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The Formation of Azomethine Dyes from 4-Anisylidene- and 4,4'-Anisylidene-bis-pyrazolones

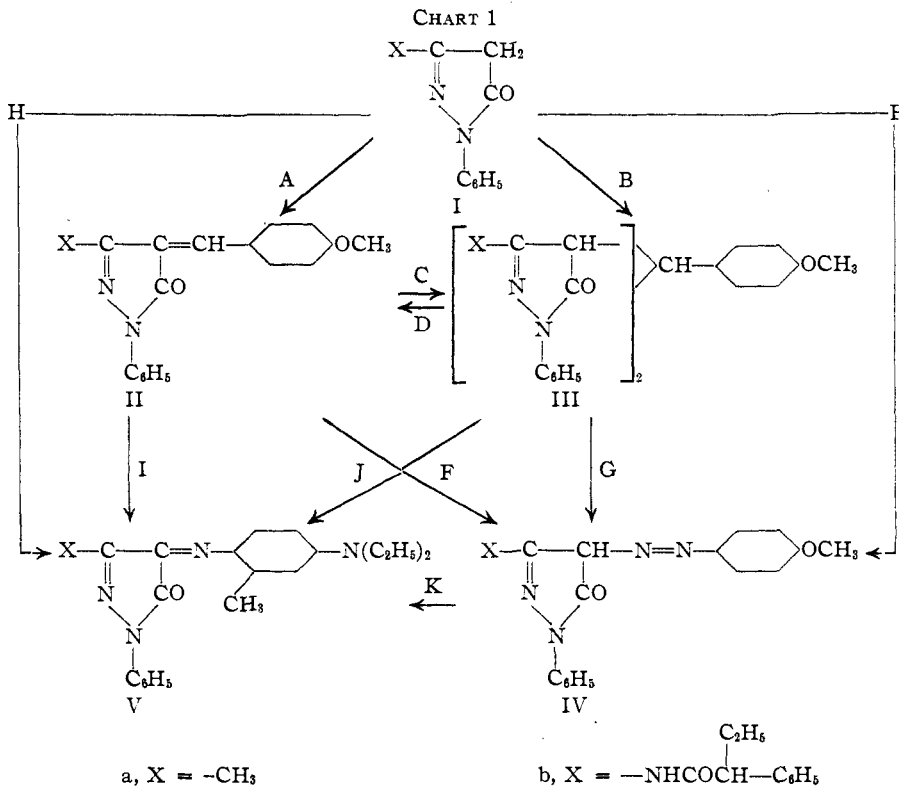
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Recent work in these Laboratories has shown¹ that certain 1-phenyl-4-aryloxy-5-pyrazolones undergo oxidative condensation with N,N-disubstituted *p*-phenylenediamines to produce azomethine dyes, the reaction involving a scission of the pyrazolone-azo linkage and replacement of the aryloxy group by the *p*-phenylenediamine residue. Earlier, it was reported that the aldehyde condensation products of the pyrazolones, both the 4-aryloxy derivatives² and the 4,4'-aryloxybis-pyrazolones,³ give rise to magenta dyes in the photographic process of color development⁴ using N,N-dialkyl-*p*-phenylenediamine developers. Our interest in the pyrazolone-azomethine dyes and their reactions⁵ has prompted us to investigate the coupling reactions of these pyrazolone-aldehyde condensation products, primarily to establish the structures of the magenta dyes formed. Two considerations made it appear probable that the magenta dyes were azomethines formed by elimination of the aldehyde residue in the coupling reaction: (1) the aldehyde residue might be expected to be more easily replaceable in the coupling reaction than an aryloxy group which can be replaced with comparative ease in some cases,¹ and (2) some of these pyrazolone-aldehyde condensation products have long been known⁶ to undergo elimination-coupling with diazonium compounds.

The ease with which the 4-aryloxy-pyrazolones undergo elimination-coupling with oxidized *p*-

phenylenediamines has been found¹ to vary widely with the nature of the substituents in the pyrazolone nucleus.⁷ Accordingly, for the present study, two pyrazolones were selected: 1-phenyl-3-methyl-5-pyrazolone (Ia), the 4-azo derivatives of which couple sluggishly, and 1-phenyl-3-(α -phenylbutyramido)-5-pyrazolone (Ib), the azo derivatives of which undergo elimination-coupling considerably more easily. Anisaldehyde was used as the aldehyde component in all cases. The reactions investigated are shown in Chart 1.

The pyrazolones (Ia and b) condense with anisaldehyde to give either the 4-anisylidene (II) or the 4,4'-anisylidene-bis (III) derivatives



in good yields, depending upon the reaction conditions used. When equimolar quantities of the reactants were heated together without solvent, as described by Tambor,⁸ the former products were obtained (Reaction A). Reaction B, leading to the bis derivatives, occurred when two moles of the pyrazolone and one mole of anisaldehyde

(1) Vitnum, Sawdey, Herdle and Scholl, THIS JOURNAL, **72**, 1533 (1950).

(2) Kendall and Collins, U. S. Patent 2,213,896 (1940).

(3) Jennings, U. S. Patent 2,294,909 (1942).

(4) Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1942, p. 393.

(5) Vitnum and Duennebier, THIS JOURNAL, **72**, 1536 (1950).

(6) Stolz, *Ber.*, **28**, 631 (1895).

(7) Merckx, *Science et ind. phot.*, [2], **21**, 45, 84 (1950), has studied the azomethine coupling of other series of methylene-azo compounds and found in these, too, a wide range of reactivities.

(8) Tambor, *Ber.*, **33**, 864 (1900).

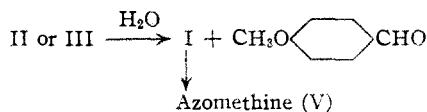
were heated in the presence of acetic acid and sodium acetate. The two condensation products were found to be readily interconvertible (Reactions C and D), II reacting with one mole of the pyrazolone to give III, and III reacting with anisaldehyde to produce II.⁹

Both series of anisylidene-pyrazolones (II and III) were found to react with *p*-methoxyphenyldiazonium chloride to give the 4-(*p*-methoxyphenylazo)-pyrazolones (IV, Reactions F and G), an exception being the reaction starting out with IIa, which was not successfully completed. Attempts were made to carry out the reverse conversion of the azo compound (IV) to the anisylidene derivatives (II and III), but no conditions were found under which this transformation could be effected.

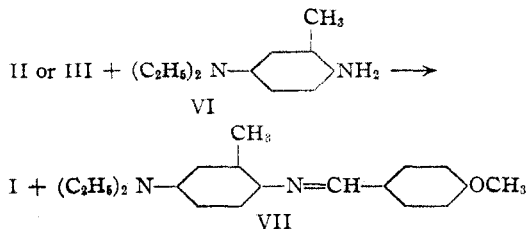
All of the anisylidene derivatives readily underwent oxidative condensation with 2-amino-5-diethylaminotoluene (Reactions I and J) to give magenta dyes. These dyes were identified as the same azomethines (V) formed from the parent pyrazolone couplers (I) under similar conditions (Reaction H), as previously described.⁵ The nature of the 3-substituent in the pyrazolone ring ($-\text{CH}_3$ or $-\text{NH-acyl}$), previously found¹ to affect strongly the coupling reactivity of the arylazopyrazolones (Reaction K), appeared to have little effect upon the ease with which the coupling of the anisylidene-pyrazolones occurred.

In formulating the mechanism by which these azomethines are formed, three possibilities must be considered:

(1) The anisylidene-pyrazolones undergo simple hydrolysis in the alkaline coupling medium, forming the parent pyrazolones which then undergo azomethine coupling.



(2) The anisylidene derivatives first react with unoxidized *p*-phenylenediamine to yield the parent pyrazolone and the *N*-anisylidene-*p*-phenylenediamine (VII).

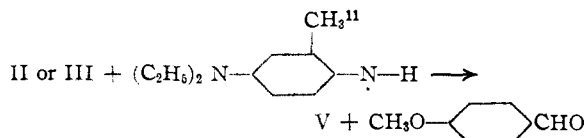


Subsequently, the Schiff base (VII) is oxidized

(9) After this paper was written, an article by Poral-Koshits and Malikova (*Izvest. Akad. Nauk S. S. R., Otdel. Khim. Nauk*, 519-528 (1948); *C. A.*, 44, 1099 (1950)) came to our attention. These authors reported the preparation of several 4-arylidene and 4,4'-arylidenebis derivatives of 1-phenyl-3-methyl-5-pyrazolone, and pointed out the interconvertibility of the two series of compounds. The details of these experiments are not yet available to us.

directly, or is hydrolyzed to VI which is oxidized, forming, in either case, a semiquinone¹⁰ which reacts with the pyrazolone, I, to produce the azomethine.

(3) The coupling reactions take place directly between the oxidized *p*-phenylenediamine and the anisylidene-pyrazolones, yielding the azomethine dyes and anisaldehyde as the products.



This reaction course is parallel to that believed to be involved in the coupling of alkylidenebis-phenols to form indoaniline dyes.¹²

In an attempt to provide a basis for deciding among these possibilities, the anisylidene-pyrazolones (II and III) were subjected to the alkaline conditions employed in the coupling reactions, omitting the *p*-phenylenediamine and the oxidizing agent (Ag^+). In other experiments, only the oxidizing agent was omitted, and air was excluded. In all these cases, the anisylidene-pyrazolones were recovered unchanged, showing that the reaction courses, (1) and (2), play little, if any, part in the azomethine dye formation. We conclude, therefore, that the direct interaction of the pyrazolone derivatives with oxidized *p*-phenylenediamine, as outlined under (3), represents the mechanism of the coupling reactions.

Experimental¹³

Except as noted below, the organic reagents employed were Eastman Kodak Co. chemicals, white label grade. Inorganic chemicals of reagent grade were used.

1-Phenyl-3-(α -phenylbutyramido)-5-pyrazolone (Ib).¹⁴—1-Phenyl-3-amino-5-pyrazolone, prepared by the method of Weissberger and Porter,¹⁵ was acylated with α -phenylbutyryl chloride. It forms white crystals from benzene, m. p. 170-171°.

1-Phenyl-3-methyl-4-anisylidene-5-pyrazolone (IIa).—A mixture of 3.5 g. (0.02 mole) of 1-phenyl-3-methyl-5-pyrazolone and 2.7 g. (0.02 mole) of anisaldehyde was heated in an oil-bath for one hour at 125°. The cooled reaction mixture was taken up in 95% ethanol from which was obtained 4.8 g. (81%) of red crystals melting at 127-128°.¹⁶ Absorption in *n*-butyl acetate: λ_{max} 356 m μ ; ϵ_{max} 3.4×10^4 .

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$: C, 73.9; H, 5.4; N, 9.6. Found: C, 74.1; H, 5.2; N, 9.4.

1-Phenyl-3-(α -phenylbutyramido)-4-anisylidene-5-pyrazolone (IIb).—The same molar quantities and procedure as those for IIa were used. The cooled reaction mixture was taken up in 200 ml. of ether, and the solution was washed twice with 10% sodium bisulfite solution, then with

(10) Michaelis, *Ann. N. Y. Acad. Sci.*, 40, 64 (1941).

(11) This structure pictures the semiquinone as the free radical, but it can equally well be formulated as the cation (see Vittum and Brown, *This Journal*, 68, 2235 (1946)). In either case, a complete formulation would have to show the several structures contributing to the resonance system.

(12) Vittum and Brown, *ibid.*, 71, 2287 (1949).

(13) Melting points given here are uncorrected.

(14) This compound was prepared for us by Dr. Howard Munro and co-workers, of these Laboratories.

(15) Weissberger and Porter, *This Journal*, 64, 2133 (1942).

(16) Tambor⁸ reported 128.5°.

water. The residue, after evaporation of the ether, was recrystallized from methanol, yielding 6.8 g. (76%) of red crystals, m. p. 162–164°; absorption in *n*-butyl acetate: λ_{\max} 369 m μ ; ϵ_{\max} 3.2×10^4 .

Anal. Calcd. for $C_{27}H_{25}N_3O_3$: C, 73.8; H, 5.9; N, 9.6. Found: C, 73.6; H, 5.7; N, 9.7.

4,4'-Anisylidenebis-(1-phenyl-3-methyl-5-pyrazolone) (IIIa).—A mixture of 3.5 g. (0.02 mole) of 1-phenyl-3-methyl-5-pyrazolone, 1.36 g. (0.01 mole) of anisaldehyde, 50 ml. of glacial acetic acid and 5 g. of anhydrous sodium acetate, was heated at the refluxing temperature for one hour. The solution was poured into water and the resulting precipitate was filtered off. Recrystallization from 95% ethanol gave 3.5 g. (76%) of white crystals with a yellowish tinge, m. p. 175–176°, turning orange at 152°. ¹⁷

Anal. Calcd. for $C_{28}H_{26}N_4O_3$: C, 72.1; H, 5.6; N, 12.0. Found: C, 71.7; H, 5.7; N, 12.0.

4,4'-Anisylidenebis-[1-phenyl-3-(α -phenylbutyramido)-5-pyrazolone] (IIIb).—1-Phenyl-3-(α -phenylbutyramido)-5-pyrazolone and anisaldehyde reacted under the same conditions used for IIIa. The crude product was slurried in 200 ml. of 95% ethanol and recrystallized from ligroin, giving a cream-white amorphous powder (71% yield) melting at 142–144°.

Anal. Calcd. for $C_{46}H_{44}N_6O_5$: C, 72.6; H, 5.8; N, 11.1. Found: C, 72.3; H, 5.8; N, 10.8.

Interconversion of 4-Anisylidene- and 4,4'-Anisylidenebis-derivatives.—The 4,4'-anisylidenebis-pyrazolones (IIIa and IIIb) were prepared from the 4-anisylidene compounds (IIa and IIb) by heating them for one hour under reflux with an equimolar quantity of the pyrazolones (Ia and Ib) in the presence of glacial acetic acid and sodium acetate. In each case, the product was worked up as described above. IIIa was obtained in 62% yield, m. p., alone and mixed with specimen prepared directly, 176–177°. IIIb was obtained in 74% yield, m. p., alone and mixed with specimen prepared directly, 142–144°.

The 4-anisylidene derivatives (IIa and IIb) were prepared from the bis-compounds (IIIa and IIIb) by heating with an equimolar quantity of anisaldehyde for one hour at 125°, working up the product, in each case, as described above. The yields of IIa and IIb, obtained in this way, were 73 and 66%, respectively. In each case, the product had the same melting point as obtained with the compound prepared directly from the pyrazolone and anisaldehyde and the melting point showed no depression when the two samples were mixed.

1-Phenyl-3-methyl-4-(*p*-methoxyphenylazo)-5-pyrazolone (IVa).—*p*-Anisidine (0.62 g., 0.005 mole) was dissolved in a mixture of 20 ml. of water and 2 ml. of concd. hydrochloric acid at 5° and diazotized with 0.37 g. (0.005 mole) of sodium nitrite in 5 ml. of water. The diazonium solution was added, with stirring, to a solution of 1.17 g. (0.0025 mole) of 4,4'-anisylidenebis-(1-phenyl-3-methyl-5-pyrazolone) (IIIa) in a mixture of 50 ml. each of 95% ethanol and pyridine. The resulting orange precipitate was collected by filtration and recrystallized from ethanol. The yield was 0.83 g. (54%) of orange crystals melting at 139–141°; absorption in *n*-butyl acetate: λ_{\max} 415 m μ ; ϵ_{\max} 2.75×10^4 .

Anal. Calcd. for $C_{17}H_{16}N_4O_2$: C, 66.2; H, 5.2; N, 18.2. Found: C, 65.7; H, 5.3; N, 18.5.

Attempts to prepare this product from 1-phenyl-3-methyl-4-anisylidene-5-pyrazolone (IIa) by the same procedure were unsuccessful. IIa was recovered unchanged from the reaction mixture.

The 1-Phenyl-3-(α -phenylbutyramido)-4-(*p*-methoxyphenylazo)-5-pyrazolone (IVb).—This compound was prepared by the preceding method in 57% yield from 1-phenyl-3-(α -phenylbutyramido)-4-anisylidene-5-pyrazolone (IIb), and in 73% yield from 4,4'-anisylidenebis-[1-phenyl-3-(α -phenylbutyramido)-5-pyrazolone]

(IIIb). It forms orange needles from 95% ethanol, m. p. 192–194°. ¹⁸

Azomethine Coupling of Anisylidene Derivatives.—Azomethine dye Va was prepared from IIa and IIIa, and dye Vb from IIb and IIIb, by reaction with 2-amino-5-diethylaminotoluene using freshly precipitated silver chloride. ¹⁹ A solution of 9.3 g. (0.055 mole) of silver nitrate in 50 ml. of water was poured slowly into a vigorously stirred solution of 3.7 g. (0.065 mole) of sodium chloride and 0.3 g. of gelatin in 20 ml. of water. To the resulting aqueous dispersion of silver chloride was added a solution of 5 g. of sodium carbonate in 20 ml. of water, followed by a solution of the anisylidene-pyrazolone (0.006 mole for IIa and IIb, 0.003 mole for IIIa and IIIb) in 20 ml. of ethyl acetate. A solution of 1.5 g. (0.007 mole) of 2-amino-5-diethylaminotoluene hydrochloride in 20 ml. of water was then added, with stirring, over a period of fifteen minutes, and stirring was continued for an additional thirty minutes. The ethyl acetate solution of the dye was separated, washed twice with an equal volume of water, and evaporated to dryness. The resulting crude dye was recrystallized from methanol to which a few drops of ammonia had been added. Yields of 65% to 85% were obtained in all cases. The dyes had the following properties:

Va.—Greenish-brown crystals, m. p. 126–127°; absorption in *n*-butyl acetate: λ_{\max} 522 m μ ; ϵ_{\max} 3.6×10^4 (secondary maximum at 448 m μ ; $\epsilon = 1.6 \times 10^4$).

Anal. Calcd. for $C_{21}H_{24}ON_4$: C, 72.4; H, 6.9; N, 16.1. Found (dye from IIa): C, 72.2; H, 7.0; N, 15.8; (dye from IIIa): C, 72.5; H, 7.1; N, 15.8.

Vb.—Lustrous green needles, m. p. 168–169°; absorption in *n*-butyl acetate: λ_{\max} 526 m μ ; ϵ_{\max} 5.2×10^4 (secondary maximum at 440 m μ ; $\epsilon = 1.0 \times 10^4$).

Anal. Calcd. for $C_{30}H_{32}O_2N_6$: C, 72.7; H, 6.7; N, 14.1. Found (dye from IIb): C, 72.7; H, 6.9; N, 14.2; (dye from IIIb): C, 72.5; H, 6.5; N, 14.5.

In order to determine the fate of the anisaldehyde residue in the coupling reaction, an additional experiment was carried out with IIb, using double the quantities stated above. The crude reaction product, after evaporation of the ethyl acetate, was subjected to steam distillation. The distillate, about 2 l. in volume, was extracted with three 200-ml. portions of ethyl acetate, and the ethyl acetate removed from the extract by distillation. The residue was taken up in acetic acid and refluxed for one hour with 1.8 g. (0.012 mole) of *p*-nitrophenylhydrazine. Anisaldehyde *p*-nitrophenylhydrazone was isolated, melting at 160–161°, ²⁰ after recrystallization from glacial acetic acid. Mixing with an authentic specimen, also melting at 160–161°, gave no depression. The dye residue from the steam distillation was worked up as described above, giving a 62% yield of Vb.

Summary

4-Anisylidene- and 4,4'-anisylidenebis-pyrazolones undergo oxidative condensation with *N,N*-disubstituted *p*-phenylenediamines to produce magenta azomethine dyes. These reactions involve a replacement of the anisylidene group by a *p*-phenylenediamine residue. The mechanism of these coupling reactions and other reactions of the anisylidene pyrazolones are discussed.

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(18) Previously reported, ¹ m. p. 194–196°, from glacial acetic acid.

(19) The procedure used ¹ for the coupling of 4-arylazopyrazolones, in which ammoniacal silver nitrate served as the oxidizing agent, was not applicable here because the 4-arylidene- and 4,4'-arylidenebis-pyrazolones are rapidly cleaved by aqueous ammonia.

(20) Shoppee (*J. Chem. Soc.*, 1225 (1931)) reported a value of 161° for this compound.

(17) Passerini and Ragni (*Gazz. chim. ital.*, **66**, 684 (1936)) reported 176°.