The same azomethine dye (X) was prepared from 1-phenyl-3-(α-phenylbutyramido)-5-pyrazolone in 53% yield.

The **azomethine dye, XIV**, was prepared from (a) 1-(*p*-nitrophenyl)-3-methyl-4-(*p*-anisylazo)-5-pyrazolone (XIII) (26% yield), as well as from (b) 1-(*p*-nitrophenyl)-3-methyl-5-pyrazolone (64% yield). It was obtained as fine reddish-brown needles with metallic reflection, m. p. 190–192°, after recrystallization from 95% ethanol. Absorption in *n*-butyl acetate: λ_{max} 540 mμ; ϵ_{max} 4.7 × 10^4.

Anal. Calcd. for $C_{21}H_{23}O_3N_5$: C, 64.1; H, 5.8; N, 17.8. Found: (a) C, 63.7; H, 6.1; N, 17.7; (b) C, 64.2; H, 5.6; N, 18.0.

Reaction of *p*-Methoxyphenyldiazonium Chloride (IX) with 2-Amino-5-diethylaminotoluene (V).—Attempts to carry out this reaction in aqueous alkaline solution yielded only tarry products unless a small amount of non-miscible solvent, such as chloroform, was added. The diazotized *p*-anisidine solution was added slowly to a cold alkaline solution of V. The reaction mixture was then subjected to steam distillation, and the chloroform layer from the distillate was separated, dried and fractionally distilled. The high-boiling fraction, on redistillation, gave a 55% yield of anisole, b. p. 153–154°, which was identified by the preparation of *p*-nitroanisole, m. p., alone and mixed with a known sample, 54°.

Acknowledgment.—The authors wish to express their appreciation to Dr. A. Weissberger, for his helpful suggestions and advice throughout the course of this work.

Summary

4-Arylazo derivatives of pyrazolones undergo oxidative condensation with N,N-disubstituted-*p*-phenylenediamine to produce magenta azomethine dyes. These reactions involve replacement of the 4-arylazo group by the *p*-phenylenediamine residue, the azomethine dye, in each case, being identical with that formed from the parent pyrazolone coupler. Several typical coupling reactions were carried out and the products identified. The mechanism of the reaction, and the effect of various types of substituents on its course, are discussed.

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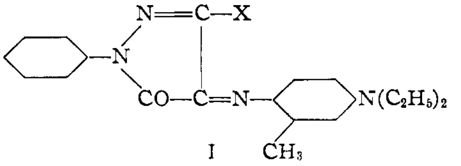
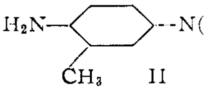
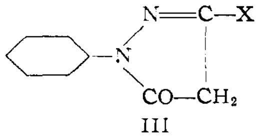
The Reaction between Pyrazolones and their Azomethine Dyes

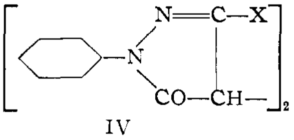
BY PAUL W. VITTUM AND FRED C. DUENNEBIER

The pyrazolone azomethine dyes, I (X may be alkyl or acylamino, for example), are representative of a large group of magenta dyes which have attained considerable importance in certain color photographic processes.[1] The dyes are formed by the process of color development,[2] involving the oxidative coupling of a developing agent, such as 2-amino-5-diethylaminotoluene (II) with the pyrazolone couplers, represented by III.


I


II


III


IV

a, X = $-CH_3$
b, X = $-NHCOC_6H_5$
c, X = $-NHCOC_6H_4Cl$-*p*

In the course of experiments with these and other closely related dyes, it was observed that rapid decolorization of the dyes occurred when their hot solutions were treated with an excess of one of the pyrazolone couplers. Since these reactions demonstrated a surprising degree of instability in the dyes, which are otherwise relatively stable, it was of interest to study the coupler-induced fading further in an attempt to determine its cause.

It was found that the dye, Ia, was faded in a few minutes by treating it with an excess of 1-phenyl-3-methyl-5-pyrazolone (IIIa) in ethyl sebacate solution at 140–145°, or more slowly in *n*-butyl acetate solution at the reflux temperature. An insoluble precipitate was formed which was identified as 4,4′-bis-(1-phenyl-3-methyl-5-pyrazolone) (IVa). Similarly, the reaction between the azomethine dye, Ib, and its parent coupler, 1-phenyl-3-benzamido-5-pyrazolone (IIIb), yielded a product giving the correct analysis for 4,4′-bis-(1-phenyl-3-benzamido-5-pyrazolone) (IVb). When the reactions were run by adding small increments of the dyes to the hot solutions of the couplers, rapid fading took place until one-third mole of the dye per mole of coupler had been added. An additional amount of dye caused the magenta color to persist even on prolonged heating.

In order to determine whether the coupler or the dye supplied the pyrazolone nuclei making up the bis-pyrazolone product, further experiments were done with 1-phenyl-3-(*p*-chlorobenzamido)-5-pyrazolone (IIIc) and the azomethine dye derived from it. When the 3-methyl dye (Ia) was faded by the chlorine-containing coupler, the insoluble

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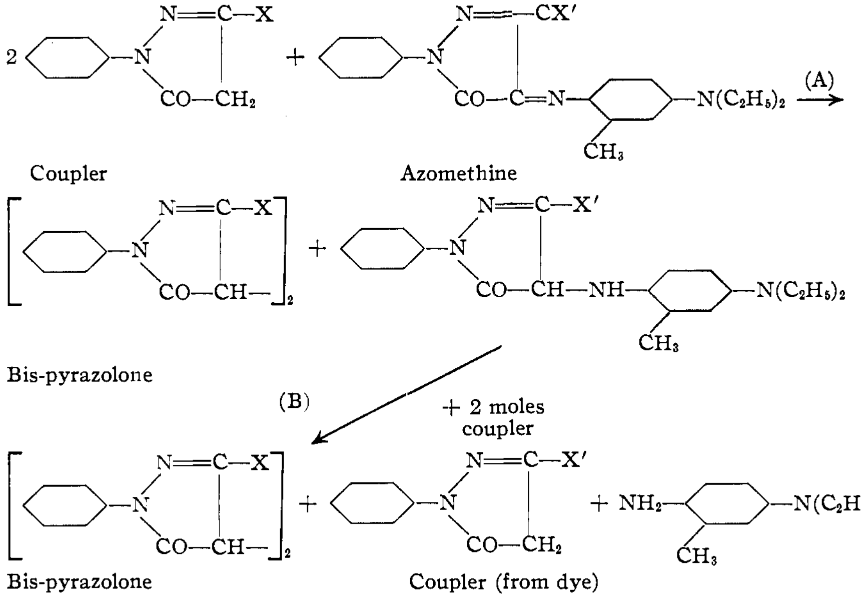
[1] Seymour, U. S. Patent 1,969,479 (1934); Weissberger and Porter, U. S. Patents 2,343,702 (1944) and 2,369,489 (1945).

[2] Fischer, U. S. Patent 1,102,028 (1914); Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1942, p. 393.

product gave a low chlorine analysis and appeared to be a mixture of the two symmetrical bis-compounds (IVa and IVc). Attempts to separate the mixture into pure fractions were unsuccessful, however. More definite results were obtained when the chlorine-containing dye (Ic) was faded with the 3-methyl coupler (IIIa). A mixture of bis-compounds was again produced, but here it could be separated into two components, one of which was pure 4,4′-bis-[1-phenyl-3-(*p*-chlorobenzamido)-5-pyrazolone] (IVc), and the other nearly pure 4,4′-bis-(1-phenyl-3-methyl-5-pyrazolone) (IVa). Furthermore, it was possible to demonstrate the presence of 2-amino-5-diethylaminotoluene (II) in this reaction mixture.

All of these results are explainable on the assumption that the dyes are reduced by the couplers according to the following sequence of reactions.



According to this scheme, the dye is reduced to the leuco form in the first step (A), and a reductive splitting of the leuco dye occurs in the second step (B) to form the pyrazolone and *p*-phenylenediamine derivative. Further support for this mechanism was obtained by preparing one of the leuco dyes (from Ia) and treating it with the corresponding 3-methylpyrazolone (IIIa). The bis-pyrazolone (IVa) and 2-amino-5-diethylaminotoluene (II) were identified as the reaction products. There was some evidence that Step A occurred more rapidly than Step B.

This reaction mechanism accounts for the fact that about three moles of coupler are required to decolorize one mole of dye, since, in the equations above, four molecules of coupler enter into the reactions, and one molecule of coupler is formed from the dye in the process. Furthermore, when the pyrazolone nucleus in the dye is different from that in the coupler used as the reducing agent, a mixture of bis-pyrazolones would be expected, since the coupler formed from the dye in Step B could take part in subsequent reduction in Step A.

Experimental[3]

Materials.—1-Phenyl-3-benzamido-5-pyrazolone (IIIb) (m. p. 220–222°) and 1-phenyl-3-(*p*-chlorobenzamido)-5-pyrazolone (IIIc) (m. p. 234–235°) were prepared by the method described by Weissberger and Porter.[4,5]

The azomethine dyes (I) were prepared by a modification of the method previously described[6] for the preparation of indoanilines. In a typical preparation, 5.22 g. (0.03 mole) of 1-phenyl-3-methyl-5-pyrazolone (IIIa) and 9.6 g. (0.045 mole) of 2-amino-5-diethylaminotoluene hydrochloride (II·HCl) were taken up in a mixture of 1 l. of ethanol, 1 l. of ethyl acetate and 1 l. of 4% ammonium hydroxide. To the above solution was added, with stirring over a period of one-half hour, a solution of 30.6 g. (0.18 mole) of silver nitrate in 500 ml. of water. Stirring was continued for one-half hour after the addition had been completed. The mixture was filtered with the aid of Celite, and the filter cake was extracted with hot ethyl acetate until all the dye was removed. Some additional dye was obtained by partially evaporating the filtrate to remove most of the solvents and then extracting with several portions of ethyl acetate. The ethyl acetate solution of the dye was filtered and evaporated to dryness. The crude dye was recrystallized from 500 ml. of boiling ethanol. The yield was 4.6 g. (44%). A second recrystallization from 300 ml. of ethanol was necessary to obtain analytically pure material (yield 3.7 g.).

The dyes had the following properties: Ia.—Small, dark, stubby needles, with yellow-green iridescence; m. p. 124–125°. Absorption in *n*-butyl acetate: λ_{max} 521 mμ; ϵ_{max} 3.6 × 10^4. *Anal.* Calcd. for $C_{21}H_{24}N_4O$: C, 72.4; H, 7.0; N, 16.1. Found: C, 72.5; H, 6.9; N, 15.9. Ib.—Small, long, purple needles with yellow-green iridescence; m. p. 207–208°. Absorption in *n*-butyl acetate: λ_{max} 526 mμ; ϵ_{max} 4.8 × 10^4. *Anal.* Calcd. for $C_{27}H_{27}N_5O_2$: C, 71.5; H, 6.0; N, 15.5. Found: C, 71.5; H, 6.2; N, 15.8. Ic.—Dark needles with yellow-green iridescence; m. p. 215–217°. Absorption in *n*-butyl acetate: λ_{max} 528 mμ; ϵ_{max} 4.9 × 10^4. *Anal.* Calcd. for $C_{27}H_{26}ClN_5O_2$: Cl, 7.3; N, 14.4. Found: Cl, 7.2; N, 14.4.

Dye-fading Experiments.—In general, 0.001 mole of the pyrazolone coupler (III) and 0.00033 mole of the azomethine dye (I) were heated in 6–8 ml. of ethyl sebacate at 140–145°. Practically complete fading of the magenta color occurred in ten to thirty minutes, with the formation of a precipitate of the bis-pyrazolone. If less coupler was used, the magenta color persisted on prolonged heating. The final reaction mixture had a brownish-yellow color which, in some cases, was deep enough to mask the point

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(3) Melting points given here are uncorrected.

(4) Weissberger and Porter, THIS JOURNAL, **64**, 2133 (1942).

(5) We are indebted to Dr. A. Weissberger and co-workers, of these Laboratories, for supplying samples of these 1-phenyl-3-acylamino-5-pyrazolones for our experiments.

(6) Vittum and Brown, THIS JOURNAL, **68**, 2235 (1946).

at which the magenta dye was completely faded. The bis-compounds were filtered off and washed with hot *n*-butyl acetate. The yields of bis-pyrazolone ranged from 60 to 70%. The results of the individual experiments are listed below under headings showing the coupler and the dye structures involved:

Ia + IIIa.—White crystals, m. p. 290° with slight decomposition, gave "pyrazole blue" when oxidized with nitrous acid,[7] a reaction characteristic of 4,4′-bis-(1-phenyl-3-methyl-5-pyrazolone).

Anal. Calcd. for $C_{20}H_{18}N_4O_2$: C, 69.3; H, 5.2; N, 16.2. Found: C, 69.3; H, 5.2; N, 16.0.

The product was identical in all respects with a sample prepared by oxidizing 1-phenyl-3-methyl-5-pyrazolone with phenylhydrazine at the boiling point, as described by Knorr.[7]

Ib + IIIb.—The product, 4,4′-bis-(1-phenyl-3-benzamido-5-pyrazolone) (IVb), was obtained as yellow crystals. Recrystallized from nitrobenzene, it melted with decomposition at about 290°. Oxidation with nitrous acid gave a blue-green compound.

Anal. Calcd. for $C_{32}H_{24}N_6O_4$: C, 69.1; H, 4.3; N, 15.1. Found: C, 68.7; H, 4.6; N, 15.4.

An attempt was made to prepare this product also by oxidizing the coupler with phenylhydrazine by the Knorr procedure.[7] A mixture of two compounds, differing in their solubility in hot nitrobenzene, was obtained. From its behavior, when oxidized with nitrous acid, the more soluble fraction appeared to be chiefly 4,4′-bis-(1-phenyl-3-benzamido-5-pyrazolone), but it could not be brought to analytical purity. The less soluble component of the mixture was soluble in dilute alkali and in pyridine. It gave an analysis corresponding to the empirical formula $C_{16}H_{13}N_4O_2$, but was not further identified.

Ic + IIIa.—The resulting mixture of bis-pyrazolones was extracted with three portions of 5% aqueous sodium hydroxide. The insoluble residue was washed twice with boiling pyridine, then with alcohol, giving red crystals, m. p. > 300°, giving an analysis correct for the structure: 4,4′-bis-[1-phenyl-3-(*p*-chlorobenzamido)-5-pyrazolone], (IVc).

Anal. Calcd. for $C_{32}H_{22}Cl_2N_6O_4$: C, 61.4; H, 3.5; Cl, 11.3; N, 13.5. Found: C, 61.3; H, 3.4; Cl, 10.9; N, 13.2.

The alkaline extract from this mixture was decolorized with Darco and acidified, giving a white crystalline precipitate. This product gave a strong "pyrazole blue" test with nitrous acid. Analysis showed it to be chiefly 4,4′-bis-(1-phenyl-3-methyl-5-pyrazolone) (IVa) contaminated with a small amount of the bis-chlorobenzamido compound or of the unsymmetrical bis-compound.

Anal. Calcd. for 14% (IVc) + 86% (IVa): C, 68.4; H, 4.99. Found: C, 68.2; H, 5.0.

Reduction of the Leuco Derivative of the Dye, Ia.—The leuco dye was most conveniently prepared by reducing 0.001 mole of dye in 25 ml. of absolute ethanol at room temperature with hydrogen at atmospheric pressure using Raney nickel as the catalyst. The colorless solution was filtered in a hydrogen atmosphere and treated with dry hydrogen chloride. The alcoholic solution was then evaporated to a small volume *in vacuo* and ether was added to precipitate the leuco dye hydrochloride, white crystals melting at about 160° (dec.). Analysis indicated about 95% purity.

For the reaction of leuco dye and coupler, 0.002 mole of the dye (Ia) in 20 ml. of *n*-butyl acetate was reduced to the leuco form, according to the above procedure. The colorless solution was filtered under hydrogen into a flask containing 0.002 mole of 1-phenyl-3-methyl-5-pyrazolone (IIIa). The solution, which colored slightly during this manipulation, was then refluxed in a hydrogen atmosphere. 4,4′-Bis-(1-phenyl-3-methyl-5-pyrazolone) (IVa) began to precipitate in a short time, but the reaction was not complete in two hours, as shown by the formation of a magenta color in the solution on exposure to air (oxidation of the leuco compound to dye). The incomplete reaction of the leuco compound under these conditions indicated that the reaction of coupler with dye (Step A) to form leuco dye is a faster reaction than that of the leuco dye with coupler (Step B). Additional evidence on this point derives from the fact that in some of the reactions where dye and coupler reacted, some magenta color developed during the isolation of the bis-compounds, indicating the presence of leuco dye in the reaction mixture.

Formation of 2-Amino-5-diethylaminotoluene (II) in the Fading Reactions.—The dye, Ia (0.003 mole), was decolorized by reaction with 1-phenyl-3-methyl-5-pyrazolone by refluxing for two hours in *n*-butyl acetate solution. The filtrate from the bis-pyrazolone was treated with 2 ml. of pyridine and 0.8 ml. of benzoyl chloride. After standing for one-half hour, the solution was washed with water and the butyl acetate was evaporated. The residue was purified by dissolving in alcohol, decolorizing the solution with Norite, filtering, and precipitating by adding water. The product, recrystallized twice from 50% ethanol, melted at 143–145°. A mixed melting point with a sample of 2-benzamido-5-diethylaminotoluene (m. p. 143–145°), made from pure 2-amino-5-diethylaminotoluene, showed no depression. 2-Amino-5-diethylaminotoluene was similarly identified among the products of reaction of the leuco dye with 1-phenyl-3-methyl-5-pyrazolone.

Summary

1-Phenyl-3-alkyl or acylamido-5-pyrazolones have been found to react with the azomethine dyes derived from them, the reactions resulting in rapid decolorizing of the dyes with the formation of 4,4′-bis-pyrazolone derivatives. The products from several of these reactions have been isolated and identified, and evidence is presented relative to the reaction mechanism.

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[7] Knorr, *Ann.*, **238**, 171 (1887).