Saturated Acetal (IV).—A 14.2-g. portion of the unsaturated alcohol (III) was refluxed until the temperature of the boiling liquid had decreased to a constant value (171°). This required ninety minutes, and the weight remained constant within 1%. The isomer was distilled at atmospheric pressure, the recovery being 12.3 g. (86%) of 1,4-dimethyl-6,8-dioxabicyclo[3.2.1]octane, a water-clear liquid having a camphoraceous odor. It was saturated with respect to Wijs reagent.

Methyl Acetal (V).—Anhydrous calcium chloride (4.5 g., 0.04 mole) was dissolved in 16 g. (0.5 mole) of methanol, and 28.0 g. (0.2 mole) of methacrylaldehyde dimer was added. The solution was kept one day at room temperature. The resulting mixture was washed free of calcium chloride by cold water, and extracted by cold, dilute potassium carbonate solution. The washed liquid was dried by potassium carbonate and fractionally distilled at 100 mm. At 124–126°, 17.2 g. (50% of the theoretical yield) of 7-methoxy-1,4-dimethyl-6,8-dioxabicyclo[3.2.1]octane was collected. This water-clear liquid had a camphoraceous odor. It was saturated, and it was recovered unchanged after having been stirred for thirty minutes with 20% aqueous sodium hydroxide at 70°. Furthermore, it was not polymerized by boron fluoride or the ethyl etherate, nor did it react with sodium at 100°.

Acknowledgment.—Thanks are due Dr. H. N. Stephens, Director of Research, Minnesota Mining & Manufacturing Company, for permission to publish these results. The authors are pleased to express appreciation also to Dr. W. E. Sohl of the Minnesota Mining & Manufacturing Company; to Dr. M. M. Baldwin of Battelle Memorial Institute; and to Dr. R. S. Shutt and Dr. Fred E. Sheibley, both formerly of Battelle Memorial Institute.

Summary

A study was made of several reactions of methacrylaldehyde dimer, 3,4-dihydro-2,5-dimethyl-1,2H-pyran-2-carboxaldehyde, characteristic of it as a vinyl-type ether and an aldehyde without α-hydrogen. The products of the Cannizzaro reaction isomerized readily into bicyclic compounds. The isomer of the alcohol was a saturated acetal, 1,4-dimethyl-6,8-dioxabicyclo-[3.2.1]octane. The isomer of the acid was a lactone which was the 7-oxo derivative of the acetal. Moreover, the 7-methoxy derivative of the acetal was obtained directly from the dimer by a mild reaction with methanol in the presence of calcium chloride.

COLUMBUS 1, OHIO RECEIVED SEPTEMBER 1, 1949

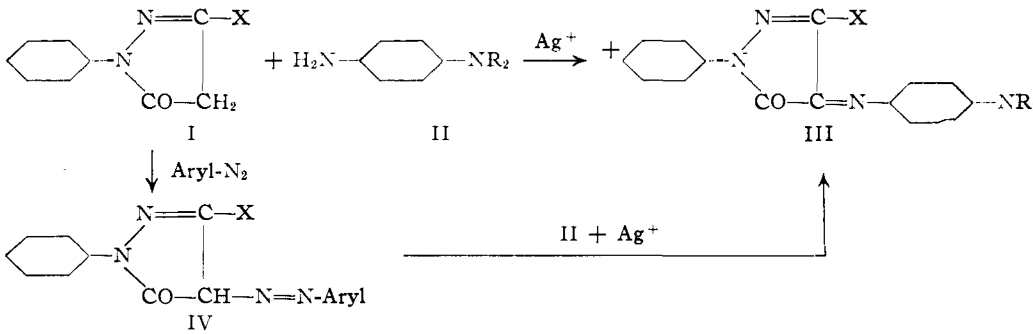
[COMMUNICATION NO. 1289 FROM THE KODAK RESEARCH LABORATORIES]

The Formation of Azomethine Dyes from 4-Arylazo-5-pyrazolones

BY PAUL W. VITTUM, GEORGE W. SAWDEY, REBECCA A. HERDLE[1] AND MARY K. SCHOLL

Pyrazolone derivatives (I, where X may be alkyl,[2] –NH$_2$[3] or –NH acyl,[3] for example) readily undergo oxidative condensation (coupling) with N,N-disubstituted-*p*-phenylenediamines (II) to form azomethine dyes (III). This dye-forming reaction, which is of importance for the production of magenta dye images in various color photographic processes,[4] is closely analogous, and probably very similar in mechanism, to that involved in the formation of an indoaniline dye from II and a phenol derivative.[5]

It has recently been found[6] that the 4-arylazo derivatives of these pyrazolone couplers (IV) can also be condensed with II under oxidizing conditions to produce azomethine dyes, the process apparently taking place by replacement of the azo group by the *p*-phenylenediamine residue. This interesting conversion of an azo dye to an azomethine, which has been found to have valuable applications in color photography,[7] appears not to have been observed previously. Accordingly, the work described in this paper was undertaken to gain a more complete understanding of the nature of the reaction.



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(1) Present address: 315 Colebrook Drive, Rochester, New York.

(2) Seymour, U. S. Patent 1,969,479 (1934).

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

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

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

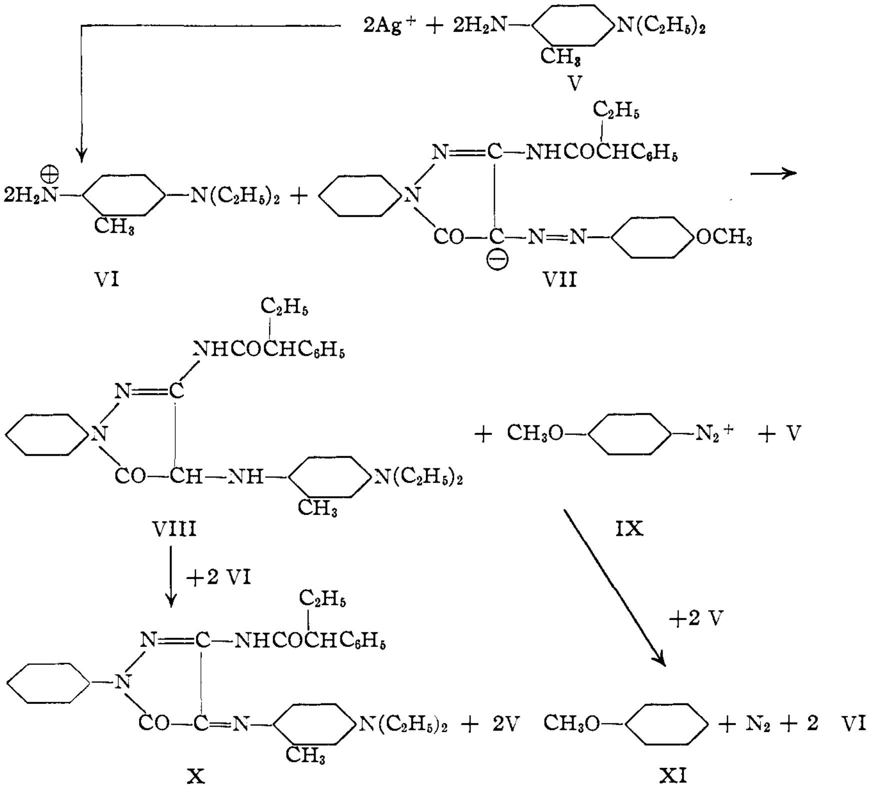
(6) Glass, Vittum and Weissberger, U. S. Patent 2,455,170 (1948).

(7) Hanson and Vittum, *PSA Journal*, **13**, 94 (1947); Hanson, U. S. Patent 2,449,966 (1948)· Hanson, *J. Opt. Soc. Am.*, in press.

1-Phenyl-3-(α-phenylbutyramido)-4-(*p*-methoxyphenylazo)-5-pyrazolone (VII) was prepared by coupling 1-phenyl-3-(α-phenylbutyramido)-5-pyrazolone with *p*-methoxyphenyldiazonium chloride. When this azo compound was treated with 2-amino-5-diethylaminotoluene (V) and silver chloride in alkaline solution, the magenta azomethine dye (X) was formed in good yield. Anisole (XI) was also isolated from the reaction mixture. It was shown that X was identical with the azomethine dye formed, under the same conditions, from the parent pyrazolone coupler.

The reaction mechanism shown in Chart I accounts satisfactorily for the formation of the products which were isolated. The first step of the coupling reaction is depicted as occurring between the arylazopyrazolone anion (VII) and the semiquinone ion (VI), the latter being formed by oxidation, by Ag^+, of the *p*-phenylenediamine (V).[8] The products of this reaction are the leuco azomethine (VIII), the diazonium ion (IX), and a regenerated molecule of the *p*-phenylenediamine,

CHART 1[9]



The subsequent oxidation of the leuco dye may take place by a direct interaction between the leuco dye and the diazonium ion, producing the azomethine, anisole and nitrogen.[10] Alternatively, the reactions can be formulated, as shown in Chart 1, as an oxidation of the leuco dye by the semiquinone (VI) and a reduction of the diazonium ion by the *p*-phenylenediamine (V). This reduction reaction, which is analogous to the reduction of diazonium compounds by hydroquinone,[11] was shown to take place under the conditions used in the coupling reaction. The experimental evidence does not permit a choice between these two possible mechanisms for the later steps of the coupling reaction. However, we prefer the scheme shown in Chart 1, in which the reactions occur through the agency of the *p*-phenylenediamine semiquinone oxidation–reduction system, since this mechanism is applicable also to the coupling reactions of parent pyrazolone couplers.

According to this reaction scheme, it would be expected that the ease of elimination of the diazonium ion from the coupler anion (VII) would be affected by structural changes tending to cause displacement of the electrons of the pyrazolone–azo bond. Thus, substituents tending to draw electrons toward the pyrazolone ring should facilitate the reaction, and those causing an electron displacement away from the pyrazolone nucleus should retard the coupling. In this connection, the following observations are pertinent:

(a) The 4-(*p*-anisylazo) derivative of 1-phenyl-3-methyl-5-pyrazolone (XII) reacts sluggishly under the conditions used here. With this compound, the formation of azomethine dye was evident from the color of the reaction mixture, but it was formed in such small amounts that it could not be readily isolated.[12] The electron-releasing nature of the 3-methyl group is believed largely responsible for this behavior.

(b) Introduction of electron-attracting groups into the 1-phenyl ring of XII enhances the

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[8] Michaelis, *Ann. N. Y. Acad. Sci.*, **40**, Art. 2, 64 (1941).

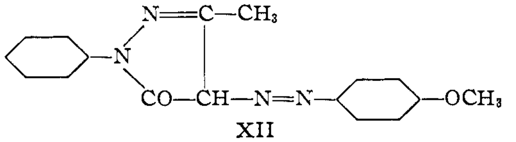
[9] In this chart, only one of the possible resonance structures is shown for VI, VII and X. A more complete formulation of the resonance system of the anion, VII, for example, would have to show also the structures in which the negative charge is carried by the carbonyl oxygen and the 2-nitrogen, respectively.

[10] F. C. Duennebier, of these Laboratories, has shown that this reaction does take place. The leuco dye (VIII) was rapidly oxidized to the azomethine (X) by treatment with *p*-methoxyphenyldiazonium chloride in alkaline solution.

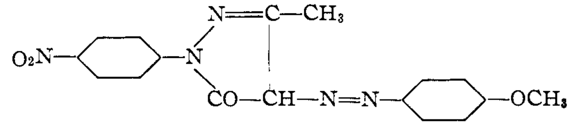
[11] Orton and Everatt, *J. Chem. Soc.*, **93**, 1021 (1908).

[12] In coupling reactions of this type, a sluggish reaction almost always leads to a low yield of azomethine dye, because the semiquinone is unstable and undergoes other reactions before the coupling reaction occurs.

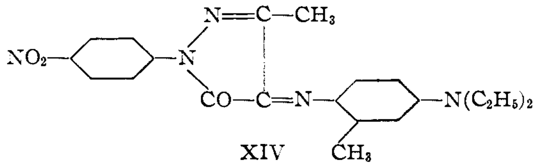
coupling reaction. Thus, the azo derivative of 1-(*p*-nitrophenyl)-3-methyl-5-pyrazolone (XIII) coupled rapidly and gave a good yield of the azomethine dye (XIV). Qualitative experiments indicated that electronegative substituents other than $-NO_2$, such as $-Cl$ and $-CN$, had the same general effect, in varying degree, in enhancing the coupling reaction.



XII

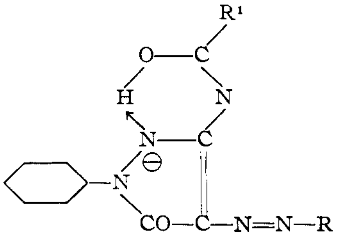


XIII



XIV

(c) The relatively high coupling reactivity of the 3-acylamidopyrazolone derivatives, compared with the 3-methyl compounds, for example, would indicate that the $-NHCOR$ group in the 3-position exerts an electron-attracting effect. This may arise because structures such as XV make a significant contribution to the state of the coupler anion. In XV, the establishment of the hydrogen bond would be expected to assist in distributing the negative charge of the anion and thus aid in polarizing the pyrazolone-azo bond in the direction favorable for the elimination of the diazonium ion in the coupling reaction.[13]



XV

(d) Qualitative experiments have indicated that electronegative substituents ($-NO_2$, halogen, $-CN$, $-SO_2NH_2$, etc.) in the arylazo radical of the 1-phenyl-3-acylamido-4-arylazo-5-pyrazolones retard the coupling reaction. Electropositive groups in the para-position, such as $-OCH_3$ and $-NHCOR$, on the other hand, increase the coupling reactivity.

Experimental[14]

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

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

1-Phenyl-3-(α-phenylbutyramido)-4-(*p*-anisylazo)-5-pyrazolone (VII).—Three and seven-tenths grams (0.03 mole) of *p*-anisidine was dissolved in 10 ml. of concd. hydrochloric acid, cooled to 0°, and diazotized with 2.2 g. (0.03 mole) of sodium nitrite in 10 ml. of water. The diazonium solution was added, with stirring, to a solution of 9.6 g. (0.03 mole) of 1-phenyl-3-(α-phenylbutyramido)-5-pyrazolone in a mixture of 30 ml. each of 95% ethanol and pyridine. The resulting orange precipitate was collected by suction filtration and recrystallized from glacial acetic acid. The yield was 11 g. (80%) of orange crystals melting at 194–196°. Absorption in *n*-butyl acetate: λ_{max} 418 mμ; ϵ_{max} 2.5 × 10^4.

Anal. Calcd. for $C_{26}H_{25}O_3N_5$: C, 68.6; H, 5.5; N, 15.6. Found: C, 68.5; H, 5.6; N, 15.9.

The same procedure was followed for the preparation of **1-(*p*-nitrophenyl)-3-methyl-4-(*p*-anisylazo)-5-pyrazolone (XIII).** The product, which was obtained in 52% yield after recrystallization from acetic acid, consisted of red crystals, m. p. 250–252°. Absorption in *n*-butyl acetate: λ_{max} 426 mμ; ϵ_{max} 2.5 × 10^4.

Anal. Calcd. for $C_{17}H_{15}O_4N_5$: C, 57.8; H, 4.2; N, 19.8. Found: C, 57.7; H, 4.5; N, 20.1.

Preparation of Azomethine Dyes.—The coupling reactions were carried out using a modification of the method previously described[5] for the preparation of indoaniline dyes. The preparation of **azomethine dye, X,** was typical. A solution of 4 g. (0.009 mole) of 1-phenyl-3-(α-phenylbutyramido)-4-(*p*-anisylazo)-5-pyrazolone (VII) in 700 ml. of ethyl acetate was stirred with a solution of 6.5 g. (0.036 mole) of silver nitrate in 500 ml. of water and 80 ml. of 28% ammonium hydroxide. To this mixture was added, dropwise, a solution of 3.9 g. (0.018 mole) of 2-amino-5-diethylaminotoluene hydrochloride (V·HCl) in 50 ml. of water. The reaction mixture was stirred for thirty minutes after the addition was completed and then filtered through a bed of Celite to remove the metallic silver which had separated. Occluded dye was washed through with small portions of ethyl acetate. The ethyl acetate layer containing the dye was separated, washed twice with water, and filtered by gravity through cotton to remove the last traces of metallic silver and water droplets. The ethyl acetate was evaporated and the crude dye was recrystallized from ligroin. The yield of greenish crystals with brown reflex (X), m. p. 169–171°, was 2.9 g. (66%). Absorption in *n*-butyl acetate: λ_{max} 529 mμ; ϵ_{max} 5.4 × 10^4.

Anal. Calcd. for $C_{30}H_{33}O_2N_6$: C, 72.7; H, 6.7; N, 14.1. Found: C, 72.3; H, 6.8; N, 14.6.

For the isolation of anisole from this coupling reaction, the same procedure was used in a larger-scale preparation (19.8 g. (0.042 mole) of VII). The ethyl acetate was evaporated carefully at normal pressure, and the residual mass was subjected to steam distillation, 5 l. of distillate being collected. The distillate was extracted with two 1-l. portions of ethyl acetate, the ethyl acetate was evaporated on a steam-bath at normal pressure, and the residual liquid was distilled. The fraction coming over between 120 and 154° was redistilled, giving 2.7 g. (60%) of anisole, b. p. 152–154°. The product was identified by the preparation of 2,4-dinitroanisole, m. p. 88–89°.[16]

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[13] It would be predicted that those substituents in the pyrazolone nucleus which affect the coupling reactivity of the 4-arylazo derivatives should exert a parallel effect upon the ionization constants of the parent pyrazolones without the arylazo group. Determination of the ionization constants for representative compounds from this series is now being carried out in these Laboratories.

[14] All melting points recorded here are uncorrected.

[15] We are indebted to Dr. Howard Munro and co-workers, of these Laboratories, for a supply of this compound.

[16] Meldola, Woolcott and Wray (*J. Chem. Soc.*, **69**, 1330 (1896)) give 88°.

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 nonmiscible 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.

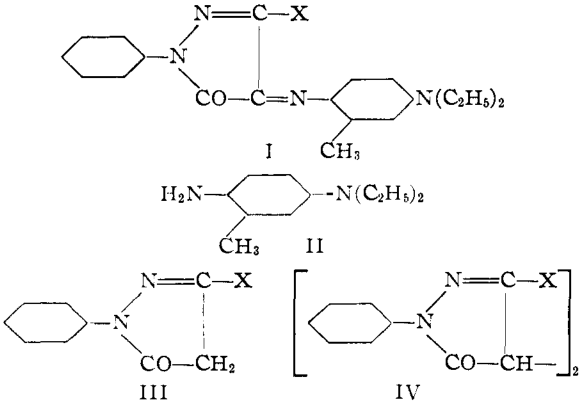
ROCHESTER, NEW YORK RECEIVED SEPTEMBER 21, 1949

[COMMUNICATION NO. 1290 FROM THE KODAK RESEARCH LABORATORIES]

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.