These crystals were nearly pure[1] *dimethylaniline benzoylchloride.*

Diethylaniline.—Crystals melting[2] at 115–120° and containing 14.20% of chlorine were obtained.

Calc. for $C_2H_5(C_2H_5)_2N.HCl$: Cl, 19.10. Calc. for $C_6H_5(C_2H_5)_2N.C_6H_5COCl$: Cl, 12.24%.

Diethylaniline benzoylchloride was present as 71% of the mixture.

Antipyrine.—Clusters of transparent needles melting at 138° to a blood-red liquid were obtained. The substance contained 11.08% of chlorine.

Calc. for $C_{11}H_{12}N_2O.C_6H_5COCl$: Cl, 10.47%.

Antipyrine benzoylchloride is very soluble in water.

Quinoline.—Precipitated slowly, reddish crystals melting at 112–116° and containing 16.10% of chlorine.

Calc. for $C_9H_7N.HCl$: Cl, 21.42. Calc. for $C_9H_7N.C_6H_5COCl$: Cl, 13.15%.

Evidently *quinoline benzoylchloride* was present as 65% of the mixture.

Pyridine.—A slow-forming precipitate containing 26.30% of chlorine was obtained.

Calc. for $C_5H_5N.HCl$: Cl, 30.69. Calc. for $C_5H_5N.C_6H_5COCl$: Cl, 16.15%.

Pyridine benzoyl chloride was present as 31% of the mixture.

α-Picoline.—Star-like clusters of needles containing 17.60% of chlorine were obtained.

Calc. for $C_5H_4N.CH_3.HCl$: Cl, 27.37%. Calc. for $C_5H_4N(CH_3).C_6H_5COCl$: Cl, 15.18%.

Picoline benzoyl chloride was present as 80% of the mixture.

SEATTLE, WASH.

THE SALTS OF ACRIDINE, PYRIDINE AND QUINOLINE.[3]

[SECOND PAPER.]

BY L. H. CONE.

Received July 20, 1914.

In a previous paper[4] some experiments were described which indicate a very close analogy between the acridyl salts, *e. g.*, salts of diphenyl acridol (I), and the salts of triphenylcarbinol and its analogues (II). The analogy lay in the character of the reaction of the respective halides with metals. Triphenylmethyl chloride and its analogues in solution react with silver and other metals to form highly unsaturated free radicals of the type of triphenylmethyl. These free radicals absorb oxygen from the air to form

---

[1] Dimethylaniline hydrochloride melts at 83–85°, Scholl and Escales, *Ber.*, **30**, 3134; Menschutkin, *J. Russ. Phys. Chem. Ges.*, **30**, 252; Perkins, *J. Chem. Soc.*, **69**, 1235; Bredig, *Ber.*, **30**, 673.

[2] Diethyl aniline hydrochloride melts at 145°, Reynolds, *J. Chem. Soc.*, **61**, 457; THIS JOURNAL, **34**, 1408 (1912).

[3] Presented at the spring meeting of the American Chemical Society, Cincinnati, April, 1914.

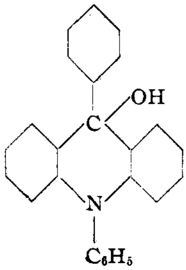
[4] THIS JOURNAL, **34**, 1695 (1912).

peroxides. It was shown that diphenylacridyl chloride and also phenyl-*N*-methylacridyl chloride, when shaken in nitrobenzene solution with molecular silver, give highly colored solutions which absorb oxygen. It was assumed that in these colored solutions free acridyl radicals were present. A quantitative study was made of these reactions and it was found that first silver, and then oxygen enter into the reactions in the proportions given in the following equations:

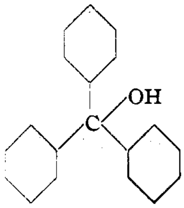
$$(a)\quad C_{25}H_{18}NCl + Ag = (C_{25}H_{18}N)— + AgCl$$

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

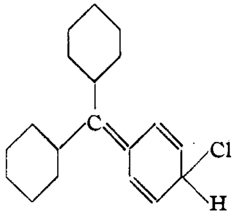
Neither the unsaturated diphenylacridyl, supposed to be formed in reaction *a*, nor its peroxide, supposed to be formed in reaction *b*, were at that time isolated, but the evidence seemed conclusive that both of these compounds were produced. This close analogy between the acridyl chlorides and the triarylmethyl chlorides in so important a reaction as the formation of free radicals seemed to warrant assigning to the colored acridyl chlorides the same type of quinocarbonium structure (IV) as that employed for the colored modifications of the more simple triarylmethyl chlorides (III).



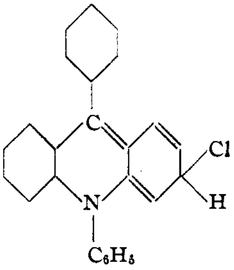
(I)



(II)



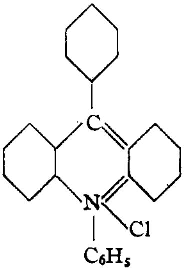
(III)



(IV)

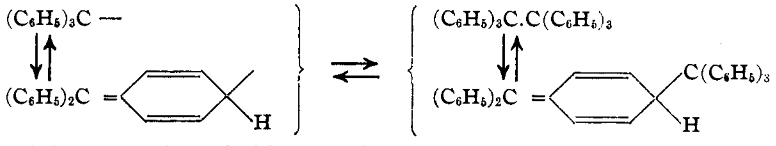
It has now been shown that the interpretation of the reaction between acridyl chlorides and metals, and then with oxygen as given in equations (*a*) and (*b*) above, is entirely correct. This has been done by actually isolating several unsaturated radicals and their peroxides. The free radicals as obtained are dark brownish red, beautifully crystalline compounds, which in solution absorb oxygen from the atmosphere rapidly to form colorless peroxides. They will also combine directly with halogens to form the corresponding halide salts. The method which has been found most satisfactory for the preparation of these free radicals is to shake a watery solution of some salt, preferably the sulfate, with zinc dust. The zinc immediately becomes covered with a dark red coating of the free radical, and if enough zinc has been added the highly colored sulfate solution is completely decolorized. The colorless watery solution of zinc sulfate can then be decanted from the zinc and free radical. On addition of benzene to the moist slime the free radical is dissolved, forming a dark red solution and the excess of zinc appears again in its normal color. The dark red benzene solution is very sensitive to oxidation. If it is shaken a moment in contact with air all of the dark red color disappears and there remains only a pale yellow or brown coloration. From this decolorized solution colorless peroxide soon begins to separate out. In some cases the peroxide is soluble enough in benzene so that it can be recovered only by evaporation of the solvent.

The feature which distinguishes the preparation of free acridyl radicals from the preparation of other triarylmethyls is the use of watery solutions of the acridyl salts instead of benzene solutions as in the other cases. This difference is rendered necessary by the complete insolubility of most acridyl salts in inert organic solvents, and by the non-solubility of the ordinary triarylmethyl chlorides in water. It seems hardly possible that these two classes of salts could all react so completely alike in such a characteristic reaction and yet belong, as is generally supposed, to distinctly different types of compounds, that is, to the quinocarbonium type for the colored forms of the triarylmethyl salts (III) and to the ammonium type for the acridyl salts (V).



(V)

In the absence of any direct experimental evidence that the acridyl salts are really of the ammonium type it seems simpler to assume that they are quinocarbonium in structure (IV) and that the formation of the free radicals consists simply in the removal of the acid radical by a metal. The intensely colored acridyl radicals are certainly analogues of triphenylmethyl. But triphenylmethyl, in solution at least, is not one single substance but is a mixture of substances in equilibrium with each other probably as expressed in the following equation:[1]



The right-hand side of this equation is the predominant one in the case

---

[1] Gomberg, This Journal, 36, 1162 (1914); Schmidlin, "Das Triphenylmethyl," p. 213.

of triphenylmethyl. The reverse is true for the acridyl radicals, the left-hand or monomolecular side being present in their solutions almost to the exclusion of the other. Of the two monomolecular forms, the upper benzoid, colorless form and the lower quinoid, colored form, the quinoid is probably the predominant one because of the intense color of the radicals and their solutions.

Experimental.

Diphenylacridol (*I*).—This compound has been prepared by Ullmann[1] and his method has in the main been followed. A few modifications of his method have increased the certainty of good results in carrying out the preparation according to Ullmann. Commercial anthranilic acid is converted by the method of Goldberg into diphenylanthranilic acid and this is then changed to *N*-phenylacridon by means of sulfuric acid. The *N*-phenylacridon is converted into diphenylacridol by means of phenyl magnesium bromide. This reaction is described in detail because Ullmann's procedure is varied considerably. The powdered acridon is added in small portions to a 10% excess of phenylmagnesium bromide dissolved in rather a large quantity of ether (one-twentieth mol in about 150 cc.). After a considerable portion of the acridon has been added, an oil begins to separate from the ethereal solution. Without making any further additions of acridon, the ether is now boiled till the oil turns to a yellow solid which can easily be powdered by means of a glass rod. The rest of the acridon is then gradually added, with boiling and shaking after each addition. After all of the acridon has been added the reaction mixture is boiled about two hours. The yellow powder in the bottom of the flask is frequently stirred in order to give the very insoluble acridon every opportunity to enter into reaction. The ether is distilled off, ice and hydrochloric acid are added to the residue and the resulting mixture is steam-distilled to remove benzene and bromobenzene. All but a small portion of the residue will dissolve in dilute acid. To the filtered, cold acid solution, which contains diphenylacridyl chloride, sodium hydroxide is then added till the liquid is decidedly alkaline. Diphenyl acridol and magnesium hydroxide separate out together. The precipitate is filtered, washed a little with approximately normal sodium hydroxide solution and dried in a steam or electric oven to avoid acid fumes. Although the acridol could be precipitated free from magnesium hydroxide by means of ammonium hydroxide, the use of this reagent is not advisable, for then an amino derivative is formed from which it is difficult to free the acridol.[2] The sodium hydroxide is left in the cake of precipitate to keep the acridol from taking up acid from the air during drying. The dried cake is broken up and extracted in a Landsiedl extractor with benzene. The benzene

---

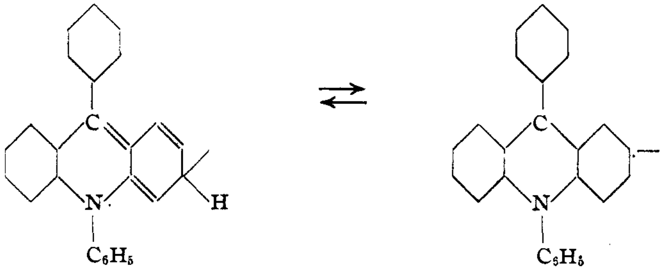
[1] *Ber.*, 40, 2520 (1907).

[2] Villiger, *Ibid.*, 45, 2910 (1912).

solution is concentrated and the acridol thrown out of solution by the addition of petroleum ether. It can thus be obtained in pure white, crystalline leaflets which melt, as Ullmann gives, at 178°. The yield is 85 to 90% of the theory as calculated from the acridon.

Diphenylacridyl Chloride (IV).—A method of preparation of diphenylacridyl chloride has been already described,[1] but a simpler method of obtaining it has now been found. From a solution of the acridol in chloroform the chloride hydrochloride, $C_{25}H_{18}NCl.HCl$, is prepared by means of acetyl chloride and hydrochloric acid gas as directed in the previous paper. The yellow crystalline chloride hydrochloride is filtered out, redissolved in chloroform and an excess of pure, dry calcium carbonate is added. The mixture is shaken for some minutes. The molecule of hydrochloric acid in the hydrochloride is quickly removed to form calcium chloride and acridyl chloride remains in solution. On concentration of the chloroform solution and gradual addition of petroleum ether, the chloride crystallizes out perfectly pure as glittering yellow plates.

Diphenylacridyl,



The action of various metals upon diphenylacridyl chloride dissolved or suspended in different solvents has been tried repeatedly. The metals which were most frequently tested were silver and mercury. Every attempt to bring about a reaction between these metals and watery solutions of the chloride failed. It was then found, as reported in the last paper, that the chloride dissolved in nitrobenzene reacts with silver, and that by long shaking the reaction can be brought to completion according to Equation *a* on page 2102. Finally it was found that warm, watery solutions of diphenylacridyl chloride are rapidly decolorized by zinc dust and that the product formed is not colorless diphenylacridane as might be expected but is a brownish red unsaturated compound, diphenylacridyl. Granulated zinc reacts slightly but the surface becomes rapidly coated over with a thin copper-like film of the free radical and further progress of the reaction ceases. Zinc dust seems to be an ideal reagent because of its very large surface. Even this large surface becomes quickly coated over by the free radical which is completely insoluble in water, and the

---

[1] This Journal, 34, 1699 (1912).

reaction stops unless a great excess of zinc dust (thirty to forty times the theoretical amount) has been used. If a fairly concentrated solution of the chloride is used, its reaction with zinc dust will go rapidly to completion only in hot water. In cold water the reaction starts but the zinc chloride formed unites with still unchanged acridyl chloride to form a rather insoluble double salt and this decreases the rate of the reaction. When the sulfate is used in place of the chloride no double salt is formed and so the reaction is very rapid.

Qualitatively, the reaction can be carried out in a test tube in the most simple manner. In fact, as a lecture room experiment to demonstrate the existence of free radicals and their properties the preparation of diphenylacridyl leaves nothing to be desired in the way of simplicity and certainty. About 1 g. of diphenylacridol is suspended in 25 cc. of water and approximately twice the amount of sulfuric acid necessary to make the normal sulfate is added. The suspension of the acridol is warmed on the steam bath with stirring till the solid has largely dissolved. To the filtered, clear yellow solution sodium hydroxide solution is cautiously added, drop by drop, till a small permanent precipitate of acridol is formed. To this normal sulfate solution 10 g. of zinc dust are added and the mixture is shaken vigorously. The reaction is complete in a fraction of a minute. The dark red slime of zinc dust and free radical settles quickly and the perfectly colorless watery layer can be poured off. The free radical does not oxidize rapidly while in the solid state and wet with water so no special precautions are necessary up to this point to prevent oxidation. The test tube containing the slime is now filled completely with benzene, closed tightly with the thumb and inverted several times. The dark red benzene solution of the free radical is then poured slowly out into a beaker. The solution decolorizes immediately to a pale yellow or brown. After fifteen or twenty minutes' standing in the open the decolorized solution becomes turbid from the separation of peroxide. Thorough decolorization of the benzene solution will take place only if pure diphenylacridol was used in the experiment.

To isolate the solid crystalline diphenylacridyl considerable care is necessary. The apparatus which has given best results in isolating the compound is the one which has been used in this laboratory for the preparation of solid triphenylmethyl. This has been illustrated and described in detail in *Berichte der deutschen chemischen Gesellschaft*, **37**, 2034. Two similar pieces of this apparatus as described there are necessary. A watery solution of the sulfate, 4 to 5 g. prepared as already described above, is poured into one apparatus. The air is displaced by carbon dioxide, and zinc dust, 15 to 20 g. slimed up with water, is added to the acridyl sulfate solution. The reaction is quickly completed by shaking. The colorless watery layer is forced out of the apparatus by means of carbon dioxide.

Warm benzene is poured in and the free radical dissolved. The colored benzene solution is decanted from the wet zinc slime over into the second apparatus, passing at the same time through a filter cartridge filled with calcium chloride but without exposing the solution to the air. The benzene solution is then concentrated under reduced pressure till crystallization begins. A volume of petroleum ether, about equal to the benzene solution remaining, is added, the apparatus is filled with carbon dioxide and put in a cool place. Crystallization is complete in relatively short time. The mother liquor is decanted off from the crystals and they are washed with low boiling petroleum ether and dried under reduced pressure. About 2 g. of the crystalline product can thus be obtained from 4 g. of the acridol.

The melting point of diphenylacridyl is *unsharp*, about 185–190°, softening below that temperature. For combustions and molecular weight determinations the diphenylacridyl was dried in a partial vacuum at 80–90° in a slow stream of carbon dioxide. It was necessary to mix the substance with a large quantity of copper oxide in the combustion tube in order to get good results as otherwise it was almost impossible to avoid too rapid decomposition.

Calc. for $C_{25}H_{18}N$: C, 90.32; H, 5.46; found: C, 90.17; H, 5.65.

Molecular weight determinations were made by the boiling point method in both benzene and chloroform solutions.

	s. grams.	S. grams.	*d*.	Mol. wt.
Benzene I	0.271	7.45	0.28°	347
II	0.201	7.45	0.19°	375
Chloroform I	0.277	22.08	0.13°	348
II	0.494	22.08	0.23°	350

Calculated for $C_{25}H_{18}N$ = 332.

These determinations show conclusively that under the conditions of the experiments above diphenylacridyl is, largely at least, in the monomolecular state. The results are all slightly higher than the calculated value (332), so there may be some indication of slight association, but boiling point determinations are not accurate enough to warrant any quantitative statement as to the amount of this association.

Diphenylacridyl dissolved in benzene unites instantly with chlorine to form yellow diphenylacridyl chloride. It also dissolves slowly in hydrochloric acid to form the chloride.

Preparation of Diphenylacridyl by Electrolysis of its Salts.—The free radical can be prepared readily by electrolysis. In this method of preparation it is best to use a solution of the neutral sulfate in the absence of all other salts. Finely powdered diphenylacridol is warmed and stirred several hours with less than the necessary amount of sulfuric acid to dissolve it all. The excess of diphenylacridol is filtered off. The sulfate solution is electrolyzed in a wide test tube with a platinum wire sealed through the bottom. Mercury, to serve as cathode, is added till the platinum wire is covered. The anode is a piece of platinum foil which is suspended in a tube of about 1 cm. diameter. To prevent free mixing of the anode and cathode liquid, the bottom of the anode tube is covered with a double layer of filter paper. The anode tube is set into the large test tube so that the filter paper comes above the mercury. Solid diphenylacridol is added to the liquid in the anode tube for the purpose of combining with acid which is produced there during the electrolysis. The test tube can readily be kept filled with carbon dioxide. 8–10 volts is sufficient for electrolysis. On closing the circuit the ammeter will jump to perhaps half an ampere, and then immediately fall back to practically zero. At the same time a copper-like film of diphenylacridyl appears over the surface of the mercury. By agitating the surface of the mercury the diphenylacridyl breaks away from the mercury in thin scales that float upward in the liquid. The current passing through the solution varies according to the extent of the mercury surface which is free from diphenylacridyl at any time. On account of the high molecular weight of the free radical, its quantity increases rapidly even though the average current is small. As thus prepared the product appears to be beautifully crystalline, but its appearance is deceptive. It is a mass of fine, irregular scales not unlike shellac. By means of suitable apparatus the diphenylacridyl can be separated from the watery sulfate solution and recrystallized from benzene and petroleum ether in the absence of air. This method of preparation is not so satisfactory as the one in which zinc dust is used.

Both the zinc dust method and the electrolytic method of preparation of diphenylacridyl serve to emphasize the metal-like character of the free radical. The salts of diphenylacridyl in watery solution are highly ionized like the salts of sodium or potassium. The precipitation of the free radical from such a solution by means of zinc dust or electrolysis is exactly like the precipitation of copper from its salts by the same methods. In thin films the free radical appears lustrous very like a metal. Like the metals, it dissolves in acids to form salts which are water-soluble. The property of electrical conductivity so characteristic of metals is, however, apparently not possessed by diphenylacridyl in the solid state.

Many attempts have been made in the past to isolate metal-like free radicals. The nearest approach to success in this direction has come in the cases of ammonium, methylammonium and tetramethylammonium amalgams.[1] A comparison of the properties of these amalgams with those of diphenylacridyl shows no such resemblances as exist between the latter compound and the triarylmethyls, so there can be no hesitation in classifying diphenylacridyl as other than an ammonium radical. The fact, however, that such a radical as diphenylacridyl with so many metallic

---

[1] McCoy and Moore, This Journal, 33, 277 (1911).

properties has been prepared, gives reason to believe that free ammonium radicals may yet be isolated and that some of them may be found to be relatively stable compounds.

Diphenylacridylperoxide.—This peroxide is obtained in good yield by exposing a benzene solution of diphenylacridyl to the air and then allowing nearly all of the benzene to evaporate at room temperature. Ether is added to the small residue of benzene, the peroxide is filtered out and washed with more ether. To further purify the still pink peroxide it is recrystallized from carbon disulfide. This is best done by extracting the fine powder in a Landsiedl extractor. It is exceedingly difficult to recrystallize the peroxide in the ordinary manner, *i. e.*, by heating a suspension of the solid and then filtering off the undissolved portion, because so very little goes into solution. In the extraction apparatus, however, as much as 1 g. can be dissolved in 100 cc. of boiling carbon disulfide if the extraction is continued two or three hours. On cooling the hot solution from the extractor the peroxide crystallizes out in fine prisms. This crystalline peroxide is pale yellow. It begins to darken at about 190° and melts between 204° and 207° according to the rate of heating. With a moderate rate of heating it will generally melt at 204°.

Calc. for $C_{50}H_{36}N_2O_2$: C, 86.17; H, 5.22; found: 86.16, 85.60 and 5.16, 5.11.

On treating the peroxide with mineral acids it goes slowly into solution to form the corresponding acridyl salts.

Diphenylacridane.—It might be expected when a watery solution of diphenylacridyl chloride is treated with zinc dust that in addition to the free radical some diphenylacridane would be formed.

$$C_{25}H_{18}NCl + Zn + HCl = C_{25}H_{18}NH + ZnCl_2,$$

the acid necessary for the reaction coming from slight hydrolysis of the chloride;

$$C_{25}H_{18}NCl + H_2O = C_{25}H_{18}NOH + HCl.$$

The formation of diphenylacridane is, however, only a minor reaction. The major part of the acridyl salt simply gives up its acid radical and forms the free acridyl radical. Out of the reaction between 4 g. of the acridyl sulfate and zinc dust, only about 0.1 g. of the acridane has been isolated. The diphenylacridane is very soluble in benzene so it will be found in the benzene-petroleum ether mother liquors from which the free radical diphenylacridyl has been crystallized. These mother liquors are allowed to evaporate to dryness and the dark residue extracted with hot ligroin, boiling between 80° and 90°. The residue remaining after evaporating the ligroin is treated with a small amount of alcohol acidulated with hydrochloric acid to remove acridol and peroxide. The insoluble portion, after cooling the alcohol, is diphenylacridane. This is recrystallized from ligroin, from which it separates as almost perfect cubes with a high refractive index, melting point 175°. On standing in the air, the crystals assume a slight yellow tinge.

Diphenylacridane can also be prepared by adding zinc dust to a boiling solution of diphenylacridol in acetic acid. The free radical, diphenylacridyl, is formed as an intermediate product, as is shown by the instantaneous production of a deep red color on adding the zinc dust. If the boiling is continued for some time with the occasional addition of zinc dust to the acid solution, the red color will be gradually discharged to a pale yellow. On pouring the acetic acid solution into water acidulated with hydrochloric acid, the diphenylacridane precipitates as colorless flakes. These, on drying and recrystallizing from ligroin, show the same properties as given above.

Calc. for $C_{18}H_{19}N$: C, 90.04; H, 5.75; found: 89.75 and 6.00.
Molecular weight: Calculated, 333; found: 331 in boiling chloroform.

Analogues of Diphenylacridyl.—The following analogues of diphenylacridol have been prepared and from them, salts, free radicals and peroxides, have been obtained: *p*-chlorophenyl-*N*-phenylacridol, *p*-methoxyphenyl-*N*-phenylacridol, 2,4-dimethoxyphenyl-*N*-phenylacridol, phenyl-*N*-methyl acridol, phenyl-*N*-ethylacridol. So far as studied, the salts of all of these acridols behave essentially as do the salts of diphenylacridol. In each case the watery solutions of the salts give a free, dark brownish red radical with zinc dust. All of these free radicals are soluble in benzene and in solution are readily oxidized to form peroxides. The salts having aliphatic radicals attached to the nitrogen atom tend to yield more of the acridane and less of the free radical than the aryl nitrogen acridyl salts. The free radicals and the peroxides obtained above will be described in the next paper.

ANN ARBOR, MICH.

THE PREPARATION OF RAFFINOSE.

BY C. S. HUDSON AND T. S. HARDING.[1]

Received August 4, 1914.

In the course of an investigation on the hydrolysis of raffinose by enzymes, it became necessary to prepare several kilograms of the sugar. A method which was devised for the purpose has proved materially preferable to the procedures recorded in the literature and its description may be useful to those requiring a supply of raffinose.

Selection of the Best Natural Source for Raffinose.

It is recorded that crystalline raffinose has been isolated from Australian

---

[1] Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, Department of Agriculture.