TABLE I
COMPARISON OF ULTRAVIOLET ABSORPTION SPECTRA OF DEHYDRORUBINIUM (IV) WITH ANALOGOUS DEHYDROBERBERINIUM SYSTEMS (V)

Dehydro-	max, mμ[a]					min, mμ			
Palmatrubinium	248	281		354	477	263		337	412
Palmatinium	246	285	328	355	464	268	306	344	404
Berberubinium	249	281		352	470	268		334	415
Berberinium[b]	246	278	310	348	460	257	290.5	332	405

[a] Except as noted, bromides were used. [b] As chloride.

Experimental[7]

3-Methoxy-2-hydroxybenzyl alcohol[8] (prepared in 68% yield by sodium borohydride reduction of the aldehyde) was converted to the bromide by treatment with phosphorus tribromide. The crude 3-methoxy-2-hydroxybenzyl bromide was not purified.

Dehydropalmatrubinium (IV. R = CH_3) Bromide.—One gram of 6,7-dimethoxyisoquinoline-1-carboxaldoxime[6] was allowed to react with 1 g. of crude 3-methoxy-2-hydroxybenzyl bromide in 7 ml. of dimethylformamide, at first for a few minutes in the steam bath, and then at room temperature for 24 hr. The yellow crystals of the crude quaternary salt were collected, washed with ether, and then cyclized by heating on the steam bath with 12 ml. of concd. hydrochloric acid. After only 10 min. red crystals started to precipitate. The mixture was cooled and the product collected and recrystallized from methanol–ethyl acetate as red needles, m.p. 218–220° dec. (sealed tube), yield 2 g. (100%).

Anal. Calcd. for $C_{20}H_{18}BrNO_4 \cdot 2H_2O$: C, 53.10; H, 4.86; N, 3.10. Found: C, 53.50; H, 4.69; N, 3.32.

The Perchlorate (IV. R = CH_3) crystallized from dimethyformamide-methanol as red needles, m.p. 313–314° dec. (sealed tube).

Anal. Calcd. for: $C_{20}H_{18}ClNO_8 \cdot 2H_2O$: C, 50.90; H, 4.66; N, 3.00. Found: C, 51.22; H, 4.86; N, 3.16.

Tetrahydropalmatrubine (I).—A suspension containing 200 mg. of dehydropalmatrubinium bromide in 150 ml. of methanol was hydrogenated at atmospheric pressure for 2 days in the presence of 40 mg. of platinum oxide catalyst. The colorless solution was concentrated under reduced pressure and the residue treated with a dilute solution of sodium carbonate and then extracted with ether. The residue obtained by evaporation of the ether was crystallized twice from dilute methanol as colorless prisms, m.p. 148° (lit.,[3] m.p. 148–149°). The base slowly develops color on storage.

Anal. Calcd. for $C_{20}H_{23}NO_4$: C, 70.38; H, 6.74; N, 4.10. Found: C, 70.33; H, 6.93; N, 3.95.

Dehydroberberubinium (IV. R—R= —CH_2—) Bromide.—Quaternization of 1.1 g. of 6,7-methylenedioxyisoquinoline-1-carboxaldoxime[5] with 1.1 g. of crude 3-methoxy-2-hydroxybenzyl bromide was carried out in 9 ml. of dimethylformamide and the product cyclized as in the case of dehydropalmatrubine. Two grams (100%) of red needles were obtained, m.p. 203–205° dec.

Anal. Calcd. for $C_{19}H_{14}BrNO_4$: C, 57.00; H, 3.50; N, 3.50. Found: C, 56.83; H, 3.63; N, 3.35.

The perchlorate (IV. R—R = —CH_2—) crystallized from dimethylformamide–methanol as red needles, m.p. 338° dec.

Anal. Calcd. for $C_{19}H_{14}NClO_8$: C, 54.35; H, 3.33; N, 3.33. Found: C, 54.48; H, 3.46; N, 3.40.

Acetyldehydroberberubinium Bromide.—Dehydroberberubinium bromide was acetylated by refluxing for 3 hr. in acetic anhydride. The product crystallized from methanol as yellow prisms, m.p. 145–146°, and slowly turned to a buff color on keeping.

Anal. Calcd. for $C_{21}H_{16}BrNO_5$: C, 57.01; H, 3.61; N, 3.16. Found: C, 57.32; H, 3.90; N, 3.15.

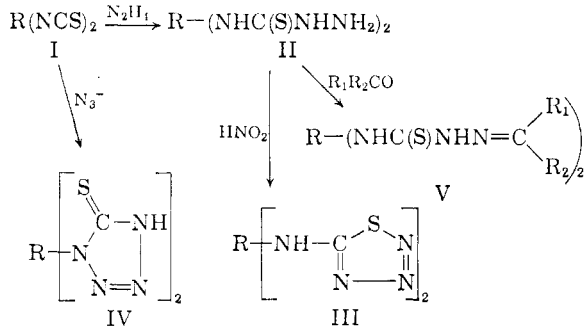
Diisothiocyanates and Derivatives[1]

EUGENE LIEBER[2] AND RALPH SLUTKIN[3]

Department of Chemistry, Roosevelt University and DePaul University, Chicago, Ill.

Received August 15, 1961

The present investigation relates to the synthesis of difunctional compounds of the aminothiatriazole and tetrazolinethione series.[4,5] For this purpose, diisothiocyanates (I) were prepared from diamines and their conversion to di-thiosemicarbazides (II), -aminothiotriazoles (III), and -tetrazoline-5-thione (IV) studied. Most of the compounds thus prepared have not been previously reported. Thiosemicarbazones (V) were prepared to characterize II.



The infrared absorption spectra of I, II, III, and IV were determined. All of the diisothiocyanates show a strong or medium band, near 2040 cm.$^{-1}$ or between 2062–2105 cm.$^{-1}$. The 2040-cm.$^{-1}$ band is slightly lower than the characteristic vibrational frequencies for the monofunctional isothiocyanates.[6] It has been suggested that the bands in the 1000–1100-cm.$^{-1}$ region are due to the isothiocyanate stretching vibration.[6] As in the monofunctional compounds[7] the S—H band (2600–

(1) The authors gratefully acknowledge the support of this investigation by the U. S. Army Research Office.

(2) To whom all correspondence should be addressed.

(3) Abstracted from the M.S. Thesis, DePaul University, Chicago, Ill., 1961.

(4) E. Lieber, C. N. Pillai, and R. D. Hites, *Can. J. Chem.*, **35**, 832 (1957).

(5) E. Lieber, C. N. Pillai, J. Ramachandran, and R. D. Hites, *J. Org. Chem.*, **22**, 1750 (1957).

(6) E. Lieber, C. N. R. Rao, and J. Ramachandran, *Spectrochimica Acta*, **13**, 296 (1959).

(7) E. Lieber, C. N. R. Rao, J. Ramachandran, and R. D. Hites, *Can. J. Chem.*, **36**, 801 (1958).

TABLE I
DIISOTHIOCYANATES R(NCS)$_2$

R	Functional Positions, (NCS)$_2$	% Yield[a]	M.P. Found	M.P. Reptd.	Ref.	Cryst. Form	Formula	N Calcd.	N Found	S Calcd.	S Found
C_6H_4	1,4	67	132	130–131	[b]	Pr. ndls.	$C_8H_4N_2S_2$				
2-Cl—C_6H_3[c,d]	1,4	59	58	[e]	[e]	Lt. yel. lftls.	$C_8H_3ClN_2S_2$	12.36	12.56	28.26	27.60
2-CH_3—C_6H_3[c]	1,4	47	75			Lt. yel. ndls.	$C_9H_6N_2S_2$	13.59	13.78	31.07	31.22
C_6H_4[f]	1,3	59	54–55	53, 55	[b]	Wh. ndls.	$C_8H_4N_2S_2$	14.58	14.70	33.33	33.25
4-Cl—C_6H_3[c,g]	1,3	60[h]	33			Wh. lflts.	$C_8H_3ClN_2S_2$	12.36	12.09	28.26	27.45
4-CH_3—C_6H_3	1,3	45	57	56	[b]	Wh. ndls.	$C_9H_6N_2S_2$	13.59	13.81	31.07	30.90
4-CH_3O—C_6H_3[c]	1,3	70	96			Lt. yel. pr.	$C_9H_6N_2OS_2$	12.61	12.42	28.83	28.65
$C_{13}H_{10}$[i,j]	4,4′	69	138–139	143–144 196	[k]	Lt. yel. ndls.	$C_{14}H_{10}N_2S_2$	9.93	10.27	22.70	22.81
$C_{14}H_{12}$[c,l]	4,4′	84	126–127			Lt. yel. ndls.	$C_{16}H_{12}N_2S_2$	9.46	9.55	21.62	21.68
$C_{10}H_6$[c,l,m]	1,5	35	177–178			Wh. ndls.	$C_{12}H_6N_2S_2$	11.57	11.41	26.45	26.59
C_2H_4	1,2	16	B.p. 100/3 mm.	B.p. 141/10 151/15	[n]	Lt. yel. liq.	$C_4H_4N_2S_2$	19.44	19.61	44.44	44.19

[a] Based on pure product. [b] O. Billeter and A. Steiner, *Ber.*, 20, 230 (1887). [c] New compound. [d] Calcd.: Cl, 15.67. Found: Cl, 15.65. [e] Not reported. [f] The monothiourethane was obtained from ethanol–acetone, m.p. 72–73°, calcd. for $C_{10}H_{10}N_2OS$; N, 11.78; S, 26.90. Found: N, 11.90; S, 26.95. [g] Calcd.: Cl, 15.67; Found: Cl, 14.98; the product tend to revert to an oil. [h] Crude. [i] Diphenylmethane, $C_6H_4CH_2C_6H_4$. [j] Calcd.: C, 63.83; H, 3.55. Found: C, 63.98; H, 3.69. [k] Ref. 9 and 11. [l] Bibenzyl group. [m] Naphthalene group. [n] Ref. 10.

2500 cm.$^{-1}$) was not evident. The absence of this band in the spectra of IV supports the structure given. The di(tetrazolinethiones) (IV) showed bands previously observed for this class.[7] Absorption bands near 1500 cm.$^{-1}$ and 1330–1370 cm.$^{-1}$ have been assigned, tentatively, to the N—C=S and C=S structures. Skeletal vibrations of the tetrazole ring are attributed to the bands near 1080 cm.$^{-1}$, 1040 cm.$^{-1}$, and 980 cm.$^{-1}$. The characteristic infrared absorption bands for III were found to be similar to those for the monofunctional derivatives.[7]

Modification of the method[4] for the preparation of substituted-5-aminothiatriazoles by the diazotization of the di(thiosemicarbazides) gave only three derivatives of acceptable analysis (Table V), although many trials were carried out. The direct reaction[4] of hydrazoic acid with the di(isothiocyanates) in a variety of solvents failed to yield any products of acceptable analysis which varied over a wide range and were not consistent. The cause for these failures are not known.

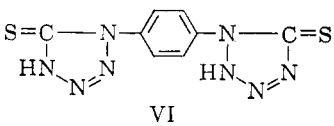
Experimental[8]

Diisothiocyanates.—The aromatic diisothiocyanates were prepared by the method of Dyson.[9,10] In those cases in which the product did not precipitate, it was recovered by neutralization of the acid solution or by extraction with organic solvents. Ethylene diisothiocyanate was prepared by the method of Klöpping.[11] The diisothiocyanates so prepared are listed in Table I. Recrystallization was from acetone or aqueous acetone. **4,4′-Di(isothiocyano)diphenylmethane** has previously been reported to have a melting point of 143–144° [9] and 196°.[12]

Dithiosemicarbazides (II).—The method of Lieber[4] was used. Dimethylformamide was used to effect recrystallization. The crude products are highly insoluble in the usual organic solvents. The crude diisothiosemicarbazide was dissolved in warm dimethylformamide, ethanol was then added to promote crystallization. Benzene or ethanol, instead of ether, can be used as the solvent for reaction. The hydrazine was occasionally added in ethanol rather than in aqueous solution, depending on the solubility requirements. The substances prepared are listed in Table II.

Thiosemicarbazones. (V).—Acetone thiosemicarbazones were prepared by refluxing the components in dimethylformamide on the steam bath for 1 hr. The ketone derivatives were recovered by pouring the clear solution into ice water. The aldehyde derivatives were recovered by diluting the dimethylformamide solution with ethanol. Recrystallizations were effected from ethanol or from dimethylformamide, adding ethanol to the latter if necessary. The compounds so prepared are summarized in Table III. All the substances summarized in this Table are new compounds. In a similar manner, hydrazones were readily prepared from benzaldehyde and other ketones and aldehydes.

Di(1-substituted tetrazoline-5-thiones) (IV).—These are prepared from I by a modification of the method of Lieber.[12] The *p*-phenylene derivative (VI) is described as typical. *p*-Phenylene diisothiocyanate (3.0 g., 0.016 mole) and 3.3 g. (0.05 mole) of sodium azide were used to 100 ml. of water and refluxed for 4 hr., the solution becoming greenish.



VI

(8) Microanalyses by Dr. C. Weiler and Dr. F. B. Strauss, Oxford, England. Melting points were determined in glass capillaries and are uncorrected. Infrared absorptions were recorded on a Perkin-Elmer Model 21 with sodium chloride optics over the range 2–15 μ using an automatic slit drive with a program of 927 and a scanning rate of twenty minutes. Liquids were handled in a demountable cell with a 0.025-mm. silver spacer. Solids were mulled in 2–3 drops of white mineral oil using sufficient sample to provide good absorption intensity. Thiophosgene was supplied by Rapter Laboratories, Chicago, Ill.

(9) G. M. Dyson, *J. Chem. Soc.*, 1702 (1924).

(10) G. M. Dyson and D. W. Browne, *ibid.*, 318 (1934).

(11) H. L. Klöpping and G. J. M. VanderKerk, *Rec. trav. chim.*, **70**, 949 (1951).

(12) F. H. McMillan and J. H. King, *J. Am. Chem. Soc.*, **72**, 4323 (1950).

TABLE II

DI(THIOSEMICARBAZIDES)

R—(NBC(S)NHNH$_2$)$_2$

R	Functional Positions	% Yield[a]	M.P.[b-d]	Formula	N Calcd.	N Found	S Calcd.	S Found
C_6H_4[e]	1,4	93	205–206	$C_8H_{12}N_6S_2$	32.79	33.10	25.10	25.20
2-ClC_6H_3[e,b]	1,4	85	193	$C_8H_{11}ClN_6S_2$	28.92	28.99	22.03	22.34
2-$CH_3C_6H_3$[e]	1,4	95	197–198	$C_9H_{14}N_6S_2$	31.11	31.00	23.70	23.96
C_6H_4[e]	1,3	95	189–190	$C_8H_{12}N_6S_2$	32.79	32.17	25.01	24.72
4-ClC_6H_3[e,g]	1,3	76	201[h]	$C_8H_{11}ClN_6S_2$	28.92	28.61	22.03	21.68
4-$CH_3C_6H_3$	1,3	86	196[i]	$C_9H_{14}N_6S_2$	31.11	30.81	23.70	23.58
4-$CH_3OC_6H_3$[e]	1,3	95	190	$C_9H_{14}N_6OS_2$	29.37	29.29	22.38	22.56
$C_{13}H_{10}$[e,j]	4,4′	94	193–194	$C_{15}H_{18}N_6S_2$	25.00	25.21	19.05	18.81
$C_{14}H_{12}$[e,k]	4,4′	88	209	$C_{16}H_{20}N_6S_2$	23.33	23.60	17.78	17.80
$C_{10}H_6$[e,l]	1,5	95	223	$C_{12}H_{14}N_6S_2$	27.45	27.20	20.92	21.11
C_2H_4[e]	1,2	85	225	$C_4H_{12}N_6S_2$	40.38	40.20	30.76	30.00

[a] Crude. [b] All recrystn. were from dimethylformamide. [c] White amorphous powder except where noted. [d] With decompn. [e] New compound. [f] Calcd.: Cl, 12.22. Found: Cl, 11.92. [g] Calcd.: Cl, 12.22. Found: Cl, 12.10. [h] Tan powder. [i] J. Klarer and R. Behnisch, Ger. Patent **832,891** (1952). [j] Diphenylmethane group. [k] Bibenzyl group. [l] Naphthalene.

TABLE III

ACETONE THIOSEMICARBAZONES

R(NHC(S)NHN=C(CH_3)$_2$)$_2$

R[a]	Functional Positions	% Yield	M.P.	Formula	N Calcd.	N Found	S Calcd.	S Found
C_6H_4	1,4	76	207–208[b,c]	$C_{14}H_{20}N_6S_2$	25.00	24.90	19.05	18.70
2-ClC_6H_3[d]	1,4	78	197–198[e]	$C_{14}H_{19}ClN_6S_2$	22.67	22.67	17.27	17.09
2-$CH_3C_6H_3$	1,4	60	187[e]	$C_{15}H_{22}N_6S_2$	24.00	24.30	18.29	17.96
C_6H_4	1,3	76	198–199[c]	$C_{14}H_{20}N_6S_2$	25.00	24.70	19.05	19.29
4-ClC_6H_3	1,3	67	189[e]	$C_{14}H_{19}ClN_6S_2$	22.76	22.80	17.27	17.10
4-$CH_3C_6H_3$	1,3	69	183–184[c]	$C_{15}H_{22}N_6S_2$	24.00	24.40	18.29	18.26
4-$CH_3OC_6H_3$	1,3	73	192[g]	$C_{15}H_{22}N_6OS_2$	22.95	22.78	17.49	17.61
$C_{13}H_{10}$[h]	4,4′	83	189–190[i]	$C_{21}H_{26}N_6S_2$	19.72	19.56	15.02	14.51
$C_{14}H_{12}$[j]	4,4′	53	208[i]	$C_{22}H_{28}N_6S_2$	19.09	18.78	14.55	14.65
$C_{10}H_6$[k]	1,5	83	210[e]	$C_{18}H_{22}N_6S_2$	21.76	21.58	16.58	16.48
C_2H_4	1,2	56	216[i]	$C_{10}H_{20}N_6S_2$	29.17	28.80	22.22	22.60

[a] New compound. [b] All m.p. all decompn. [c] White amorphous powder. [d] Calcd: Cl, 9.58. Found: Cl, 9.73. [e] Gray powder. [f] Calcd.: Cl, 9.58. Found: Cl, 9.31. [g] White ndls. [h] Diphenylmethane group. [i] Light yellow crystals. [j] Bibenzyl group. [k] Naphthalene.

TABLE IV

DI(TETRAZOLINETHIONES)

R[a]	Functional Positions	% Yield	M.P.	Formula	N Calcd.	N Found	S Calcd.	S Found
C_6H_4	1,4	93	210[b]	$C_8H_6N_8S_2$	40.33	40.50	23.00	22.98
2-ClC_6H_3[c]	1,4	60	173	$C_8H_5ClN_8S_2$	35.84	36.02	20.48	20.40
2-$CH_3C_6H_3$	1,4	81	190	$C_9H_8N_8S_2$	38.36	37.96	21.92	21.73
C_6H_4	1,3	76	179	$C_8H_6N_8S_2$	40.33	41.00	23.00	23.20
4-ClC_6H_3[d]	1,3	61	160	$C_8H_5ClN_8S_2$	35.84	35.35	20.48	19.30
4-$CH_3C_6H_3$	1,3	60	180	$C_9H_8N_8S_2$	38.36	38.20	21.92	21.58
4-$CH_3OC_6H_3$	1,3	67	126	$C_9H_8N_8OS_2$	36.36	36.55	20.78	20.76
$C_{13}H_{10}$[e]	4,4′	82	188	$C_{15}H_{12}N_8S_2$	30.43	30.20	17.39	17.51
$C_{14}H_{12}$[f]	4,4′	53	191	$C_{16}H_{14}N_8S_2$	29.32	29.21	16.76	16.78

[a] New compound. [b] All detonate or decompose violently. [c] Calcd.: Cl, 11.36. Found: Cl, 11.70. [d] Calcd.: Cl, 11.36. Found: Cl, 11.42. [e] Diphenylmethane. [f] Bibenzyl.

The alkaline solution was filtered, extracted twice with ether to remove unchanged isothiocyanate, and acidified with concd. hydrochloric acid (Congo red paper), giving a creamy white solid. The yield was 4.1 g. (93%) melting with detonation at 205°. Recrystallization from ethanol gave white leaflets which detonated at 208°.

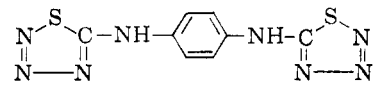
Anal. Calcd. for $C_3H_6N_8S_2$: C, 34.52; H, 2.17; N, 40.27; S, 23.04; neut. equiv., 139. Found: C, 34.50; H, 2.40; N, 40.50; S, 22.98; neut. equiv., 137.

The ultraviolet absorption was taken with a Beckman DU spectrophotometer at a concentration of 11 mg./ml. in 95% ethanol; λ_{max} was 228 mμ; log ϵ_{max} 4.40.

The ditetrazolinethiones derived from diphenylmethane and bibenzyl, because of solubility considerations, were prepared in a benzene–water two-phase system, with recovery of the product from the aqueous alkaline layer.

The di(tetrazolinethiones) are listed in Table IV.

Di(aminothiatriazoles) (III).—These were prepared by a modification of the method of Lieber.[4] The procedure for the



VII

p-phenylene derivative (VII) is typical. The *p*-phenylenedi(thiosemicarbazide), 0.6 g. (0.0023 mole), was dissolved in

TABLE V
DI(AMINOTHIATRIAZOLES)

R[a]	Functional Positions	% Yield	M.P[b]	Formula	N Calcd.	N Found	S Calcd.	S Found
C_6H_4	1,4	80	180	$C_8H_6N_8S_2$	40.33	40.25	23.00	22.90
C_6H_4	1,3	82	162	$C_8H_6N_8S_2$	40.33	40.30	23.00	22.85
$C_{13}H_{10}$[c]	4,4′	86	148	$C_{15}H_{12}N_8S_2$	30.43	30.10	17.39	17.20

[a] New compound. [b] With detonation. [c] Diphenylmethane.

25 ml. of dimethylformamide, cooled to 5°, and agitated by a magnetic stirring bar. There was then added 4 ml. of 4 *N* hydrochloric acid and 0.4 g. (0.006 mole) of sodium nitrite in 5 ml. of water over a 10-min. period. A yellow-green solid precipitated immediately. The reaction was maintained at 5–10° for 20 min. The crude product, 0.51 g. (80%), was recovered as a greenish powder, detonating at 160°. Recrystallization was effected by dissolving in 15 ml. of dimethylformamide, decolorizing with charcoal, filtering, and then diluting with ethanol. A light tan powder, detonating at 180° was obtained. The di(aminothiatriazoles) are listed in Table V.

(13) E. Lieber and J. Ramachandran, *Can. J. Chem.*, **37**, 101 (1959).

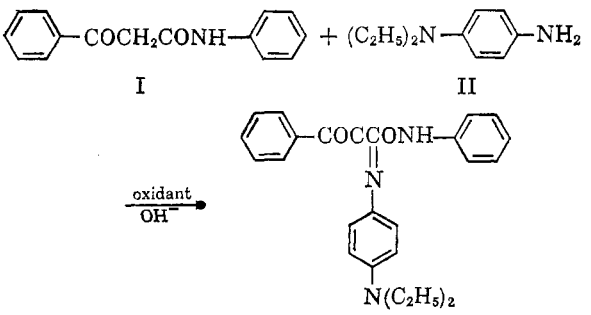
Formation of Quinoxalone Dye in the Color Photographic Coupling Reaction

PAUL M. MADER

Communication No. 2230 from the Kodak Research Laboratories, Rochester, N. Y.

Received September 25, 1961

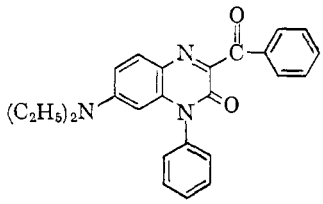
A large class of the compounds ("couplers") giving yellow color photographic image dyes contain the grouping, —$COCH_2CONH$—.[1] Reaction of the oxidized *p*-phenylenediamine derivative developing agent at the activated methylene group of such a coupler gives azomethine dye, as shown.



III

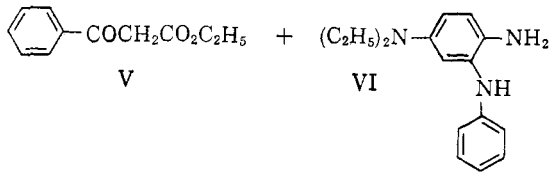
When couplers of this class react with oxidized color developing agents in dilute solution, it is often observed[2] that, in addition to the azomethine dye, a yellow dye of another type is produced. This dye differs from the azomethine dye in its fluorescence, smaller value of λ_{max}, and greater slope of the absorbance *vs.* λ curve on the long wave length side of λ_{max}. The present communication gives a proof of structure or a representative of this type of dye and evidence for a mechanism by which it forms.

On the basis of the fluorescence and absorption spectra, it was suggested[3] several years ago that the fluorescent, yellow dyes formed along with the yellow azomethine dyes are quinoxalones. For example, I and II would give IV. Structure IV

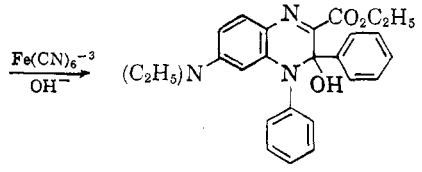


IV

has now been verified by means of the following alternative synthesis:



V VI



VII

Irradiation of the yellow pseudo base, VII, in solution converts it to IV, identical with the fluorescent dye obtained from I and II.

The oxidative condensation of dicarbonylmethylene compounds with *p*-phenylenediamines having a monosubstituted amino group *ortho* to the unsubstituted amino group has been described by Schmidt *et al.*[4] The products are yellow in the presence of alkali and magenta under neutral or weakly acidic conditions. The new dye VII shows this typical behavior. Schmidt *et al.*[4] proposed that in the magenta form the dyes have a quinoxalinium structure, whereas in the yellow form they exist as the corresponding pseudo bases (1,2-

(1) P. W. Vittum and A. Weissberger, *J. Phot. Sci.*, **2**, 81 (1954).
(2) G. H. Brown, private communication.
(3) P. W. Vittum, private communication.
(4) W. A. Schmidt, V. Tulagin, J. A. Sprung, R. C. Gunther, R. F. Coles, and D. E. Sargent, *Ind. Eng. Chem.*, **45**, 1726 (1953).