[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

# Effect of Substituents on the Structure of the Dipyrrylmethenes. Some Relationships between the Dipyrryl- and the Triphenylmethane Dyes[1,2]

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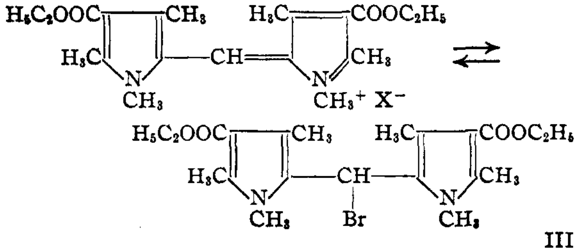
Although a large number of dipyrrylmethene salts having a wide variety of substituents on the pyrrole rings have been prepared for the purpose of synthesizing naturally occurring pyrrole pigments,[3] the correlation of the effect of substitution and a study of the significance of these compounds to the general theory of organic dye salts has not been undertaken. General observations on the behavior of this large body of pigments has led to the conclusion that the dipyrrylmethene salts are best represented as coplanar resonating ionic structures (I), Chart I.

CHART I



III

I $X = Br^-$
II $X = ClO_4$

Thus, from the standpoint of structure, color and general dye characteristics these salts are closely related to the triphenylmethane dyes. However, there is a marked difference between these two classes of dyes in their behavior toward hydroxyl ions. Treatment of the dipyrrylmethene salts with alkali yields, in a great number of cases, stable highly colored free bases (VI, Chart II), whereas similar treatment of the triphenylmethane dyes yields colorless covalent carbinol bases instead of the corresponding Homolka bases. Such anhydro bases are not readily formed in the triphenylmethane series and go over into the colorless carbinols in the presence of hydroxyl ion. The dipyrryl carbinols, on the other hand, are practically unknown and have been suggested by several authors[3,4,5,6] as unstable intermediates in the preparation of methene salts by certain pyrrole condensations. In one instance,[7] a dipyrryl carbinol ether was isolated by treatment of a methene salt with alcoholic potassium hydroxide.

Recently, the authors prepared a stable carbinol from a di-N-methyl methene perchlorate II.[8] This system is similar to dimethylamino substituted triphenylmethane dyes in that it cannot exist in the form of a free base. Since the carbinol derivative was so unusual in the pyrrole series, a careful study of the properties of the parent methene salts was made. Evidence was found suggesting the existence of a covalent form of the di-N-methyl dipyrrylmethene bromide III. Thus, the unusual features of this methene system which gave rise to stability of the covalent carbinol also exerted their influence on the structure of the methene halide. Since the electronic interpretation of the effect of alkyl substitution on the nitrogens required that the stability of the ionic form of this system be enhanced, an explanation of the exactly opposite effect observed was sought elsewhere and found in a scale model of the coplanar resonating ion.

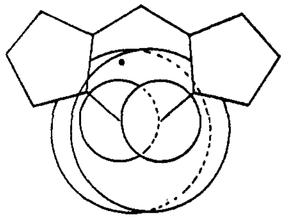


Fig. 1.

The strong interference of the methyl groups requires that the normal bond distances and angles, van der Waals radii and the normal coplanar configuration of the pyrrole rings be distorted in the resonating ion. These modifications must subtract from the usual stabilization due to resonance, thereby leading to a decrease in the margin of energy between the un-ionized covalent methyl bromide and the ionic form. Unfortunately, the covalent dipyrrylmethyl bromide could not actually be isolated in this case and therefore it seemed desirable to investigate the general effects of substitution on the structure of these pyrrole dyes and to attempt the preparation of a colorless covalent dipyrrylmethyl halide. The success of such an undertaking would be expected to lead to an explanation of the relationship of these compounds to the triphenylmethane dyes.

This paper reports the preparation of two covalent dipyrryl methyl bromides and presents a series of other derivatives which demonstrate the effect of pyrrole substituents on the structure of these methene dyes. All of the dipyrrylmethene salts and the dipyrrylmethyl halides were prepared by bromination of the corresponding di-

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[1] Studies in the Pyrrole Series. XI; Paper X, Corwin and Brunings, THIS JOURNAL, **64**, 2106 (1942).

[2] A portion of this paper was presented at the Buffalo meeting of the American Chemical Society, September, 1942.

[3] Fischer and Orth, "Chemie des Pyrrols," Bd. II, p. 3., Akad. Verlag, Leipzig, 1937.

[4] Fischer and Fries, *Z. physiol. Chem.*, **231**, 231 (1935).

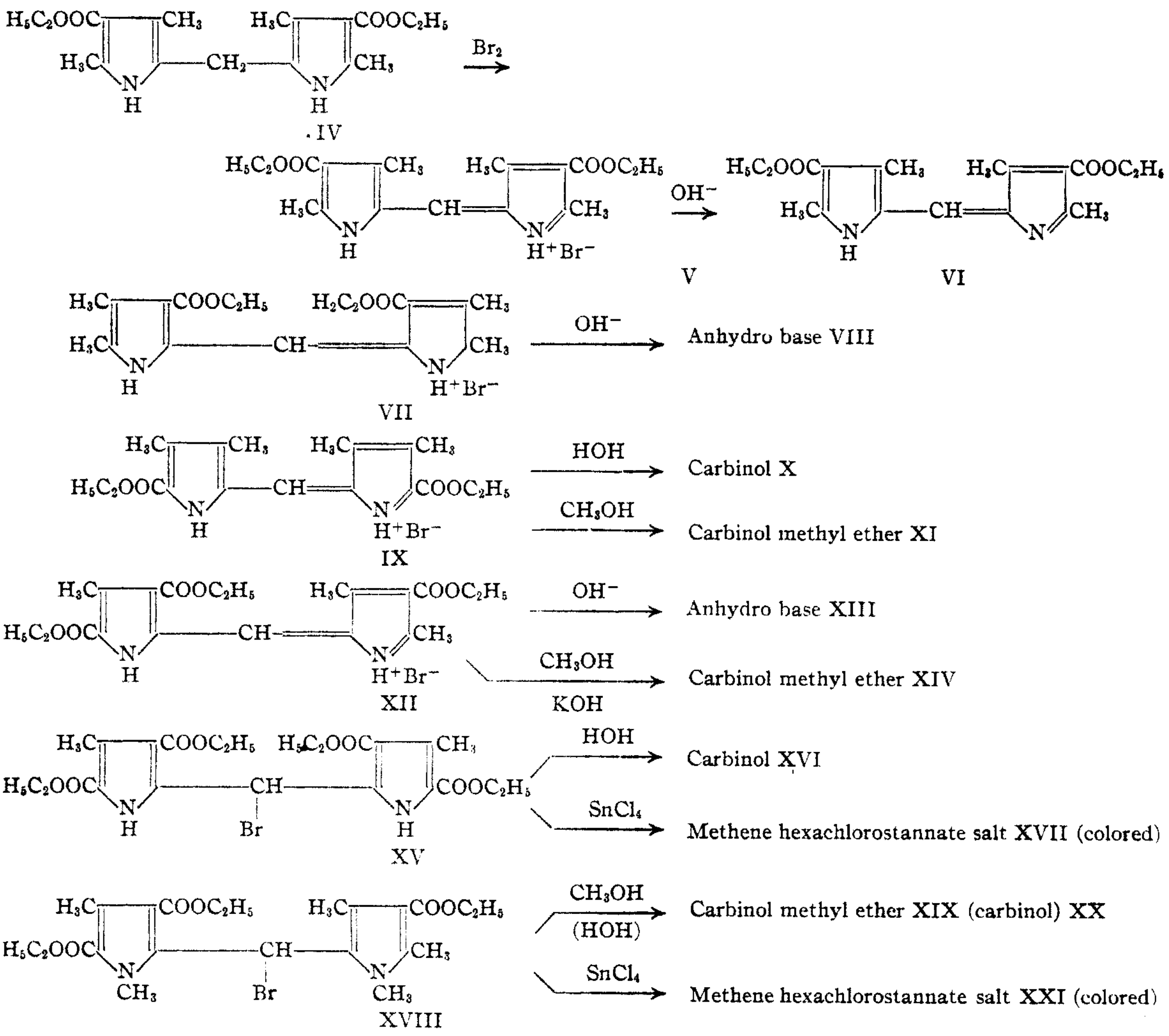
[5] Fischer and Scheyer, *Ann.*, **434**, 237 (1923).

[6] Corwin and Andrews, THIS JOURNAL, **58**, 1086 (1936).

[7] Corwin and Andrews, *ibid.*, **59**, 1975 (1937).

[8] Brunings and Corwin, *ibid.*, **64**, 593 (1942).

CHART II



pyrrylmethane leuco bases in carbon tetrachloride solution. Each methene was studied with respect to its behavior toward hydroxyl ion and alcoholic potassium hydroxide. The results are described by the structural formulas and equations in Chart II.

A comparison of the behavior of the methene bromides V, VII, and IX demonstrates the importance of the position of groups on the tendency toward stable dipyrryl carbinol formation. The methenes (V and VII) having a single carbethoxy group in either of the beta (3 or 4) positions of each pyrrole ring yield stable methene free bases VI and VIII in the manner of a great variety of these compounds. The $\alpha,\alpha'$-dicarbethoxy methene IX, on the other hand, gives a quite stable colorless dipyrryl carbinol X by merely suspending the highly colored methene crystals in neutral water, while the dipyrryl carbinol methyl ether XI is obtained by dissolving the methene in methanol. Thus it may be argued that carbethoxy groups in the alpha positions increase the tendency toward covalency in these systems. The special effect of the alpha carbethoxy groups was first noted by H. Fischer[9,10,11] who stated that $\alpha,\alpha'$-dicarbethoxy methanes do not yield methenes by oxidation (ferric chloride) but rather tetrapyrrylethanes. Since the $\alpha,\alpha'$-dicarbethoxy methene hydrobromide IX was prepared by oxidation of the corresponding methane with bromine, it represents an exception to this empirical rule. However, it should be pointed out that the conditions (solvent, oxidizing agent, temperature, etc.) of the reaction used in this work are quite different from those employed by Fischer in the oxidation of dipyrrylmethanes.

The effect of the alpha-carbethoxy group would suggest that substitution of carbethoxy groups for methyl groups on the pyrrole rings generally leads to stabilization of the covalent forms of the methenes. This reasoning is substantiated by the

(9) Fischer and Baumgartner, *Ann.*, **493**, 1 (1932).

(10) Fischer and Halbig, *ibid.*, **447**, 125 (1926).

(11) Fischer-Orth, "Chemie des Pyrrols," Bd. II, p. 6, Akad. Verlag. Leipzig, 1937.

previously reported isolation of a stable carbinol ether from the tricarbethoxy dipyrrylmethene XII in which the additional effect of a single carbethoxy group has been introduced. The prime importance of the alpha carbethoxy groups is stressed by the fact that this methene having only one carbethoxy group in the alpha position yields the usual methene free base XIII on treatment with alkali.

By utilizing the strong effect of the carbethoxy groups in both of the alpha positions and the additional effect of substituting carbethoxy groups in the 3 and 3′ positions it was possible to prepare the colorless covalent dipyrrylmethyl bromide XV. The behavior of this compound is analogous to that of the well-known triphenylmethyl bromide and, like the parent compound of the triphenylmethane dyes, it may be converted into the colored ionic form by treatment with anhydrous stannic chloride. Actually the bromine in this compound is more tightly held than in the case of triphenylmethyl bromide and treatment with strong acids leads to only weak coloration.

A further consideration of this series of compounds shows that for any given methene system the structure will depend on the nature of the anion. Thus, methene XII requires the basicity of the methoxyl group in order to stabilize the covalent form, while in the presence of hydroxyl ion the methene reverts to the free base XIII. In the case of methene IX both hydroxyl and methoxyl ion stabilize the covalent form. Finally, the tetracarbethoxy system XV remains in the covalent form even in the presence of the weakly basic bromide ion.

Now, since compound XII, containing three carbethoxy groups, shows its tendency toward covalent structures only in the form of its carbinol ether, it might be argued that the introduction of steric hindrance by methylation of the nitrogens would so decrease the stability of the coplanar ionic form that even the methene bromide would exist in the covalent dipyrryl halide structure. This prediction is fully borne out by the preparation of the colorless di-N-methyl dipyrrylmethyl bromide XVIII. Once again this compound is analogous to triphenylmethyl bromide and is converted to a highly colored form by solution in strong acids or by treatment with anhydrous stannic chloride. The bromine in this derivative is less tightly bound than in the case of the tetracarbethoxydipyrrylmethyl bromide XV and the carbon–bromine bond is hydrolyzed by water so rapidly that great care must be exercised in protecting the compound from the atmosphere in preparing it for analysis.

The present series coupled with the previously reported data on the di-N-methyl dipyrrylmethene system I permits the following conclusions: (1) the structure of the dipyrrylmethenes is profoundly influenced by the substituents on the pyrrole rings; (2) the position of the substituents is critical; (3) substitution of carbethoxy groups increases stability of the colorless covalent form of the methene; conversely alkyl substitution favors the ionic salt structure; (4) alkyl substitution on the pyrrole nitrogens results in steric interference causing a decrease in the stability of the ionic coplanar form and is, therefore, opposite to the effect predicted on the basis of the electrical effect of alkyl groups.

Now, these observations are almost precisely those which have been made in the triphenylmethane series and the effects in both classes of dyes are supported by the same electronic interpretations. Finally, a consideration of the structural differences of the two systems leads to a satisfactory explanation of the relationships discussed in the early part of this paper.

The tendency of the triphenylmethyl halides toward ionic dissociation is explained by the resonance stabilization of the carbonium ion. Essentially the resonance forms of the ion describe the ability of the system to distribute the positive charge on the ortho and para positions of the phenyl groups and the bridge carbon atom. By substituting amino or dimethylamino groups in the para position of the benzene rings we convert the triphenylmethyl halide system into dye salts (pararosaniline, crystal violet, etc.). The positive charge is now shared by the amino nitrogens and the coplanar resonating cation is highly stabilized since the energy of positively charged nitrogen is lower than that of positively charged carbon. On the other hand, if carboxy groups are substituted in the para positions, we should expect the resulting structures to be covalent and therefore colorless. Some para carboxy substituted triphenyl carbinols and triphenylmethyl halides have been prepared and are, in fact, colorless covalent compounds.[12,13,14] The tendency of the carbethoxy groups to enter into resonance with the benzene rings by the withdrawal of electrons opposes the withdrawal of electrons from the triphenylmethyl system required for ionization of the halogen. The substitution of alkyl groups which are electron repelling by inductance would be opposite in effect to the carboxyl substitution and should increase the stabilization of the ionic form although their influence would be small. On the basis of qualitative measurements the tritolylmethyl halides are found to be more dissociated than the parent triphenylmethyl halide.[15,16,17]

Now it is well known that only para substituted triphenylmethenes are chromophoric dye systems. This suggests that the position of substitution in the benzene rings is critical. It was Baeyer and Villiger who first recognized the importance of position of substitution in the triphenylmethyl

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(12) Hamilian, *Ber.*, **19**, 3071 (1886).

(13) Limpricht, *Ann.*, **299**, 295 (1898).

(14) Gomberg, THIS JOURNAL, **26**, 1520 (1904).

(15) Gomberg, *ibid.*, **26**, 1517 (1904).

(16) Mothwurf, *Ber.*, **37**, 3153 (1904).

(17) Norris, *Am. Chem. J.*, **38**, 629 (1907).

system.[18] These investigators prepared a series of ortho, meta and para methoxy derivatives and devised a rough quantitative method for comparing the tendency toward ionization of the carbinols. They observed that the degree of ionization of *p,p′,p″*-trianisylcarbinol in a mixture of concentrated acetic and sulfuric acids was many times greater than that of the parent triphenyl carbinol; the ortho derivative was much less ionized than the para, while meta derivatives were hardly more ionized than triphenyl carbinol. The very weak effect of ortho substitution was not considered surprising by these authors and since that time it has been considered axiomatic that only para substitution gives triphenylmethane dyes.

On the basis of the electronic interpretation of the effect of these groups we should expect meta substitution to be relatively ineffective in influencing the structure of these dyes, but there is no apparent reason why ortho substitution should not be as potent as para in stabilizing the resonating cation. However, if we construct a model of the triphenyl carbonium ion (Fig. 2) similar to the type drawn for the di-N-methyl dipyrrylmethene[8] (Fig. 1), assuming coplanarity of the system and utilizing the accepted bond angles and distances in aromatic molecules, strong overlapping of the van der Waals radii of the ortho hydrogens is observed. This steric hindrance of the ortho hydrogens has been pointed out recently by G. N. Lewis,[19] who suggests that deviation of the phenyl groups from complete coplanarity gives rise to isomerism in the triphenylmethane dyes. He finds evidence of two forms of crystal violet in the shoulder of its absorption maximum in the visible. It is not necessary to assume that this steric interference of the ortho hydrogens makes the concept of the resonance stabilized cation untenable since by bending of the carbon–hydrogen bonds, penetration of the van der Waals radii, and slight deviation from coplanarity the conditions of aromaticity can be approached. But these factors of accommodation can only occur with an expenditure of energy which must be subtracted from the energy of resonance stabilization. Replacement of the ortho hydrogens with still larger groups will decrease the resonance stabilization even more and it is not unreasonable to assume that this steric effect will eventually nullify whatever other influence the ortho substituent might have. The magnitude of the energy necessary to accommodate such sterically hindered structures and for that matter the resonance energy of an unhindered system has not been determined and can only be inferred by comparison of the chemical and physical properties of a series of compounds.

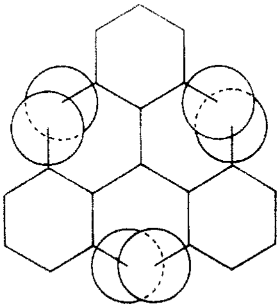
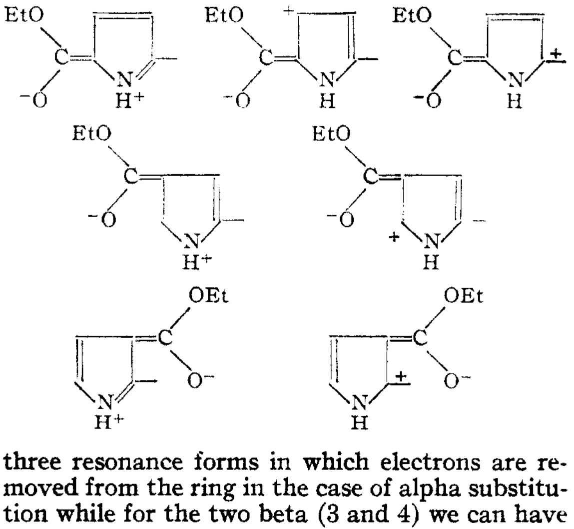


Fig. 2.

The foregoing interpretation of the relationships in the triphenylmethane dyes provides an explanation of the observations on the dipyrrylmethenes reported in this paper. Thus, it is the pyrrole nitrogens with their ability to stabilize the positive charge of the cation by resonance which are responsible for the ionic character and finally the color of the dipyrrylmethene pigments. We may say that a pyrryl group is equivalent to a para aminophenyl group in stabilizing the carbonium ion. This tendency of the pyrrole rings to supply electrons for the ionization of the halogens in the dipyrrylmethyl halides will be opposed by the substitution of carbethoxy groups in the pyrrole rings. That the position of these groups is critical is apparent from an inspection of the resonance forms which can be written for the three types of carbethoxy substituted pyrrole rings in Chart III. It is observed that we can write three resonance forms in which electrons are removed from the ring in the case of alpha substitution while for the two beta (3 and 4) we can have only two. Thus, the alpha carbethoxy group will be most potent in attracting electrons from the dipyrrylmethyl system and, therefore, most effective in stabilizing the covalent colorless form of the methene halides. It may be equally well argued that the carbethoxy group increases the positive character of the methene bridge carbon, thereby strengthening the carbon–halogen bond with respect to ionic cleavage. Consideration of the interaction of the carbethoxy group with

CHART III



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(18) Baeyer and Villiger, *Ber.*, **35**, 3019 (1902).

(19) Lewis, Magel and Lipkin, THIS JOURNAL, **64**, 1774 (1942).

pyrrolenyl forms in the methene system shows that the β-carbethoxy can interact to give a higher energy form (two positive charges on one pyrrole ring) while the α-carbethoxy cannot. Again the difference favors a greater effect of the α-carbethoxy group in stabilizing the covalent form. A more careful analysis of all the possible resonance forms of the whole methene structure including higher energy forms will give a more accurate value of the ratio of effectiveness of the three positions and will, indeed, indicate differences between the two beta (3 and 4) positions. However, such an analysis is unnecessary for the large effects observed in the present study, but may be helpful in explaining fine differences in properties such as absorption spectra.

If we compare models of the N-free dipyrrylmethene ion (Fig. 1) and the triphenyl carbonium ion (Fig. 2), we observe that the interference of the hydrogens ortho to the bridge carbon is somewhat less for the former. This difference, however, is small and would represent only a minor contribution to the comparative effectiveness of dipyrryl groups in stabilizing the carbonium ion. Now in the formation of the free base of the dipyrrylmethene one of the hydrogens on the nitrogens is lost and with it the steric hindrance. Moreover, the distances are now favorable for the formation of an intramolecular six membered chelate ring involving the pyrrole nitrogens (Chart IV). Thus an additional factor must be added to the resonance stabilization of the free base structure. In the case of the corresponding Homolka bases of the triphenylmethane dyes the normal steric repulsion of the ortho hydrogens is not released, nor does the possibility of intramolecular chelation exist. A consideration of the geometry of the resonating ions, therefore, gives us two factors which account for the ready formation of free bases in the pyrrole series and the relative instability of the Homolka bases of the triphenylmethane dyes.

CHART IV

The authors are indebted to the Rockefeller Foundation for a research grant which has made this investigation possible.

## Experimental Section

**Preparation of 3,5,3′,5′-Tetramethyl-4,4′-dicarbethoxydipyrrylmethene Hydrobromide (V).**—A solution of 0.350 g. of 3,5,3′,5′-tetramethyl-4,4′-dicarbethoxydipyrrylmethane (II) in 500 cc. of dry carbon tetrachloride was prepared by refluxing the finely divided methane in the solvent for several hours. After the solution had been brought to room temperature 0.16 g. of bromine in 2 cc. of carbon tetrachloride was run in quickly while the flask was twirled. The solution was allowed to stand in the ice box overnight, after which time 0.390 mg. of fine red needles (92% of the theoretical) was filtered from the solution. The free base (VI) was obtained by shaking a chloroform solution of the hydrobromide salt with calcium hydroxide. The long red needles were recrystallized from benzene-hexane; m. p. (dec.) 189–190°.

**3,3′-Dicarbethoxy-4,5,4′,5′-tetramethyldipyrrylmethene Hydrobromide (VII).**—A solution of 1 g. of the corresponding dipyrrylmethane[20,21] in 100 cc. of dry carbon tetrachloride was placed in a 200-cc. Erlenmeyer flask; 0.51 g. of bromine in 5.1 cc. of carbon tetrachloride was run in quickly while the flask was twirled and the solution was allowed to stand several hours in the ice box; 0.910 g. of deep red crystals was obtained on filtration. Addition of petroleum ether to the mother liquors gave an additional 0.150 g. of the methene salt; total yield, 87%. The free base VIII was prepared by shaking a chloroform solution of the hydrobromide salt with calcium hydroxide.[22,23] Recrystallization from benzene–hexane gave beautiful orange-red crystals; m. p. (dec.) 164–165°.

**3,4,3′,4′-Tetramethyl-5,5′-dicarbethoxydipyrrylmethene Hydrobromide (IX).**—The corresponding dipyrrylmethane[24,25] (5 g.) was dissolved in one liter of dry carbon tetrachloride. After the solution had been brought to room temperature, 2.55 g. of bromine in 25.5 cc. of carbon tetrachloride was added rapidly with stirring. A rich crop of brilliantly colored crystals appeared in a few minutes. After cooling in an ice box 5.9 g. of fine red needles was filtered off; yield, 96%. The dipyrrylmethene salt decomposed at 160–165°. *Anal.* Calcd. for $C_{19}H_{25}N_2O_4Br$: C, 53.65; H, 5.93. Found: C, 53.64; H, 5.94. All attempts to prepare the free base yielded the dipyrrylcarbinol (X).

**3,4,3′,4′-Tetramethyl-5,5′-dicarbethoxydipyrrylcarbinol (X).**—The corresponding dipyrrylmethene salt (1 g.) was suspended in about 50 cc. of water, the mixture shaken thoroughly and allowed to stand overnight. The brilliant red color of the suspended crystals faded slowly until after six hours only a faint pink remained. The easily filtrable precipitate weighed 0.830 g. Recrystallization from benzene yielded a beautiful white compound melting with decomposition at 185–186°. *Anal.* Calcd. for $C_{19}H_{26}N_2O_5$: C, 62.97; H, 7.23. Found: C, 63.25; H, 7.18.

**3,4,3′,4′-Tetramethyl-5,5′-dicarbethoxydipyrrylcarbinol Methyl Ether (XI).**—The corresponding dipyrrylmethene salt (IX) (200 mg.) was dissolved in boiling anhydrous methanol. The red color of the methene disappeared rapidly and on cooling, 150 mg. of pearly crystals precipitated; yield, 85%. The material melts sharply with decomposition at 169–170°. *Anal.* Calcd. for $C_{20}H_{28}N_2O_5$: C, 63.81; H, 7.50. Found: C, 63.93; H, 7.46.

Both the dipyrrylmethyl carbinol (X) and the dipyrrylmethyl methyl ether (XI) described above may be converted back to the corresponding dipyrrylmethene hydrobromide (IX) by dissolving them in dry carbon tetrachloride and saturating the solution with dry gaseous hydrogen bromide. The identity of the methene salt was checked by analysis.

**3,5,4′-Trimethyl-4,3′,5′-tricarbethoxydipyrrylmethene Hydrobromide (XII).**—The corresponding dipyrrylmethane[26,27] (500 mg.) was dissolved in 500 cc. of dry carbon tetrachloride; 0.2 g. of bromine in 5 cc. of carbon tetrachloride was added quickly with stirring at room temperature. After standing several hours in the cold 500 mg. of fine orange red needles was filtered from the solution; yield, 83%. Conversion of the methene salt to the base (XIII) by the method described above gave a compound identical with the methene base prepared by several independent methods; m. p. (dec. ) 125–126°.

**3,5,4′-Trimethyl-4,3′,5′-tricarbethoxydipyrrylcarbinol Methyl Ether (XIV).**—This compound was prepared by the method described by Corwin and Andrews.[28]

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[20] Fischer and Nenitzescu, *Ann.*, **443**, 124 (1925).

[21] Fischer and Walach, *ibid.*, **450**, 127 (1926).

[22] Fischer and Beller, *ibid.*, **444**, 247 (1925).

[23] Fischer and Nussler, *ibid.*, **491**, 167 (1931).

[24] Fischer and Nenitzescu, *ibid.*, **443**, 124 (1925).

[25] Buc, Dissertation, The Johns Hopkins University, 1939

[26] Fischer and Halbig, *Ann.*, **447**, 132 (1926).

[27] Corwin and Ellingson, THIS JOURNAL, **64**, 2098 (1942).

[28] Corwin and Andrews, *ibid.*, **59**, 1978 (1937).

**3,3′,5,5′-Tetracarbethoxy-4,4′-dimethyldipyrrylmethyl Bromide (XV).**—A solution of 10 g. of the corresponding dipyrrylmethane[26,29,30] (thoroughly desiccated) in one liter of dry carbon tetrachloride was prepared in a 1.5 liter filter flask equipped with a one-holed rubber stopper containing a calcium chloride drying tube. The sidearm of the filter flask was tightly sealed with a piece of rubber tubing and a screw clamp; 3.5 g. of bromine in 35 cc. of dry carbon tetrachloride was run in rapidly with stirring and the flask quickly stoppered. The addition of the bromine caused no cloudiness and the color of the solution was simply that of the added bromine. Even after six hours an appreciable amount of bromine remained unreacted. After standing twenty-four hours the stopper was replaced by a rubber stopper containing a capillary with a drying tube attached to the end. The flask was then hooked up to a water pump by means of an intervening drying tube, and the carbon tetrachloride removed at room temperature. The slightly colored crystalline residue was recrystallized from dry benzene–hexane (purified); yield, 10.6 g. or 90%. Repeated recrystallization from benzene–hexane gave 8.0 g. of analytically pure compound; m. p. (dec.) 132–133°. The compound turns pink at 128–130°. *Anal.* Calcd. for $C_{23}H_{29}N_2O_8Br$: C, 51.02; H, 5.40; Br, 14.26. Found: C, 51.09; H, 5.42; Br, 15.45 (± 1%).

In the process of purification it was observed that benzene solutions of the dipyrrylmethyl bromide (XV) became highly colored when heated to the boiling point of benzene; on cooling, this color disappears. The same phenomenon was reported by Gomberg for the tritolylmethyl halides in benzonitrile.[31] It was also observed that cold colorless solutions of the dipyrrylmethyl bromide were capable of imparting a definite orange-red color to filter paper and to textiles in general. The color imparted to wool was the most intense.

When the dipyrrylmethyl bromide was dissolved in concentrated sulfuric acid only a weak coloration occurred. Chloroform solutions on the other hand became intensely colored when anhydrous stannic chloride was added. This color vanished immediately when water was added to the solution. The assumed dipyrrylmethene hexachlorostannate salt (XVII) was not isolated.

**1,3,5,1′,4′-Pentamethyl-4,3′,5′-tricarbethoxydipyrrylmethyl Bromide (XVIII).**—A solution of 3.9 g. of the corresponding dipyrrylmethane[27] (thoroughly desiccated) was prepared in a 500-cc. Erlenmeyer flask. 1.47 g. of bromine in 14.7 cc. of carbon tetrachloride was run in rapidly while the flask was twirled. After the addition the flask was stoppered immediately, and then placed in a desiccator and allowed to stand overnight. After this time a small amount of red oil had collected on the sides of the flask; the solution itself was clear. The following operations were then carried out in a dry air chamber. A nitrogen tank with a glass top and arm holes served as a dry air chamber. Compressed air, conducted through a tall column of calcium chloride, was passed through the chamber for one-half hour before operations were begun and continued until completed. The solution was transferred to a one-liter flask equipped with a one-holed rubber stopper containing a capillary with a drying tube attached to the end. The filter flask was then hooked up to a water pump by means of an intervening drying tube and the carbon tetrachloride pumped off at room temperature. The pink colored crystalline residue, weighing 3.5 g., was placed in an Erlenmeyer flask equipped with a tight fitting rubber stopper. The crystals were then covered with dry benzene–hexane in the ratio of ten to one, the flask well stoppered, and removed from the dry air chamber. After replacing the stopper with an air reflux condenser equipped with a drying tube, the mixture was gently refluxed until solution was complete. The flask was once again stoppered with a drying tube, returned to the dry air chamber and allowed to stand until crystallization was complete. Soft almost colorless crystals were then painfully collected on a Büchner funnel in the dry air chamber. The material melted, turning blood red at 135–136°.

*Anal.* Calcd. for $C_{23}H_{31}N_2O_6Br$: C, 54.01; H, 6.11; Br, 15.63. Found: C, 54.28; H, 6.11; Br, 16.11 (± 1%). It is absolutely necessary to follow the above precautions for the exclusion of water vapor in order to obtain analytical material. By merely suspending the compound in water and filtering over fifty per cent. of the bromine is lost.

The dipyrrylmethyl bromide readily dissolves in concentrated sulfuric and perchloric acid to yield brilliantly colored solutions. Likewise, the same intense color is obtained when a chloroform solution of the bromide is treated with anhydrous stannic chloride. Dilution of the acid solutions and addition of water to the stannic chloride solution discharges the color.

**1,3,5,1′,4′-Pentamethyl-4,3′,5′-tricarbethoxydipyrrylcarbinol Methyl Ether (XIX).**—This derivative was obtained by simply dissolving the corresponding dipyrrylmethyl bromide in hot methanol and allowing the solution to cool. The compound was recrystallized several times from the same solvent; m. p. 93–94°. *Anal.* Calcd. for $C_{24}H_{34}N_2O_7$: C, 62.32; H, 7.41. Found: C, 62.48; H, 7.42.

## Summary

1. The effect of substituents on the structure of the dipyrrylmethenes has been studied by comparing the properties of a variety of these pigments.

2. It has been shown that the ionic character of the dipyrrylmethene halides is strongly dependent on the nature and position of the substituents on the pyrrole rings.

3. Several new dipyrryl carbinols have been prepared.

4. Two colorless dipyrrylmethyl bromides have been synthesized. These compounds, which are analogous in structure and behavior to triphenylmethyl bromide, have not been observed heretofore in the pyrrole series.

5. It has been shown that steric interference of hydrogens or substituents ortho to the bridge carbon atom exerts a strong influence on the structure of both the triphenyl and dipyrrylmethane dyes.

6. The present observations on the dipyrrylmethenes and previously established data on the triphenylmethane series have been correlated on the basis of a common electronic interpretation. A comparison of the structural geometry of the two dye systems completes the relationship.

BALTIMORE, MD. RECEIVED SEPTEMBER 17, 1943

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(29) Corwin, Bailey and Viohl, THIS JOURNAL, **64**, 1270 (1942).

(30) Fischer and Ernst, *Ann.*, **447**, 158 (1926).

(31) Gomberg, *Ber.*, **35**, 2404 (1902).