "Carboniumsalzformeln ein richtiger Gedanke ausgedrückt werden soll."

It is the purpose of this paper to describe certain experimental evidence that has been obtained which shows the very strong analogy between the derivatives of the triphenylcarbinols and the xanthenols on the one hand and those of the acridols on the other hand, and also to show that this analogy extends still further to the salts of pyridine and quinoline but does not include the open chain ammonium salts.

C-Phenyl-N-phenylacridol Chloride Hydrochloride,



Diphenylacridol was prepared by the action of phenylmagnesium bromide upon N-phenyl acridone. It has been prepared by Ullmann[1] and there is nothing to be added to his description of the compound. In a previous paper[2] it was shown that diphenylacridol unites readily with hydrochloric acid to form the colored chloride hydrochloride above, which is analogous to the similar hydrochlorides of the xanthenols and of the methoxytriphenylcarbinols. This hydrochloride is best prepared as follows: Diphenylacridol is dissolved in the smallest possible volume of chloroform, a few cubic centimeters of acetyl chloride are added, and then the solution is saturated with hydrochloric acid gas. Benzene is slowly added to the chloroform solution till crystallization begins. After a considerable quantity of crystals have separated out petroleum ether is added with stirring. The product separates out in glittering yellow plates, or, if the addition of petroleum ether has been too rapid, in very fine needles. The yield is quantitative, provided enough petroleum ether has been added to throw all of the crystals out of solution. The product as thus obtained shows upon analysis somewhat high values for hydrochloric acid. This is due to the fact that the hydrochloride adds a third molecule of hydrochloric acid, presumably to the nitrogen atom, as this third molecule of acid is held with about as little tenacity as, *e. g.*, hydrobromic acid in the hydrobromide of triphenylamine. A few hours drying of the crystals in a good vacuum over fresh soda lime leaves a product which gives sharp analysis for the chloride hydrochloride.

Calculated for $C_{25}H_{19}NCl_2$: Cl, 17.55. Found, 17.23.

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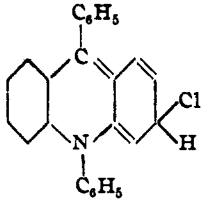
[1] *Ber.*, 40, 2520 (1907).

[2] *Ann.*, 370, 205 (1909).

C-Phenyl-N-phenylacridol Chloride,



The hydrochloric acid is held very firmly in the above hydrochloride. It may, however, be removed by heating the compound in a vacuum at 150–160° during an hour, or more rapidly by dissolving the hydrochloride in water and then adding salt to the solution, when the crystallin chloride separates out. The last method is accompanied by considerable loss and the product obtained is contaminated with salt. To finally purify the compound, whether prepared by heating or from water, it is necessary to recrystallize it from chloroform by the addition of benzene and petroleum ether, and then to dry it in a vacuum at 100° to remove solvent of crystallization. The product as thus prepared is a lemon yellow powder which is insoluble in benzene and petroleum ether, but easily soluble in water, alcohol, nitrobenzene and chloroform. The product does not melt at the boiling point of sulfuric acid.

Calculated for $C_{25}H_{18}NCl$: Cl, 9.64. Found, 9.37.

The Action of Molecular Silver.—The above chloride dissolves in nitrobenzene to a lemon yellow solution. When molecular silver is added to this solution a brown layer immediately begins to form over the surface of the metal. In a few hours the entire solution will change to a deep clear brown with a slight greenish fluorescence. Repeated examinations of the silver residue remaining after the brown color has reached the maximum of intensity showed that the solid contained no silver chloride. The nature of the reaction taking place was entirely dark till it was revealed by a series of quantitative experiments of which the following serves as an example: 0.1774 gram of the acridol chloride and 0.3272 gram of molecular silver were sealed with nitrobenzene and shaken during a week. The solution became intensely brown. The solid residue in the tube was filtered off. It consisted of pure silver which weighed 0.025 gram less than the original amount taken. To the filtered nitrobenzene solution benzene and petroleum ether were added, and a small quantity of a crystallin precipitate was obtained, which proved to be a double salt of silver chloride with diphenylacridol chloride. If it is assumed that the reaction of silver with diphenylacridol chloride takes place in the same manner as it does with triphenylchlormethane and that an unsaturated compound analogous to triphenylmethyl is formed, the following equations would explain the loss in weight of the metallic silver and the formation of the double salt:

$$(a)\quad C_{25}H_{18}NCl + Ag = (C_{25}H_{18}N) — + AgCl$$
$$(b)\quad C_{25}H_{18}NCl + AgCl = C_{25}H_{18}NCl.AgCl.$$

The amount of silver necessary to complete the reaction in the above experiment, according to the equations, is 0.0266 gram, whereas the amount actually used was 0.025 gram. If this interpretation of the reaction is correct, it is exactly analogous to the reaction between triphenylchlormethane and metallic zinc. In this reaction triphenylmethyl and zinc chloride are first formed and then zinc chloride unites with some of the unchanged triphenylchlormethane to form a double salt.

The Silver Chloride Double Salt.—Further evidence in favor of the above interpretation is given by the following experiment: 0.3882 gram of diphenylacridol chloride and 0.5605 gram of silver chloride were sealed with nitrobenzene and shaken during a week. The solution darkened only very slightly. During the shaking 0.1487 gram of silver chloride went into solution, while if a double salt is formed according to equation (*b*) 0.1514 gram should have gone into solution. To the filtrate from the undissolved silver chloride, benzene and petroleum ether were added when fine, yellow needles and plate crystals separated out, in all, 0.470 gram out of a possible 0.530 gram of double salt.

This crystallin silver chloride double salt is only slightly darker in color than the acridol chloride from which it was prepared. It dissolves fairly well in chloroform and nitrobenzene and also gives a clear solution in acid-free water and alcohol. If a drop of nitric acid be added to its water solution, instant precipitation of silver chloride takes place, or, if its water solution be allowed to stand, gradual separation of silver chloride takes place. It is probably due to the formation of this silver chloride double salt, that silver nitrate gives no immediate precipitation with water solutions of diphenylacridol chloride unless nitric acid is added. The double salt was analyzed by precipitating the silver chloride with nitric acid and then titrating the chlorine in the filtrate.

Calculated for $C_{25}H_{18}NCl.AgCl$: AgCl, 28.06; Cl, 6.93.
Found: AgCl, 27.53; Cl, 6.78.

The Unsaturated Compound.—If the reaction between diphenylacridol chloride and silver proceeds according to equation (*a*) and (*b*), then beside the double salt formed there must be produced an unsaturated analog of triphenylmethyl. The deep brown solution resulting from shaking phenylacridol chloride with silver does not change very much in color on exposure to the air, and no insoluble peroxide separates out as is the case with triphenylmethyl solutions. Nevertheless, a measurable, though not large, absorption of oxygen by the brown solution could be demonstrated. It was therefore concluded that during the long shaking the unsaturated compound had polymerized to some more stable substance. If this is the correct explanation, the only way in which the unsaturated compound could be quantitatively oxidized would be at the instant of its formation. The reaction was therefore further investigated in the following manner.

Diphenylacridol chloride was sealed with silver and nitrobenzene in an atmosphere of oxygen. The container was immersed in water at a definit temperature at the time of sealing and the barometric pressure was read. Tubes were shaken varying lengths of time and each was examined separately. · The sealed capillary end of the tube was connected with a gas buret. The container was brought back to the same temperature at which it had been sealed, the barometer again read, and the end of the capillary was broken off inside of the rubber tubing and the volume of oxygen absorbed was measured.

During ten days 0.6797 gram of substance was shaken as above. Twelve cc. of oxygen at 24° and 735 mm. or 0.0153 gram were absorbed. If the reaction took place according to (*a*) and (*b*) and then the unsaturated compound produced in (*a*) absorbed oxygen to form a peroxide of the type of triphenylmethyl peroxide as follows:

$$(c)\quad 2(C_{25}H_{18}N) —+ O_2 = (C_{25}H_{18}N).O — O.(C_{25}H_{18}N),$$

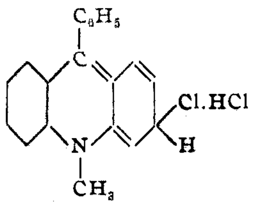
then the theoretical amount of oxygen necessary in the above experiment would be 0.0148 gram instead of 0.0153 gram as found. A number of similar experiments have shown that the amount of oxygen absorbed is generally higher than the amount calculated according to equations (*a*, *b*, and *c*) combined. This is due to the gradual decomposition of the silver chloride double salt in the presence of silver, resulting in the formation of more of the unsaturated compound than that called for by equations (*a* and *b*). This was proven in two ways: first, if the acridol chloride is shaken with silver for a much longer period of time the reaction can be driven to where almost twice the amount of oxygen called for by equations (*a*, *b* and *c*) is absorbed; second, if the crystallin double salt of diphenylacridol chloride and silver chloride be shaken with molecular silver in an atmosphere of oxygen, the unsaturated compound is again formed and oxygen is absorbed. It must therefore be concluded that the silver chloride double salt suffers slight dissociation into its components when dissolved in nitrobenzene.

0.6469 gram of the acridol chloride in nitrobenzene solution when shaken six weeks with excess of silver absorbed 0.023 gram of O. Calc. by equations (*a*, *b* and *c*) 0.014 gram, for complete reaction 0.028 gram.

0.2771 gram of silver chloride double salt during 3 weeks shaking with silver absorbed 0.007 gram of O. Calc. 0.011 gram.

The reaction of other metals with diphenylacridol chloride is the same as that described for silver. The fact that diphenylacridol chloride is a colored compound and is undoubtedly in the quinoid state, as shown in its formula above, does not seem to make the character of its reactions different from those of the benzoid, colorless triphenylchloromethane. It cannot be positively concluded from this that metals will react with both the benzoid and quinoid forms of the halides under consideration, for there is the possibility that in solution a small portion of triphenylchloromethane may be in the quinoid state or a small portion of the diphenylacridol chloride may be in the benzoid form. Whichever form metallic silver reacts with, the equilibrium would be so disturbed that the reaction would proceed to the same type of end products. Optical studies and the studies of the time rates of the two reactions are methods by which this question may be answered.

C-Phenyl-N-methylacridolchloride Hydrochloride,



Phenylacridine was prepared according to Bernsthen[1] from benzoic acid and diphenylamine. This was methylated by means of methyl sulfate in nitrobenzene solution.[2] From the sulfate thus obtained the C-phenyl-N-methylacridol was freed by means of alkali and then purified by recrystallization from benzene. Starting from pure C-phenyl-N-methylacridol the preparation of its chloride hydrochloride and its normal chloride is entirely analogous to the preparation of the corresponding derivatives of the N-phenyl compound already described. The chloride hydrochloride as freshly prepared always contains more than two atoms of chlorine, probably for the same reason as given under the corresponding phenyl derivative. This excess of hydrochloric acid is more difficult to remove than from the corresponding phenyl compound, but after standing over soda lime in a good vacuum during several days the residue analyzes sharply for the chloride hydrochloride.

Calculated for $C_{20}H_{17}NCl_2$: Cl_2, 20.73. Found: 20.74.

The hydrochloric acid in this hydrochloride is not held as firmly as it is in the corresponding phenyl derivative, for it can be removed by passing air through a suspension of the substance in toluene heated to 90–100°. The hydrochloric acid thus removed was determined by passing the air through silver nitrate solution.

Calculated for $C_{20}H_{18}NCl.HCl$: HCl, 10.66. Found: 10.54.

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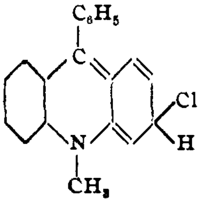
[1] *Ann.*, **224**, 13 (1884).

[2] *Ber.*, **42**, 873 (1909).

C-Phenyl-N-methylacridol Chloride,



This simple chloride is prepared from the hydrochloride by driving off the hydrochloric acid in the manner above described, or in the same way as the chloride of the corresponding phenyl derivative.

Calculated for $C_{20}H_{16}NCl$: Cl, 11.60. Found: 11.48.

In appearance the N-methyl derivative resembles the corresponding phenyl derivative and its solubilities are about the same, except that it is not so soluble in nitrobenzene. When mercury or silver is added to a nitrobenzene solution of the chloride a green cloud begins to form over the metal, and in a few hours the solution becomes so dark that it is transparent in thin layers only. This green color of the phenyl-N-methylacridol analog of triphenylmethyl is strikingly different from the brown of the corresponding N-phenyl derivative. The reactions taking place in the nitrobenzene solution are entirely similar to those already described for the N-phenyl derivative. The silver chloride double salt of the N-methyl derivative is less stable than the double salt of the phenyl derivative, so that the reaction with metals goes to completion sooner than with the phenyl compound.

A solution of 0.8581 gram of phenyl-N-methylacridol chloride in nitrobenzene was sealed with silver and oxygen, and shaken during three weeks. Silver chloride corresponding to 0.2044 gram of silver was formed and 23.5 cc. of oxygen at 24° and 740 mm. were absorbed. The 0.2044 gram of silver changed to silver chloride indicate that 0.5789 gram of the acridol chloride had been changed to the unsaturated compound, and this should absorb 23.71 cc. of oxygen while the amount actually absorbed was 23.5 cc.

The experiment was repeated continuing the shaking during 6 weeks.

0.8218 gram substance absorbed 0.0393 gram of oxygen.

Calculated for complete change of all the chloride into a peroxide, 0.043 gram.

The silver chloride double salt of phenyl-N-methylacridol chloride was prepared by shaking a nitrobenzene solution of the acridol chloride with silver chloride and precipitating the crystallin double salt from solution, with benzene and petroleum ether. This double salt is a yellow, crystallin powder, soluble without decomposition in warm nitrobenzene but not very soluble in cold. It is difficult to prepare a clear water solution of it as hydrolysis is so rapid that the solution quickly becomes turbid from the separation of silver chloride. When prepared as above, the salt holds nitrobenzene very firmly, probably as solvent of crystallization, so that it is necessary to dry it in a vacuum at 110–120°.

Calculated for $C_{20}H_{16}NCl.AgCl$: AgCl, 31.96; Cl, 7.90.
Found: AgCl, 32.29; Cl, 7.12.

Other derivatives of the acridols are now being studied and as far as the work has progressed they all behave very similarly to the two compounds already described. From the work given in this paper it is apparent that the acridols as a class belong to the same type of compounds as the triphenylcarbinols and the xanthenols.

Salts of Pyridine and Quinoline.—There still remains to be investigated the relationship between the salts of the acridols and those of pyridine and quinoline. Following it is shown that certain reactions common to the halides of the triphenylcarbinols, the xanthenols and the acridols are characteristic of the salts of pyridine and quinoline also, and further that these same reactions are not characteristic of the ammonium salts. Thus far only quaternary salts of pyridine and quinoline have been studied.

Pyridine methyl iodide dissolves only slightly in nitrobenzene. If mercury or molecular silver is added to such a solution, or better to a suspension of the finely powdered salt in nitrobenzene, a brown ring will slowly form over the surface of the metal, or, if the solution is warmed, brown clouds will rise from the metal. This reaction is entirely analogous to the reaction of the salts of the acridols with metals described above. It consists in the removal of halogen from the pyridine salt with the formation of an unsaturated compound as represented by the following equation:

$$(1)\ (C_5H_5N.CH_3)I + Ag = (C_5H_5NCH_3)^- + AgI.$$

The metal halide thus formed unites with some of the still unchanged pyridine methyl iodide to form a double salt, which afterwards slowly decomposes in the presence of silver to form more of the unsaturated compound.

$$(2)\ C_5H_5N.CH_3I + AgI = C_5H_5NCH_3I.AgI.$$

If the reaction is carried out in the presence of oxygen the unsaturated compound is oxidized, presumably according to the following equation:

$$(3)\ 2(C_5H_5NCH_3)^- + O_2 = (C_5H_5NCH_3).O.O.(C_5H_5NCH_3).$$

The following two experiments illustrate the behavior of pyridine methyl iodide with metals and oxygen:

A suspension of 2.0812 gram of pyridine methyl iodide in nitrobenzene was shaken during one week with excess of silver in an oxygen atmosphere. The solution became dark brown and some sticky organic matter separated out on the sides of the tube. Seventy-two and eight-tenths cc. of oxygen were absorbed at 23° and 737 mm., or 0.093 gram. If the reaction proceeded according to equations (1, 2 and 3), 0.075 gram of oxygen should have been absorbed, and if the reaction had progressed to completion with total decomposition of the double salt of silver iodide then 0.150 gram should have been absorbed.

0.8505 gram of substance was shaken as above during three weeks. 51.85 cc. of oxygen were absorbed at 25.5° and 740 mm., or 0.066 g. For complete reaction theory requires 0.062 g. of oxygen.

In the first experiment the reaction had gone somewhat beyond the stage represented by the equations (1, 2 and 3), and in the second experiment apparently time enough had elapsed for the reaction to go to completion.

Quinoline methyl iodide behaves entirely like the corresponding pyridine derivative. It is easily soluble in nitrobenzene to a light orange colored solution. Metals react rapidly with this solution giving an intense, deep red color, which as the reaction progresses takes on a purplish tinge. The solution is not decolorized by oxygen nor is the formation of the color inhibited by the presence of oxygen, thus indicating that the peroxide or its decomposition products are colored substances, just as is the case with the acridols and the salts of pyridine.

1.6748 grams of quinoline methyl iodide in nitrobenzene solution were shaken with excess of silver in the presence of oxygen during ten days. 38.4 cc. of oxygen were absorbed at 25° and 737 mm., or 0.0491 gram. For complete reaction in which the silver iodide double salt had been decomposed, 0.0988 gram should have been absorbed.

1.7590 grams substance in nitrobenzene as above were shaken three weeks. 73 cc. of oxygen were absorbed at 22° and 740 mm., or 0.094 gram. Calculated for complete reaction, 0.103 gram.

1.6094 grams substance were shaken during one month as above. 0.0878 gram of oxygen was absorbed. Calculated for complete reaction, 0.095 gram.

From these three experiments it is apparent that the first stage of the reaction, resulting in the formation of the unsaturated compound and the silver iodide double salt, goes rapidly, but that it takes a very long time for the second part of the reaction, that of the double salt with silver, to go to completion.

Nitrobenzene is not the only solvent in which the reaction may be carried out. It goes equally well in quinoline but slower in alcohol. In both solvents a deep red color is produced which in the case of quinoline is tinged with purple. Even in benzene, in which quinoline methyl iodide is insoluble, the reaction with silver proceeds slowly. The suspended solid turns black and considerable oxygen is absorbed. A suspension of the silver iodide double salt of quinoline methyl iodide in nitrobenzene gradually reacts with molecular silver, the solution turns red, and oxygen is absorbed.

It is well at this point to say a word about the double salts of the halides of quinoline and pyridine with the corresponding silver halides. Strange to say, these double salts have not as far as the author knows been observed, yet their formation takes place very readily. If silver nitrate is added to a neutral solution of quinoline or pyridine methyl iodide in water or alcohol, the precipitate formed is not pure silver iodide, but a mixture of that with the double salt of silver iodide and the pyridine or quinoline salt. No attempt has been made to prepare these double salts of the pyridine and quinoline salts in a pure state as they are very insoluble in all reagents.

A number of open chain ammonium salts, as, *e. g.*, benzyldimethylphenylammonium chloride, and tetramethylammonium iodide, in nitrobenzene solution, were shaken varying lengths of time with molecular silver. Not the slightest indication of any reaction could be detected.

A further study of the salts of pyridine and quinoline is now being carried on. It is not deemed advisable to write structural formulas for these salts till a larger number of their derivatives have been studied, and some definit evidence has been obtained as to which carbon atom is the center of their basicity.

Summary.

It has been shown in this paper that the halogen salts of phenylacridol, pyridine and quinoline react with silver to form silver halides and unsaturated compounds similar to triphenylmethyl, which unsaturated compounds readily absorb oxygen just as does triphenylmethyl. It has also been shown that open-chain ammonium salts do not react in this way.

It was concluded that the salts of acridine, pyridine and quinoline are probably quinocarbonium salts because of their analogy to the derivatives of the triphenylcarbinols and the xanthenols, and not ammonium salts as hitherto assumed.

Hitherto, undescribed silver chloride double salts of the salts of the acridols have been prepared and studied and it has been shown that silver iodide forms double salts with the iodides of pyridine and quinoline.

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BIOCHEMICAL AND BACTERIOLOGICAL STUDIES ON THE BANANA.

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Received October 11, 1912.

In an earlier paper[1] compiled analyses were presented to show the composition of ripe bananas and that the essential change during ripening is a transformation of starch into soluble carbohydrates with a decrease in the total carbohydrates. Using the relative amounts of soluble and insoluble carbohydrates present in a given fruit as an index to the degree of ripeness attained, experimental evidence was presented to show the effect of various abnormal conditions upon the ripening process. Fruits

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[1] *J. Biol. Chem.*, 1, 4 and 5, 1906.