cold hydrochloric acid. The organic layer was removed and the water was extracted with ether. The ether was combined with the benzene–toluene layer and the whole was dried with anhydrous sodium sulfate, then distilled; yield 5.0 g. of viscid, light yellow oil of b.p. 162–164° (3 mm.). That this was the desired ester was proved: (a) by oxidation to benzoic acid with permanganate; (b) by nonreaction with phenyl isocyanate; (c) by saponification to an acid of m.p. 156–157.5°. The melting point of 5-phenyl-3-methyl-2,4-pentadienoic acid (various geometric isomers) is given[8] as 153, 156–157, 124, 160°.

Ethyl 4-(1-Hydroxycyclohexyl)-3-methylcrotonate.—Comparable details were used as in the last experiment, starting with 9.3 g. of cyclohexanone and 12 g. of the iodo ester. Distillation of the products yielded a 4.7-g. fraction boiling from 95–127° (3 mm.). On standing overnight, it became purple in color. It was then dissolved in ether and the solution decolorized with an aqueous solution of sodium thiosulfate and dried with anhydrous sodium sulfate. Redistillation gave 0.6 g. boiling at 100–110° (2 mm.) and 3.1 g. boiling at 112–116° (2 mm.). Analysis of the ester indicated that it was still slightly contaminated with the iodo ester.

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 67.60; H, 8.56.

α-Benzylidene-γ-ethynyl-γ-valerolactone.—γ-Ethynyl-γ-valerolactone was prepared by Kreimeier's method[9] from levulinic acid, acetylene and sodamide in liquid ammonia. It was collected at 108–109° (21 mm.).

A fine suspension of 2.3 g. (0.1 mole) of sodium shot was prepared in dry toluene in a flask protected from atmospheric moisture. After cooling, 5.8 ml. of absolute alcohol was added. Before the sodium had completely dissolved, 12.4 g. of γ-ethynyl-γ-valerolactone was added to the cold mixture. After stirring for 10 minutes, 10.6 g. (0.1 mole) of freshly distilled benzaldehyde was slowly dropped into the mixture, which was cooled in an ice-bath and stirred during the addition and for a subsequent 3 hours, then allowed to stand overnight.

The mixture was then poured into dilute acetic acid, shaken for 15 minutes, and the toluene layer was dried and cooled. The resulting precipitate was collected, washed in ether with aqueous sodium carbonate, then was recrystallized from aqueous alcohol. This yielded 2.1 g. of white needles, m.p. 85–86°. By concentrating the mother liquor, a further 1.4-g. quantity of crystals was obtained.

When treated with alcoholic silver nitrate and with potassium mercuriiodide, the compound gave positive tests for acetylenic hydrogen.

Anal. (By T. S. Ma) Calcd. for $C_{14}H_{12}O_2$: C, 79.21; H, 5.66. Found: C, 79.64; H, 5.89.

γ-Acetyl-γ-valerolactone.—To a solution of 1.5 g. of mercuric oxide dissolved in a mixture of 8.3 g. of concentrated sulfuric acid and 49.7 ml. of water was slowly added 16.3 g. of γ-ethynyl-γ-valerolactone. The resulting reaction was exothermic, and a white precipitate of the mercury salt formed. After all was added, the mixture was refluxed for 3 hours. An additional 5 cc. of sulfuric acid was added, and refluxing was continued 5 hours more. At this point, solution had been effected, leaving only a small residue of reduced mercury salts. The mixture was filtered and neutralized with concentrated aqueous potassium hydroxide added dropwise until the solution was nearly neutral. The precipitated inorganic salts were removed and the solution was repeatedly extracted with ether. After drying the ether extract with anhydrous sodium sulfate, the solvent was removed and the residue distilled at 23 mm. A 2.5-g. fraction was collected up to 126°, then 9.3 g. from 126–132° most of it coming over at 130–132°.

Redistillation of the higher boiling fraction gave the keto lactone as a colorless, water-soluble liquid boiling at 115–116° (10 mm.).

Anal. (By T. S. Ma) Calcd. for $C_7H_{10}O_3$: C, 59.12; H, 7.04. Found: C, 59.90; H, 7.13.

Semicarbazone.—A mixture of 0.5 g. of the lactone, 0.5 g. of anhydrous sodium acetate and 0.5 g. of semicarbazide hydrochloride in 5 ml. of water was allowed to stand overnight. The resulting precipitate weighed 0.6 g. and, after recrystallization from water, melted at 182–183°.

Anal. Calcd. for $C_7H_{10}O_3$: N, 21.11. Found: N, 21.49, 21.68.

2,4-Dinitrophenylhydrazone.—About 0.6 g. of the ketone, 0.4 g. of 2,4-dinitrophenylhydrazine and 25 ml. of ethanol were brought to boiling and 0.5 ml. of concentrated hydrochloric acid was added. After the solution had cooled, 0.5 g. of precipitate was collected. This derivative melted at 147–148° after two crystallizations from ethanol.

Anal. (By Mr. Krzywicki) Calcd. for $C_{13}H_{14}N_4O_6$: N, 17.38. Found: N, 18.37, 18.17.

EVANSTON, ILLINOIS RECEIVED JULY 28, 1950

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[8] Kohler and Heritage, *Am. Chem. J.*, **43**, 485 (1910): Auwers, *J. prakt. Chem.*, **105**, 380 (1922); Kuhn and Hoffer, *Ber.*, **65**, 651 (1932).

[9] Kreimeier, U. S. Patent 2,122,719, July, 1938.

[COMMUNICATION NO. 1362 FROM THE KODAK RESEARCH LABORATORIES]

Azomethine Dyes. I. Color and Constitution of Pyrazolone Azomethine Dyes

BY G. H. BROWN, B. GRAHAM, P. W. VITTUM AND A. WEISSBERGER

Azomethine dyes have been prepared from 2-amino-5-diethylaminotoluene and twenty-six pyrazolones, and their absorptions have been determined in three solvents covering a range of dielectric constant. Explanation of the absorption data is based on the assumption that the two absorption bands occurring in the visible region of the spectrum are x- and y-bands, and the effects of structural changes in the pyrazolone nucleus on these bands are explained qualitatively in terms of the resonance systems involved. The x-band (λ_{max} *ca.* 530–550 mμ) appears to be associated with excitation involving large contributions from structures in which the pyrazolone 2-nitrogen atom is negatively charged, while the y-band (λ_{max} *ca.* 440–450 mμ) is associated with excitation involving structures in which the negative charge is carried largely by the carbonyl-oxygen atom. Polarization of the 1,5-lactam group of the pyrazolone ring, and the steric arrangement of the dye molecule are shown to be important factors in determining the absorption.

The pyrazolone azomethine dyes (III) have received considerable attention since Seymour described[1] their use as the magenta dyes in certain color photographic processes. In these color processes the dyes are formed during color development[2,3] by oxidative condensation of a pyrazolone (I) with an N,N-disubstituted *p*-phenylenediamine (II), and numerous investigations[4] and patents[5] have been concerned with the effect of structural changes in the pyrazolone upon the ability to undergo the azomethine coupling reaction and upon the properties of the resulting dyes.

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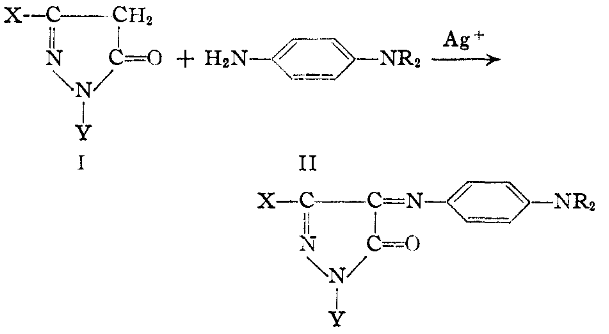
[1] M. W. Seymour, U. S. Patent 1,969,479 (1934).

[2] R. Fischer, U. S. Patent 1,102,028 (1914).

[3] C. E. K. Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1942, p. 393.

[4] A. Weissberger and H. D. Porter, THIS JOURNAL, **64**, 2133 (1942); **65**, 52, 732, 1495, 2180 (1943); **66**, 1849 (1944).

[5] For example, U. S. Patents 2,200,924 and 2,213,986 (1940); 2,311,081, 2,311,082 and 2,334,495 (1943); 2,343,702, 2,343,703, 2,348,463, 2,353,205 and 2,354,552 (1944); 2,367,523 and 2,369,489 (1945); 2,403,329 (1946); 2,435,550, 2,437,063 and 2,439,098 (1948).



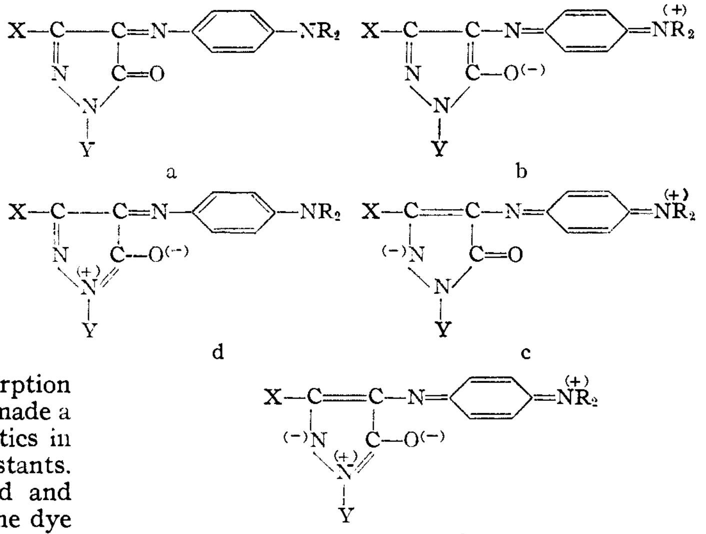
It was pointed out[6] some years ago that one of the characteristics of the absorption of the pyrazolone azomethine dyes is the presence of two distinct absorption bands in the visible region: the primary band in the green region ($\lambda_{\max}$, *ca.* 530–550 mμ), and a secondary band of lower intensity in the blue ($\lambda_{\max}$, *ca.* 440–450 mμ). The secondary band, which is disadvantageous in the photographic application of these dyes, can be reduced in intensity by modifications in the pyrazolone coupler.[6] More recently, Gerbaux has described[7] the absorption of a large number of pyrazolone azomethine dyes. His data confirm the presence of the two absorption bands, and show that the two bands respond more or less independently to changes in structure and solvent.

In an attempt to gain an understanding of the electronic mechanism governing the absorption of the pyrazolone azomethine dyes, we have made a detailed study of their absorption characteristics in solvents covering a wide range of dielectric constants. A large group of pyrazolones was prepared and each of them was converted to an azomethine dye by oxidative condensation with 2-amino-5-diethylaminotoluene. The dyes are listed in Table I, along with pertinent physical and analytical data. The absorption spectra of each dye were measured in cyclohexane, *n*-butyl acetate and methanol, leading to the values given in Table II for $\lambda_{\max}$ and $\epsilon_{\max}$ of the primary and secondary bands.

According to Lewis and Calvin,[8] absorption of light by a planar molecule having no center of symmetry involves vectorized electronic activations associated with electric moments oriented normal to each other in the plane of the molecule. If these activations lead to excited states differing sufficiently in energy, two absorption bands result. The band with the longer wave length (lower energy), called the *x*-band, is associated with activation in the direction of greatest polarizability in the molecule, while the shorter wave-length band, the *y*-band, arises from activation at right angles to this direction. This interpretation has been applied, with very satisfactory results, to complex absorption spectra in many widely differing series of compounds.[9]

The most probable structures contributing to the resonance hybrid of a pyrazolone azomethine dye are represented by IVa, b, c, d and e.

Consideration of this system has led us to the view that the two absorption bands in the visible region are *x*- and *y*-bands. Analogous to the cases of other non-ionic dyes, the visible absorption of these azomethines is assumed to be associated with resonance among structures falling into two groups: IVa and d, on the one hand, and IVb, c and e, on the other. The structures of the latter group are characterized by the charge separation occurring along the ***conjugated system*** between the electron-donating $-NR_2$ group of the *p*-phenylenediamine system and the electron-attracting centers in the pyrazolone: the carbonyl-oxygen atom (IVb) and the 2-nitrogen atom (IVc and e). If the accumulation of negative charge on the oxygen and on the nitrogen requires different amounts of energy, excitation would lead, according to the Lewis–Calvin theory, to two spectral bands arising from electric moment vectors corresponding roughly to the electronic oscillations: [IVa and d ⟷ IVb (negative charge on O)] and [IVa and d ⟷ IVc and e (negative charge on N)]. This picture, although greatly over-simplified, provides a qualitative basis for explaining the effects of structural and environmental factors upon the absorption spectra of these dyes.



IV

In order to assign the direction of electronic oscillation associated with each of the two bands, we must consider the energy differences among the structures involved, *i.e.*, between IVa and d, and IVb, on the one hand, and between IVa and d, and IVc and e, on the other. In IVa and d, the *p*-phenylenediamine ring is benzenoid, whereas in all of the other structures, it is quinonoid. The major contribution to the resonance hybrid is therefore probably made by the structures IVa and d. Of the structures in which the *p*-phenylenediamine ring is quinonoid (IVb, c and e), IVb, might be considered, at first glance, to be the most stable,

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[6] H. D. Porter, P. W. Vittum and A. Weissberger, U. S. Patent 2,343,704 (1944).

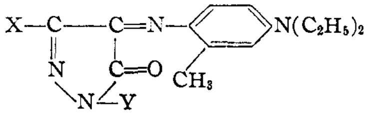
[7] R. Gerbaux, *Bull. soc. chim. Belg.*, **58**, 498 (1949).

[8] G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939).

[9] L. N. Ferguson (*ibid.*, **43**, 385 (1948)) has cited the literature on *x*- and *y*-bands. More recent applications have been made by H. P. Koch (*J. Chem. Soc.*, **1123** (1948)) and by Y. Hirshberg and R. N. Jones (*Can. J. Research*, **27**, 437*b* (1949)).

TABLE I

PHYSICAL PROPERTIES OF DYES



No.	Substituents X	Y	M. p., °C.	Crystallized from	Appearance of crystals	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1	CH_3	H	195–196	Benzene	Dark red	66.2	66.6	7.4	7.2	20.6	20.7
2	C_6H_5	H	209–210	Benzene	Dark green, metallic reflection	71.8	71.6	6.6	6.8	16.8	16.6
3	H	C_6H_5	134–135	Ethanol	Dark green gold refl.	71.8	71.7	6.6	6.7	16.8	17.1
4	CH_3	C_6H_5	129–130[a]	Ethanol	Dark red, green refl.	72.4	72.4	6.9	6.9	16.1	16.3
5	$C(CH_3)_3$	C_6H_5	131–132	Ethanol	Long green needles	73.8	73.9	7.7	7.8	14.4	14.7
6	n-$C_{15}H_{31}$	C_6H_5	44–45	Ethanol	Brick red	77.2	77.2	9.6	9.7	10.3	10.3
7	C_6H_5	C_6H_5	166–167	Cyclohexane	Dark brown, bronze refl.	76.1	76.4	6.4	6.3	13.7	13.6
8	α-Furyl	C_6H_5	191–192	Cyclohexane	Dark brown, bronze refl.	72.0	72.2	6.0	6.0	14.0	14.0
9	$CH_2CO_2C_2H_5$	C_6H_5	96–97	Ethanol	Dark green, metallic refl.	68.6	68.9	6.7	6.9	13.3	12.9
10	$CO_2C_2H_5$	C_6H_5	161–162	Ethanol	Dark green	67.9	68.1	6.5	6.5	13.8	14.1
11	$CONH_2$	C_6H_5	210–211 (dec.)	Ethyl acetate	Dark green	66.8	67.1	6.1	6.4	18.6	18.8
12	NH_2	C_6H_5	169–170[b]	Ethanol	Green needles	68.8	68.6	6.6	6.7	20.1	20.1
13	NHC_6H_5	C_6H_5	173–174	Ethanol	Dark purple needles	73.4	73.6	6.4	6.5	16.5	16.3
14	$NHCOCH(C_2H_5)C_6H_5$	C_6H_5	171–172[c]	Ethanol	Green needles	72.8	73.2	6.7	6.6	14.1	14.3
15	CH_3	p-ClC_6H_4	169–170	Ethanol	Yellow green	65.8	65.7	6.1	5.9	14.6	14.8
16	CH_3	o-ClC_6H_4	148–149	Ethanol	Magenta plates	65.8	66.3	6.1	6.0	14.6	14.7
17	CH_3	2,4-$Cl_2C_6H_3$	141–142	Cyclohexane	Purple plates	60.4	60.3	5.3	5.1	13.4	13.5
18	CH_3	2,4,6-$Cl_3C_6H_2$	176–177	Ethanol	Light red, powdery	55.8	55.9	4.7	4.7	12.4	12.4
19	CH_3	p-$NO_2C_6H_4$	189–190[d]	Ethanol	Dark brown, gold refl.	64.1	64.0	5.9	5.8	17.8	17.9
20	CH_3	p-HO_2C–C_6H_4	243–245	Ethanol	Dark red needles	67.3	67.2	6.2	6.0	14.3	14.5
21	CH_3	p-H_2NO_2S–C_6H_4	229–230 (dec.)	Ethanol	Gold needles	59.0	59.2	5.9	5.9	16.4	16.7
22	CH_3	p-H_2N–C_6H_4	189–190	n-Butanol	Purple	69.4	69.2	6.9	7.1	19.3	19.2
23	CH_3	p-NC–C_6H_4	201–202	Ethanol	Dark green needles	70.8	70.5	6.2	6.2	18.8	18.6
24	CH_3	2'-Quinolyl	200–201	Ethanol	Reddish purple	72.1	71.9	6.3	6.4	17.5	17.8
25	CH_3	3'-Quinolyl	153–154	Ethanol	Purple needles	72.1	72.0	6.3	6.4	17.5	17.5
26	CH_3	2'-Benzothiazolyl	204–206	Ethanol	Reddish purple needles	65.2	65.5	5.7	5.8	17.3	17.1

[a] Previously reported by Gerbaux,[7] 129–132°; by Vittum and Duennebier (THIS JOURNAL, **72**, 1536 (1950)), 124–125°. Gerbaux[7] reported 148–150°. [c] Previously reported by Vittum, Sawdey, Herdle and Scholl (THIS JOURNAL, **72**, 1533 (1950)), 169–171°. [d] Previously reported by Vittum, Sawdey, Herdle and Scholl (*loc. cit.*), 190–192°.

References to pyrazolones (Column 1) used in synthesis of dyes:
(1) T. Curtius and R. Jay, *J. prakt. Chem.*, **39**, 52 (1889).
(2) T. Curtius, *ibid.*, **50**, 515 (1894).
(3) L. Claisen and E. Haase, *Ber.*, **28**, 35 (1895).
(4) Eastman Organic Chemicals, Number 1397.
(5) E. Wahlberg, *Ber.*, **44**, 2074 (1911).
(6) B. Helferich and H. Köster, *ibid.*, **56**, 2091 (1923).
(7) L. Knorr and C. Klotz, *ibid.*, **20**, 2546 (1887).
(8) S. S. Sandelin, *ibid.*, **33**, 493 (1900).
(9) H. v. Peckmann, *Ann.*, **261**, 171 (1891).
(10), (11), (12) and (13) A. Weissberger and H. D. Porter, THIS JOURNAL, **64**, 2135 (1942).
(14) Reference *c*, above.
(15) and (16) J. van Alphen, *Rec. trav. chim.*, **64**, 109 (1945).
(17) F. D. Chattaway and C. R. N. Strouts, *J. Chem. Soc.*, **125**, 2423 (1924).
(19) J. Altschul, *Ber.*, **25**, 1853 (1892).
(20) A. Michaelis and H. Horn, *Ann.*, **373**, 214 (1910).
(21) G. B. Crippa and S. Maffei, *Gazz. chim. ital.*, **72**, 97 (1942).
(22) German Patent 61,794, *Frdl.*, **3**, 926 (1890–94).
(24) R. G. Fargher and R. Furness, *J. Chem. Soc.*, **107**, 699 (1915).
(26) Bayer, *et al.*, U. S. Patent 2,073,600; *C. A.*, **31**, 3300 (1937).

because of the greater electronegativity of oxygen compared with nitrogen, and because of the aromaticity of the pyrazole system. However, the greater number of possible structures when the formal charge is attached to the 2-N atom (IVc and e), of which IVe also fulfills the conditions for an aromatic character of the pyrazolone ring, indicates that a hypothetical hybrid of structures IVc and e, would be of lower energy than a hypothetical isolated structure, IVb.

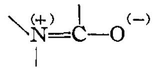
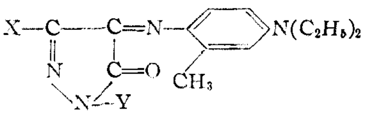
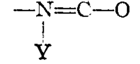
Viewed in another way, polarization of the lactam system of the pyrazolone ring to  $\diagdown\overset{(+)}{N}{=}\overset{|}{C}{-}O^{(-)}$ (IVd and e) produces a net negative charge on the oxygen atom. In the excitation process, therefore, higher energy would be involved in accumulating, on the oxygen, an additional negative charge, *viz.*, that coming from the charge separation through the conjugated system. Moreover, the positive charge on the 1-N atom resulting from polarization of the lactam group will facilitate, by an inductive effect, the accumulation of the negative charge on the 2-N atom. Thus, according to this interpretation, the lactam group of the pyrazolone ring plays an important part in the resonance system of the azomethine dyes. The electron mobility in this group is well

TABLE II

ABSORPTION OF DYES



No.	Substituents		λ_{max} in mμ						$\epsilon_{max} \times 10^{-4}$					
			Primary band			Secondary band			Primary band			Secondary band		
	X	Y	Cyclohexane	*n*-Butyl acetate	Methanol	Cyclohexane	*n*-Butyl acetate	Methanol	Cyclohexane	*n*-Butyl acetate	Methanol	Cyclohexane	*n*-Butyl acetate	Methanol
1	CH_3	H	504	517	539	443	445	441	1.7	2.5	3.0	1.3	1.6	1.1
2	C_6H_5	H	520	532	554	443	450	448	...	2.4	2.9	1.9	1.7	1.4
3	H	C_6H_5	520	546	573	447	449	422	2.2	3.3	4.1	1.3	0.8	0.6
4	CH_3	C_6H_5	499	522	539	444	448	444	2.9	3.6	3.8	2.2	1.6	1.3
5	$C(CH_3)_3$	C_6H_5	502	528	546	444	448	446	1.9	2.7	2.8	2.1	1.8	1.5
6	*n*-$C_{15}H_{31}$	C_6H_5	498	522	541	446	450	445	2.5	3.0	3.2	1.9	1.4	1.1
7	C_6H_5	C_6H_5	514	537	554	450	455	452	2.2	3.1	3.4	1.8	1.3	1.4
8	α-Furyl	C_6H_5	520	541	560	447	450	447	2.7	3.6	3.9	1.6	1.3	1.2
9	$CH_2CO_2C_2H_5$	C_6H_5	505	530	548	444	449	445	3.3	3.9	4.3	1.8	1.4	1.2
10	$CO_2C_2H_5$	C_6H_5	535	557	575	460	465	462	2.9	4.0	4.1	1.9	1.5	1.2
11	$CONH_2$	C_6H_5	...	565	583	...	460	456	...	3.8	4.5	...	1.2	1.0
12	NH_2	C_6H_5	492	506	524	430	430	423	3.7	4.1	3.9	1.4	1.2	0.8
13	NHC_6H_5	C_6H_5	504	522	533	434	432	426	4.0	4.7	4.4	1.1	0.9	0.7
14	$NHCOCH(C_2H_5)C_6H_5$	C_6H_5	512	526	543	440	440	437	5.2	5.2	5.0	1.3	1.0	0.8
15	CH_3	*p*-ClC_6H_4	503	526	541	444	445	442	3.3	3.9	3.9	1.9	1.5	1.3
16	CH_3	*o*-ClC_6H_4	506	525	547	442	446	440	2.7	3.4	4.3	1.9	1.5	1.1
17	CH_3	2,4-$Cl_2C_6H_3$	510	529	549	442	446	442	3.0	3.6	4.5	1.6	1.4	1.1
18	CH_3	2,4,6-$Cl_3C_6H_2$	511	530	551	442	444	442	3.2	4.1	4.8	1.7	1.3	1.0
19	CH_3	*p*-NO_2–C_6H_4	520	539	546	445	448	446	3.9	4.7	4.7	1.7	1.4	1.3
20	CH_3	*p*-HO_2C–C_6H_4	...	530	540	...	446	444	...	3.9	4.0	...	1.5	1.4
21	CH_3	*p*-H_2NSO_2–C_6H_4	...	532	545	...	446	444	...	4.1	4.3	...	1.5	1.3
22	CH_3	*p*-NH_2–C_6H_4	496	514	535	444	448	444	...	3.6	3.8	...	1.7	1.2
23	CH_3	*p*-NC–C_6H_4	516	535	546	444	445	443	3.5	4.4	4.5	1.7	1.4	1.3
24	CH_3	2′-Quinolyl	509	536	549	446	448	445	2.8	3.9	4.8	1.9	1.5	1.3
25	CH_3	3′-Quinolyl	508	530	546	446	448	444	3.7	4.4	4.7	2.0	1.5	1.3
26	CH_3	2′-Benzothiazolyl	517	540	556	441	442	440	3.7	5.0	5.4	1.3	1.1	1.0

known, and it has recently been established[10] that, in spite of the close proximity of the charges, structures containing the group  $-\overset{(+)}{\underset{\underset{Y}{|}}{N}}=\overset{|}{C}-\overset{(-)}{O}$ make important contributions to the resonance hybrids of antipyrine and some of its derivatives. In the pyrazolone azomethine dyes, the internal polarization of the lactam group provides a "buffering" mechanism by which the capacity of the carbonyl-oxygen atom to attract electrons, as conditioned by the structural features of the dye molecule or by the environment, can be satisfied without involving, to the full extent, the electrons associated with the charge separation through the conjugated system. These considerations make it reasonable to assume that excitation involving structures IVc and e, leads to the lower-energy primary band (*x*-band) and that excitation involving IVb, leads to the secondary band of lower intensity (*y*-band).

The absorption data collected in Table II support these suggestions. Considering first one of the simplest dyes in the series, that from 1-phenyl-5-pyrazolone (No. 3) for which the absorption curves are shown in Fig. 1, it is to be noted that the *x*-band undergoes a strong bathochromic shift with increasing dielectric constant of the solvent. This behavior parallels that generally observed with non-ionic dyes, whose resonance hybrids receive the major contributions from uncharged structures.[11]

The *y*-band, however, undergoes a hypsochromic shift of smaller magnitude, an effect which is probably associated with the degree of polarization of the lactam group in the different solvents. Thus, the more polar solvents cause electron displacement from the 1-N atom, increasing the contribution of the resonance structures IVd and e. The resulting increased negative charge on the carbonyl-oxygen atom increases the energy associated with the *y*-band activation, giving rise to lower λ_{max}. At the same time, the increased positive charge on the 1-N atom inductively facilitates the *x*-band activation, an additional factor in reducing λ_{max} of the *x*-band.

In studying the effects produced upon the absorption by substituents in the 3-position of the pyrazolone ring, attention is directed first to the *x*-band. The values in Table III show that the tendency of the 2-nitrogen atom to accept a negative charge, and therefore the stability and contribution of structures IVc and e, are affected directly by the substituent in the 3-position. Electron-releasing substituents reduce the contribution of these structures, and λ_{max} of the *x*-band is lowered accordingly. The effectiveness of the different

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(10) R. D. Brown, A. A. Hukins, R. J. W. Le Fèvre, J. Northcott and I. R. Wilson, *J. Chem. Soc.*, 2812 (1949).

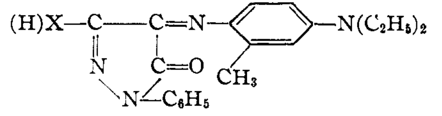
(11) L. G. S. Brooker and R. H. Sprague, THIS JOURNAL, **63**, 3214 (1941).

groups, as determined from the absorptions of cyclohexane solutions, is shown in Table III. The sequence of substituents shown there represents a plausible arrangement for an electronegativity scale if it is kept in mind that a mesomeric effect of the 3-substituent can influence directly the electron density on the 2-nitrogen atom, as shown by the three important structures, IVa, b and d. Strongly electron-attracting groups in the 3-position, such as $-CONH_2$ and $-CO_2C_2H_5$, have the opposite effect and cause an increase in λ_{max} of the x-band.

In the more polar solvents, the sequence is followed closely, with the exceptions italicized in Table III. These deviations are probably caused by the increased polarization of the X–C bond in the 3-position in the more polar solvents. Since the C–N bond is less polarizable than the C–C bond, the groups attached through –N show smaller shifts of λ_{max}. (see Table IV). The reversal of the order of $-C_{15}H_{31}$ and $-CH_3$ in methanol can be ascribed to the greater polarizability of the former group. The large shift of the compound containing the difficultly polarizable C–H bond in the 3-position is due to steric effects which are explained later.

TABLE III

CHANGE IN λ_{max} WHEN H IS REPLACED BY X



No.	Substituent X	x-band Cyclohexane	x-band n-Butyl acetate	x-band Methanol	y-band Cyclohexane	y-band n-Butyl acetate	y-band Methanol
12	NH_2	−28	−40	−49	−17	−19	+ 1
6	n-$C_{15}H_{31}$	−22	−24	−32	− 1	+ 1	+23
4	CH_3	−21	−24	*−34*	− 3	− 1	+22
5	$C(CH_3)_3$	−18	−18	−27	− 3	− 1	+24
13	NHC_6H_5	−16	*−24*	*−40*	−13	−17	+ 4
9	$CH_2CO_2C_2H_5$	−15	−16	−25	− 3	0	+23
14	$NHCOCH(C_2H_5)C_6H_5$	− 8	*−20*	*−30*	− 7	− 9	+15
7	C_6H_5	− 6	− 9	−19	+ 3	+ 6	+30
8	α-Furyl	0	− 5	−13	0	+ 1	+25
10	$CO_2C_2H_5$	+15	+11	+ 2	+13	+16	+40
11	$CONH_2$	...	+19	+10	...	+11	+34

The response of the y-band to these structural changes is not so regular. In a polar solvent (last column, Table III), a bathochromic shift of the y-band occurs when the H atom in the 3-position is replaced by any other group. This effect is probably caused by the steric factors discussed later. In solvents of lower dielectric constant, the 3-substituents shift the y-band in the same direction as the x-band, but to a considerably smaller extent. The fact that the effect on the y-band is so much smaller suggests that the 3-substituents exert their effect upon the carbonyl-oxygen atom chiefly by induction through the pyrazolone ring, the mesomeric effect being small because the group in the 3-position is conjugated with the oxygen only in the two structures IVc and e. Accordingly, the main effect of an electron-releasing substituent in the 3-position is to produce an increased negative charge on the 2-nitrogen, which, in turn, increases, by an inductive effect, the polarization of the lactam group. The end result, then, is a lowering of the λ_{max} of the y-band because the contribution of IVb is decreased, while that of IVd is increased. Electron-attracting substituents in the 3-position work in the opposite direction and cause a bathochromic shift of the y-band.

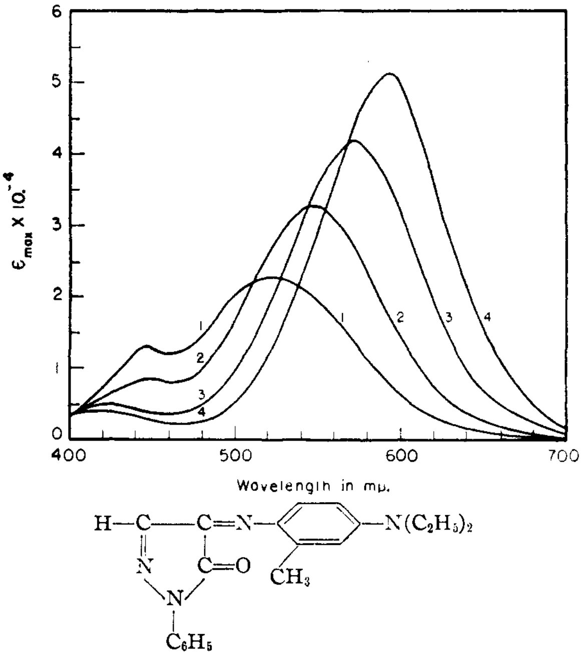
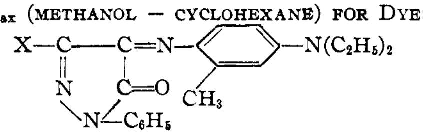


Fig. 1.—Absorption of dye in different solvents: 1, cyclohexane; 2, n-butyl acetate; 3, methanol; 4, 50% aqueous methanol.

The substituents in the 3-position have a remarkable influence on the relationship between absorption characteristics and polarity of solvent. Representative data bearing on this point are given in Table IV. The dye having X = H is seen to be distinct from all the others in that its x-band undergoes a somewhat larger bathochromic shift, and its y-band a very much larger hypsochromic shift, when the dielectric constant of the solvent is increased. The smaller shift of the x-band when the 3-position is occupied by a substituent other than H is ascribed to a shielding effect; the larger groups reduce the accessibility of the 2-nitrogen atom to the oriented polar solvent molecules. It would not be expected that this effect should be large, since, in the cyclic system of the pyrazolone, the nitrogen

TABLE IV

$\Delta\lambda_{max}$ (METHANOL − CYCLOHEXANE) FOR DYES



No.	Substituent X	x-band	y-band
3	H	53	−25
5	$C(CH_3)_3$	44	+ 2
6	n-$C_{15}H_{31}$	43	− 1
9	$CH_2CO_2C_2H_5$	43	+ 1
4	CH_3	40	0
7	C_6H_5	40	+ 2
8	α-Furyl	40	0
10	$CO_2C_2H_5$	40	+ 2
12	NH_2	32	− 7
14	$NHCOCH(C_2H_5)C_6H_5$	31	− 3
13	NHC_6H_5	29	− 8

atom should be fairly well exposed even with large groups in the 3-position.

It is more striking that the action of all 3-substituents other than H, regardless of their electronic nature, is to make λ_{max} of the *y*-band nearly independent of the polarity of the solvent (Table IV). Thus, while the *y*-band of the dye having X = H undergoes a hypsochromic shift of 25 mμ when the solvent is changed from cyclohexane to methanol, the *y*-bands of the other dyes in this group are virtually unaffected. An explanation for this observation is to be found in the manner in which the size of the group in the 3-position determines the steric configuration of the dye molecule. Figure 2 represents a scale model of these azomethines; although this scale model cannot be accepted as more than an estimate, it serves to indicate some of the steric factors which are involved.[12] Coplanarity of the benzene and pyrazolone rings is requisite for resonance through the conjugated system of the dye molecule, and, under this restriction, the benzene ring must occupy one of the two locations, A or A′, relative to the pyrazolone ring. These two locations appear to be about equal, with respect to steric interference, when a hydrogen atom occupies the 3-position on the pyrazolone ring. When larger groups are present here, however, it is seen that steric interference is so large when the benzene ring is at A′ that this configuration would be very unlikely.[13] Hence, it may be assumed that when substituents other than hydrogen are attached to the 3-carbon atom of the pyrazolone ring, the benzene ring is constrained to occupy the location A, and in this location it effectively shields the oxygen atoms from the approach of the solvent molecules.[14] The stabilization of the negative charge on the oxygen by the polar solvent is thereby greatly reduced, and as a consequence λ_{max} of the *y*-band becomes nearly independent of the nature of the solvent.

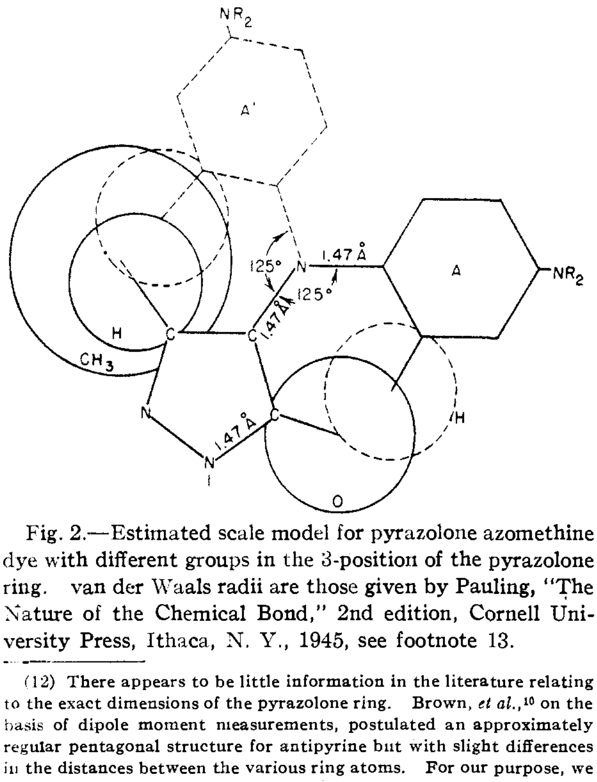


Fig. 2.—Estimated scale model for pyrazolone azomethine dye with different groups in the 3-position of the pyrazolone ring. van der Waals radii are those given by Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., 1945, see footnote 13.

We turn now to a consideration of the changes in absorption brought about by structural variations involving the 1-position of the pyrazolone. In contrast to the strong influence of substituents at the 3-carbon atom, groups attached to the 1-nitrogen atom have little effect in displacing the absorption bands. Thus, a comparison of the two pairs of dyes, 1 and 4, and 2 and 7, shown in Fig. 3, shows that replacement of a hydrogen by a phenyl group in the 1-position produces only very small changes in the values of λ_{max} for the *x*- and *y*-bands, and within each pair the absorption curves are very similar.

A more extensive series demonstrating the action of 1-substituents comprises dyes 15 to 26, all of which have a methyl group in the 3-position and

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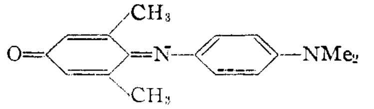
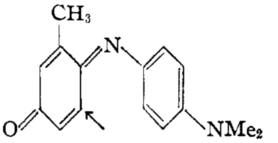
(12) There appears to be little information in the literature relating to the exact dimensions of the pyrazolone ring. Brown, *et al.*,[10] on the basis of dipole moment measurements, postulated an approximately regular pentagonal structure for antipyrine but with slight differences in the distances between the various ring atoms. For our purpose, we have constructed the pyrazolone ring as a regular pentagon, having established from scale models that small changes in the ring bond distances and angles have little effect upon the steric hindrance factors of interest for the present discussion. The size of the angle made by the ring-N-ring bonds is important, however, since, as this angle approaches 180°, the hindrance effect should disappear. Wiegand and Merkel (*Ann.*, **550**, 175 (1942)) concluded, on the basis of absorption and thermal analysis, that benzalaniline has a linear arrangement of the $=N-C_6H_5$ group, although dipole moment data of earlier investigators (V. de Gaouck and R. J. W. Le Fèvre, *J. Chem. Soc.*, **741** (1938)) indicated a stilbene-like structure for this compound. A closer analogy for the azomethine dyes is afforded by the indoanilines. Vittum and Brown (This Journal, **69**, 152 (1947)) showed that the ring -CH₃ groups in the dye



produce a striking effect upon the absorption which could only be interpreted as arising from prevention of coplanarity of the two rings by the methyl groups, resulting in inhibition of resonance. Scale model studies show that the steric effects which were observed with this indoaniline dye would not exist if the ring-N-ring bonds were linear. Similarly, the azomethines under discussion here would not be expected to show the shielding effect unless the bond angle through the central nitrogen atom was less than 180°. Accordingly, we have pictured this angle as 125°, corresponding to the value for the $C_6H_5-N=N$ bond angles in *cis*-azobenzene (J. M. Roberston, *J. Chem. Soc.*, **232** (1939)). The length of the ring-N bonds is also significant in this connection, since the longer they are, the smaller must be the ring-N-ring bond angle to produce a given steric interference. We have used here the normal single-bond distance, although the bonds would undoubtedly be somewhat shorter because of their partial double-bond character.

(13) Brunings and Corwin (This Journal, **64**, 593 (1942)) have pointed out the mechanisms by which steric interference in a dye molecule can be relieved, *viz.*, by penetration of van der Waals radii, by loss of planarity, or by increasing bond lengths or angles. However, with the azomethines as well as with the indoanilines, the possibility exists for the dye to assume an alternate configuration relatively free from interference. Thus, while the dimethyl derivative of phenol blue shows marked effects of steric hindrance (see footnote 12), the monomethyl derivative shows a completely normal absorption behavior (Vittum and Brown, ref. 15). In this case, it must be assumed that the dye has the configuration



rather than the alternate configuration with the methyl group at the position indicated by the arrow.

(14) The effect of relatively small groups in hindering the approach of solvent molecules to a phenolic hydroxylic group has been described by Golumbic, Orchin and Weller, This Journal, **71**, 2624 (1949), and by Orchin and Golumbic, *ibid.*, **71**, 4151 (1949).

which are to be compared with dyes 1 and 4. The introduction of the electron-attracting groups, –Cl, $-NO_2$, $-CO_2H$, $-SO_2NH_2$ and –CN, into the 1-phenyl group produces a bathochromic shift of the *x*-band but little, if any, effect on the position of the *y*-band. Similar results are observed when the 1-phenyl group is replaced by the more strongly electron-attracting heterocyclic groups: 2′- and 3′-quinolyl, and 2′-benzothiazolyl. When the electron-supplying $-NH_2$ is substituted into the 1-phenyl ring, a small hypsochromic shift of the *x*-band results, the position of the *y*-band again being unchanged. With all of the dyes in this series, λ_{max} of the *y*-band is virtually unaffected by solvent changes; the presence of the 3-methyl group gives rise to the shielding effect of the benzene ring on the carbonyl–oxygen atom.

These shifts of the absorption bands, brought about by substituents in the phenyl ring attached to the 1-N atom, are in the direction to be expected on the basis of the factors discussed above. If, for example, an electron-attracting substituent is introduced, the positive charge on the 1-N atom is increased, and this, by an inductive mechanism, facilitates the accumulation of the negative charge on the 2-N atom, leading to a bathochromic shift of the *x*-band. A similar inductive effect upon the carbonyl–oxygen atom is much smaller because of the intervening carbon atom and, as a result, the position of the *y*-band is not greatly affected. It is to be noted that the effect of these substituents in the 1-phenyl ring cannot be transmitted either to the 2-nitrogen or to the carbonyl-oxygen atom by a mesomeric effect without exceeding the octet of the 1-N atom.

The general shape and width of the absorption bands exhibited by the dyes in Table II vary rather widely. While extensive correlation does not seem possible, it appears to be generally true that the introduction of relatively bulky groups into the 3-position of the pyrazolone produces a broadening of the absorption curve and a flattening on the long wave-length side. An example of this behavior is seen in the curves in Fig. 3, which show that dyes having a 3-phenyl group give distinctly flatter absorption curves than the corresponding dyes with a 3-methyl group. This effect is also shown by the furyl dye (No. 8), and to a very marked extent by the dye containing a *t*-butyl group (No. 5). Mere weight of the substituent group does not cause the effect, as is shown by the dye with a pentadecyl group (No. 6), which is almost identical in absorption with the 3-methyl dye (No. 4). In some of these cases, at least, it seems probable that the effect of broadening of the absorption band is due to the Lewis and Calvin "loose-bolt" effect,[8] whereby loosely conjugated groups, of large mass or held by weak constraints, cause a dissipation of the energy of electronic excitation, giving rise to lower-energy atomic vibrations, the process resulting in a broadening of the absorption band. However, a more detailed study of the azomethine dyes would be needed to provide a clear picture of the factors governing the shape and width of the absorption bands.

The data relating to the extinctions of the various dyes also cannot be explained at the present time, although a general pattern is to be seen in the ϵ_{max} values listed in Table II. The response of the *x*- and *y*-bands to solvent changes is particularly noteworthy. In nearly every case, the *x*-band is increased in extinction as the dielectric constant of the solvent is raised; the extinction of the *y*-band, on the other hand, is reduced, even though, as we have seen, the λ_{max} of the *y*-band is usually affected only slightly under the same circumstances. The ratio of the ϵ_{max} values for the *x*- and *y*-bands, which is of great practical significance in the photographic application of these dyes, is found to vary within wide limits. Thus, the dye from 1-phenyl-3-methyl-5-pyrazolone (No. 4) gives a ratio of ϵ_{max} values of 1.34 in cyclohexane solutions, while the dye having a 3-acylamido group (No. 14) has a ratio of 4.77. Theoretical interpretation of these and other phenomena concerning the extinction values must await a better understanding of the factors controlling intensity of light absorption.

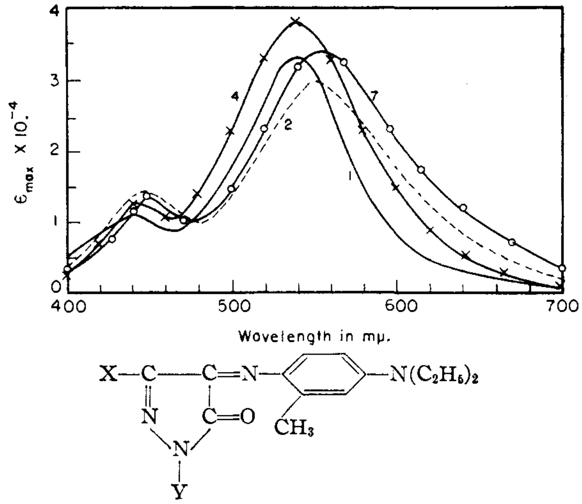


Fig. 3.—Absorption of dyes in methanol: 1, X = CH_3, Y = H; 2, X = C_6H_5, Y = H; 4, X = CH_3, Y = C_6H_5; 7, X = C_6H_5, Y = C_6H_5.

Experimental

Preparation of Pyrazolones.—Most of the pyrazolones used in the synthesis of the dyes were prepared by the methods described in the literature. References are given under Table I. The following couplers have not been previously reported:

Pyrazolone	Dye no. (Table I)	M. p., °C.	Yield, % Crude	Yield, % Final	Analysis, % Calcd.	Analysis, % Found
1-(2,4,6-Trichlorophenyl)-3-methyl-5-	18	184–186	88	50	N, 10.1 Cl, 38.4	10.1 38.1
1-(4-Cyanophenyl)-3-methyl-5-	23	172–174	79	66	N, 21.0	20.8
1-(3-Quinolyl)-3-methyl-5-	25	163–164	50	41	N, 18.6	18.3

Equimolecular portions of the hydrazine and ethyl acetoacetate were mixed at room temperature and stirred until a solid mass had formed. This mass was treated with an equal volume of alcohol containing 2% acetic acid. After 4 hours, the resulting solution was warmed to the reflux temperature and poured into three times its volume of a hot Na_2CO_3 solution. This solution was kept at a slow boil in an open beaker for 30 minutes before it was treated with decolorizing carbon, filtered and acidified. The couplers thus obtained were crystallized from a minimum amount of alcohol, giving the crude yields reported in the above table. They were then recrystallized from alcohol to constant melting point (final yield).

1-Phenyl-3-carbethoxy-5-pyrazolone.—This compound, used to prepare Dye 10, was previously prepared from ethyl oxalacetate. The following procedure uses the sodium salt of the ester, thus making the isolation of the ester unnecessary. Sodium ethyl oxalacetate, 210 g. (1 mole), was suspended in 1500 ml. of boiling alcohol. Phenylhydrazine, 119 g. (1.1 moles), was added and, after 2 minutes, all the salt was dissolved and 100 ml. of acetic acid was added. This solution was boiled for one-half hour, being concentrated thereby to one-half of its original volume. Water (30 ml.) was added and the solution was cooled. The precipitate was collected and washed with 1 l. of 40% alcohol (300 ml. on filter, 600 ml. by trituration, and then 100 ml. on filter). This was crystallized from 2 l. of xylene to give 173 g. (75%) of the pyrazolone melting at 182–184°.

1-Phenyl-4-carbethoxy-5-pyrazolone.—This intermediate, used in the preparation of the pyrazolone for Dye 3, was prepared formerly by the cyclization of diethylphenylhydrazonomethylene malonate at 170–175°. The cyclization can be effected more easily. The hydrazono compound (110 g.) was suspended in a solution of 25 g. of Na_2CO_3 in 1.3 l. of water and refluxed for 2 hours. The solution was treated with 5 g. of Darco, filtered, and acidified with HCl. The product was washed on the filter with water and dried. The yield was 90 g. (98%) of crude material, melting at 113–114°.

Preparation of Azomethine Dyes.—The azomethine dyes were prepared by the method previously described[15] for the preparation of indoanilines, an alkaline solution of the pyrazolone and 2-amino-5-diethylaminotoluene being oxidized with freshly precipitated, finely divided silver chloride. Each of the crude dyes, except No. 11 which was too insoluble, was first subjected to a preliminary purification by chromatographic adsorption. For this purpose, the crude dye (from 0.025 mole of pyrazolone) was dissolved in 50 to 100 ml. of acetone. The resulting solution was brought to a volume of 200 ml. with benzene and passed through a column, approximately 4 cm. in diameter and 45 cm. in length, packed with Doucil.[16] The chromatogram was developed and the main magenta band was finally eluted with a mixture of acetone and benzene in the same proportions used for dissolving the dye. In all cases, a small amount of yellow dye[17] passed rapidly through the column, followed by the main heavy magenta band. A dark-colored, tarry residue was retained in the upper half of the column after all of the magenta dye had been eluted. The solution of the magenta dye was then evaporated to dryness and the dye was brought to analytical purity by repeated recrystallization. The yields of purified dyes were 25 to 50% in most cases, no special precautions having been taken to avoid losses, since the main interest was in obtaining highly pure samples.

Spectrophotometric Measurements.—All the spectrophotometric measurements were made on 3.0×10^{-5} M solutions in 1-cm. cells, using the General Electric Automatic Recording Spectrophotometer. The solvents used were checked for purity by ultraviolet absorption measurements.

Acknowledgment.—The authors are grateful to Mr. E. E. Richardson for preparing the many spectrophotometric curves required in this work.

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[15] P. W. Vittum and G. H. Brown, THIS JOURNAL, **68**, 2235 (1946).

[16] Sodium aluminum silicate, obtained from the Philadelphia Quartz Co.

[17] Identified in earlier unpublished work as 4,4'-bis-(diethylamino)-2,2'-dimethylazobenzene. Gerbaux[7] also isolated *p,p'*-bis-(dialkylamino)-azobenzene derivatives from the pyrazolone-coupling reaction mixtures.

ROCHESTER, N. Y. RECEIVED AUGUST 23, 1950

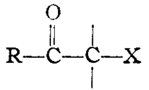
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

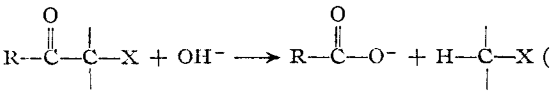
Mechanism of the Hydrolytic Cleavage of Carbon–Carbon Bonds. I. Alkaline Hydrolysis of β-Diketones[1]

BY RALPH G. PEARSON AND EVAN A. MAYERLE

The rates of alkaline hydrolysis of acetylacetone, methylacetylacetone and dimethylacetylacetone have been studied over a wide range of concentrations, and the "true" rate constants for the reactions have been calculated.

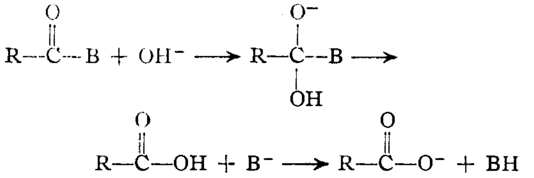
The mechanism appears to involve reactions of the neutral diketone molecule with either one or two hydroxide ions for acetylacetone and methylacetylacetone, but with only one hydroxide ion for dimethylacetylacetone. The "acid" and "ketone" cleavages of acetoacetic ester are commented upon.

Substances of the general formula  $R{-}\overset{O}{\overset{\|}{C}}{-}\underset{|}{\overset{|}{C}}{-}X$ where X is a suitable activating group are readily cleaved by aqueous alkali to give salts of carboxylic acids.



$$R{-}\overset{O}{\overset{\|}{C}}{-}\underset{|}{\overset{|}{C}}{-}X + OH^- \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}O^- + H{-}\underset{|}{\overset{|}{C}}{-}X \quad (1)$$

The group X must be a strong electron-attracting group such as nitro, carbonyl, carbalkoxyl or, in some cases, quaternary nitrogen. Halogen is effective if three atoms are alpha to the carbonyl.[2] It is reasonable to expect that the mechanism of this hydrolysis is analogous to that of the similar saponification of esters. Hauser and his co-workers[3] have written for example



$$R{-}\overset{O}{\overset{\|}{C}}{-}B + OH^- \longrightarrow R{-}\underset{OH}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}{-}B \longrightarrow$$

$$R{-}\overset{O}{\overset{\|}{C}}{-}OH + B^- \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}O^- + BH \quad (2)$$

for the mechanism of both reactions, B^- being either an alkoxyl ion or a displaceable carbanion such as $^-CH_2COCH_3$. An investigation, however, of the kinetics of alkaline hydrolysis of some 2-ketoalkylpyridinium salts[4] and of chloral hydrate[5] showed that the variation of the rate of cleavage with hydroxide ion concentration did not correspond to the demands of mechanism (2).

These compounds (and two of the β-diketones reported here) are acids capable of being ionized by alkali, the quaternary salts because of the α-hydrogen, and chloral hydrate because of the acidic hydroxyl. Furthermore, their acid strengths are such that the reaction

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[1] Abstracted from the M.S. thesis of Evan A. Mayerle, Northwestern University, 1950.

[2] For general reviews see Fuson and Bull, *Chem. Revs.*, **15**, 275 (1934), and Kröhnke and Heffe, *Ber.*, **70**, 864 (1937).

[3] Hauser, Swamer and Ringler, THIS JOURNAL, **70**, 4023 (1948).

[4] Pearson and Dillon, *ibid.*, **70**, 1933 (1948).

[5] Gustafsson and Johanson, *Acta Chem. Scand.*, **2**, 42 (1948).