

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,  
No. 455]

RESEARCHES ON THIAZOLES. VI. A NEW GROUP OF DYES  
FROM POISON GASES THROUGH THE 2-AMINOTHIAZOLES  
AS INTERMEDIATES. THE PREPARATION OF  
THIAZOLE DYES OF DOEBNER VIOLET TYPE<sup>1,2</sup>

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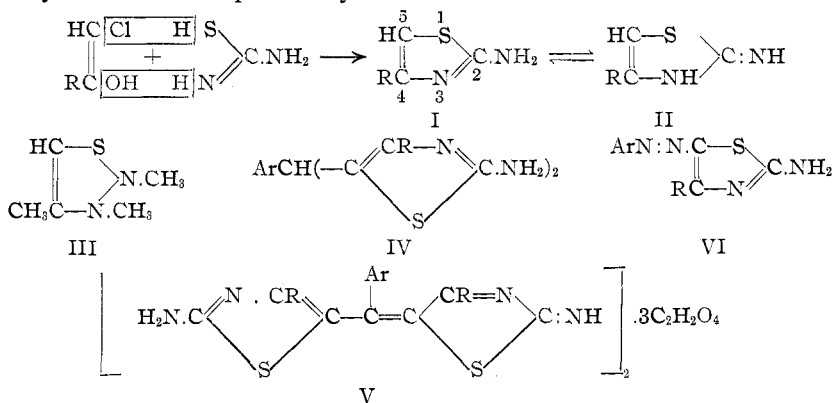
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Introductory

Halogenated aldehydes and ketones of the type  $\text{RCO} \cdot \text{CH}_2\text{X} \rightleftharpoons \text{RC}(\text{OH}) : \text{CHX}$  ( $\text{X} = \text{halogen}$ ) include some of the most powerful lachrymatory compounds known, such as the halogenated acetones and chloroacetophenone used during the war as "tear gases."

Many years ago it was discovered<sup>3,4</sup> that 2-aminothiazoles are obtained easily from such compounds by condensation with thio-ureas.



Ar = simple or substituted aromatic radical. R = H, alkyl or aryl group.

Hantzsch and Weber<sup>5</sup> and others<sup>3,4,6,7,8,9,10,11</sup> subsequently studied

<sup>1</sup> Presented before the Division of Dye Chemistry at the meeting of the American Chemical Society, Washington, D. C., April 23, 1924.

<sup>2</sup> The chloroacetophenone necessary for this investigation was presented by the Chemical Warfare Service, United States Army, through the courtesy of Brig.-Gen. Amos A. Fries, Chief, to whom our grateful acknowledgments are due.—M. T. B. and M. C.

<sup>3</sup> Traumann, *Ann.*, **249**, 35 (1888).

<sup>4</sup> Popp, *Ann.*, **250**, 273 (1889).

<sup>5</sup> Hantzsch and Weber, *Ber.*, **20**, 3121 (1887).

<sup>6</sup> Wohmann, *Ann.*, **259**, 277 (1890).

<sup>7</sup> Schatzmann, *Ann.*, **261**, 8 (1891).

<sup>8</sup> Näf, *Ann.*, **265**, 109 (1891).

<sup>9</sup> Hantzsch and Schwab, *Ber.*, **34**, 834 (1901).

<sup>10</sup> Young and Crookes, *J. Chem. Soc.*, **89**, 59 (1906).

<sup>11</sup> Morgan and Morrow, *ibid.*, **107**, 1291 (1915).

various 2-aminothiazoles and came to the conclusion that such compounds existed in the two tautomeric forms represented by Formulas I and II.

Traumann<sup>12</sup> prepared the trimethyl derivative (III), and made the following statement concerning it: "A Thiazole Green, corresponding to Malachite Green or to Thiophene Green, could not be obtained from this dimethyl base, which is not to be wondered at in view of the disappearance of the supposititious analogy of this base to dimethylaniline. In general, trithiazylmethane dyes appear not to exist, probably because the *para* position is lacking in the azoles. Thus, the joint oxidation of thiazylamines with methylthiazylamine by the action of mercuric chloride, etc., likewise yields no trace of dye."

This pronouncement does not agree altogether either with our own views concerning the dye possibilities of these aminothiazoles or with our experimental results, for it has been observed frequently that sulfur in cyclic union is the equivalent of the  $-\text{CH}:\text{CH}-$  group, as is well illustrated in the close parallelism in physical and chemical properties between the benzene and thiophene series, or between the thiazoles themselves and the corresponding pyridines. The 2-aminothiazoles, therefore, carry the amino group in a position which is to all intents and purposes *para* to Position 5.

In support of this assumption, we have succeeded in condensing these 2-aminothiazoles with aromatic aldehydes, in the presence of hydrochloric acid, to mono-aryldithiazylmethanes (IV), from which the corresponding carbinols and dyes (V) have been obtained. Such condensations were accomplished with 2-aminothiazoles carrying alkyls instead of aryls in Position 4, thus demonstrating the fact that this condensation with aromatic aldehydes was not dependent upon an aryl group in that position, that such a group did not participate in the reaction, and that therefore the attachment of the aldehyde residue was at Position 5.

The leuco bases so obtained were generally colorless or pale yellow, the carbinols red-black and the dyes (oxalates) green-black.

A comparison of certain properties of these new products with those triphenylmethane derivatives of analogous structure discloses an interesting resemblance. The leuco bases in both cases form crystalline addition products with benzene. Both groups of dyes form dark green crystals, those of the thiazole type being smaller, darker and of less marked coppery luster. The Malachite Green dyes are easily soluble in water, the thiazoles less readily; addition of excess of ammonium hydroxide precipitates the carbinol in both instances as a dark solid. Both dye silk, wool or mordanted cotton a green, the thiazoles giving a bluer and duller shade and being tinctorially weaker. Both are fugitive in direct sunlight and both give red solutions in an excess of concd. hydrochloric acid.

<sup>12</sup> Traumann, *Ann.*, **249**, 50 (1888).

Although of Doebner Violet type, in the sense that the thiazole amino groups are unalkylated, these compounds give green dyeings, a bathochromic effect which doubtless is to be ascribed to the sulfur present in the molecule. Just as there is not any very striking difference between the shade produced by Doebner Violet itself and that produced by its derivative carrying a dimethylamino group in the *para* position on the free phenyl group, so here the shade is not greatly altered by using *p*-dimethylamino-benzaldehyde, in place of benzaldehyde as the condensing agent.

As mentioned, the dyes prepared so far are inferior to Malachite Green, but the work is being continued with especial reference to the connection between structure and tinctorial properties, and in the hope that some useful products may be discovered.

Further, we have learned that the aminothiazoles may be used as couplers for diazotized amines, and a number of new red azo dyes (VI) have been prepared in this way.

Experiments are being conducted also to determine to what extent other reactions of the aromatic amines can be duplicated with these aminothiazoles, and whether the aminopyridines behave similarly or not.

### Experimental Part

**2-Aminothiazole** was prepared from the dichloro ether and thio-urea by the method of Traumann,<sup>3</sup> yield, 60%; m. p., 92° (corr.). Traumann found a melting point of 90°.

A red azo dye was obtained from this thiazole by coupling it with diazotized *p*-nitro-aniline. So far as we are aware, it has not been shown previously that 2-aminothiazoles could function thus as couplers in the production of azo dyes, although it has been known for many years that they themselves could be diazotized and combined with other couplers.

Attempts to secure the 2-cyanothiazole from the amine through the diazo reaction proved futile.

**4-Methyl-2-aminothiazole**, from molecular equivalents of chloro-acetone and thio-urea, was purified by distillation under diminished pressure, and then formed colorless crystals, m. p. 42° (corr.), which changed quite rapidly to a dark red or brown tar on standing.

This thiazole was prepared first by Tscherniac and Norton,<sup>18</sup> who christened it "Rhodanpropimin." It was investigated later by others also,<sup>8,9,10,14</sup> who likewise recorded the melting point as 42°.

**Di(4-methyl-2-aminothiazyl-5)phenylmethane (IV)**.—A mixture of two moles of the methylaminothiazole, 1 mole of benzaldehyde and  $\frac{2}{3}$  mole of hydrochloric acid was refluxed for three hours at 145°, and was then cooled, dissolved in alcohol, ammonium hydroxide added to alkaline reaction and the product diluted with sufficient water to precipitate the leuco base. This was collected, dried and purified by repeated crystallization from benzene. Microscopic, brownish crystals resulted, which melted with decomposition at about 180° (corr.), after previous sintering at a much lower temperature; yield, 55%. They dissolved readily in alcohol, acetone, aniline or diphenyl-

<sup>18</sup> Tscherniac and Norton, *Ber.*, **16**, 345 (1883).

<sup>14</sup> Hantzsch, *Ber.*, **25**, 3283 (1892).

methane; but slightly in chloroform, benzene, toluene or xylene; and were practically insoluble in water. For analysis, the crystals were dried for 48 hours at 105°.

*Anal.* Calc. for  $C_{15}H_{16}N_4S_2$ : S, 20.27. Found: 20.15.

An alcoholic solution of this leuco base when oxidized by lead dioxide and hydrochloric acid gave a purplish-red solution, but no attempt was made to isolate either the carbinol or the dye.

4-Phenyl-2-aminothiazole was discovered by Traumann,<sup>3</sup> who prepared it from chloro-acetophenone and thio-urea, and gave its melting-point as 147°. We followed his method, with a few minor modifications, and purified our product by repeated crystallization from alcohol. Colorless, transparent, short needles were obtained, m. p. 152.5° (corr.), of faint but agreeable odor, soluble in boiling water, in alcohol, ether or benzene; yield, 90%.

The hydrochloride and acetyl derivative were also prepared and found to agree with Traumann's description of them, except that we obtained a melting point of 212.3° (corr.) for our acetyl derivative, whereas the value he reported was 208°.

Nitration of this acetyl derivative was attempted by various methods, but no nitration occurred and the aminothiazole itself was recovered unchanged (except for hydrolysis of the acetyl group).

Similar lack of success attended our efforts to convert the aminothiazole into the corresponding nitrile, through the diazo reaction. The purpose of these experiments was to secure a 4-phenylthiazole-2-carboxylic acid, in order to compare its pharmacological properties with those of other compounds of cinchophen type.

4-Phenyl-2-*p*-nitrobenzalaminothiazole.—In the absence of mineral acid, Hantzsch and Schwab<sup>9</sup> have shown that aminothiazoles undergo the normal condensation with aromatic aldehydes to Schiff bases.

*p*-Nitrobenzaldehyde (4.53 g.) and the phenylaminothiazole (5.3 g.) condensed smoothly when heated together in alcoholic solution. The crude product was purified by repeated crystallization from alcohol. There resulted small, lustrous, orange needles; m. p., 156.8° (corr.); yield, 21%.

*Anal.* Calc. for  $C_{18}H_{10}O_2N_4S$ : S, 10.40. Found: 10.22.

Under similar conditions, piperonal did not condense with the thiazole.

Di(4-phenyl-2-aminothiazyl-5)phenylmethane (IV).—A mixture of 51.54 g. of 4-phenyl-2-aminothiazole, 14 g. of benzaldehyde and 31.5 g. of concd. hydrochloric acid was refluxed for three hours at 145°. It was then made alkaline with sodium hydroxide, unchanged benzaldehyde was blown out by a current of steam and the impure leuco base removed and purified by crystallization from alcohol. This gave colorless, rhombic plates, which sintered to a gray solid at 181° (corr.), softened at about 207° and melted with decomposition at 221° (corr.); yield, 95%.

*Anal.* Calc. for  $C_{26}H_{20}N_4S_2$ : S, 14.56. Found: 14.26.

It was very easily soluble in ethyl acetate, moderately in alcohol, toluene or xylene, less readily in ether, acetone or benzene and practically insoluble in water.

Oxidation of this compound by potassium permanganate in neutral, alkaline or acid solution gave benzoic acid as the only insoluble product. Fusion with potassium hydroxide yielded benzoic acid and a small quantity of unidentified tarry material.

When this substance was diazotized and coupled with suitable amines, phenols or their sulfo acids, new azo dyes were produced.

CARBINOL.—To a cooled solution of 13 g. of the base in 5.8 g. of concd. hydrochloric acid and 500 cc. of alcohol, 10 cc. of 40% acetic acid was added, followed by 7.5 g. of lead dioxide. This mixture was stirred continuously and the temperature maintained at 5°. When the oxidation was complete, the mixture was filtered, an ex-

cess of ammonium hydroxide added to the filtrate, the latter diluted and left overnight to precipitate the carbinol. The precipitate was removed, dried and purified by crystallization from toluene. There resulted a reddish-black solid that sintered slightly when heated and then melted sharply with decomposition at 197.3° (corr.); yield, 90%.

*Anal.* Calc. for  $C_{25}H_{20}ON_4S_2$ : S, 14.05. Found: 13.85.

It was soluble also in alcohol, acetone, ether or chloroform and practically insoluble in ligroin. From all solvents tried, it separated in an amorphous or pulverulent condition.

**DYE (OXALATE).**—To a solution of the carbinol (13 g.) in the minimum amount of acetone, there was added an aqueous solution of oxalic acid (7.2 g.) and ammonium oxalate (0.7 g.). The color of the solution changed immediately to green. On spontaneous evaporation of the solvent, the dye separated. It was purified by crystallization from dil. alcohol and then appeared as a very dark green powder.

*Anal.* Calc. for  $2C_{25}H_{18}N_4S_2 \cdot 3C_2H_2O_4$ : S, 11.17. Found: 11.38.

The dye was difficultly soluble in water, but dissolved more freely in the presence of some acetic acid and was soluble in dil. alcohol. It dyed wool or mordanted (tanned) cotton, a dull bluish-green.

A dyed wool sample was subjected to the following tests.

*Fastness to Light.*—Exposed to direct sunlight for three weeks, the color faded to a pale green.

*Washing.*—When the sample was left for 15 minutes in a 0.5% soap solution at 40°, the color altered but little and there was but slight bleeding.

*Milling.*—When the sample was left for 10 minutes in a 0.5% soap solution containing 0.4% of sodium carbonate solution, the color changed somewhat, but bleeding was only slight.

*Perspiration Test.*—The sample was impregnated with a solution containing 100 g. of common salt and a like amount of acetic acid per liter. It was then rolled up with white wool and white cotton and left in a stoppered bottle for 24 hours. The color change was slight, but the bleeding was more marked.

*Stoving.*—The sample was subjected to the fumes of sulfur dioxide for 12 hours. The color was bleached, but was restored by washing with dil. acetic acid and water.

*Carbonizing.*—The sample was saturated with a 5% solution of sulfuric acid, wrung out and dried between undyed woolen material at about 100°. It was then passed through a cold solution of sodium hydroxide (6° Tw.), rinsed and dried. The color was altered, but there was very little bleeding.

*Bleaching.*—The sample was immersed for 15 minutes in a solution (0.25° Tw. = d. 1.001) of bleaching powder. The color was bleached, but was restored by treatment with dil. acetic acid and rinsing with water.

*Fastness to Alkali.*—The sample was moistened with 6 N sodium hydroxide solution, allowed to dry and then brushed off. The color changed to red, but regained its original green shade when treated with dil. acid and rinsed.

In tinctorial power, beauty of shade, solubility in water and cost, the dye is decidedly inferior to Malachite Green.

**Di(4-phenyl-2-aminothiazyl-5)-p-chlorophenylmethane**, from the thiazole and *p*-chlorobenzaldehyde, was purified by crystallization from dil. acetone and then formed colorless, lustrous, short needles, or prismatic plates, which began to sinter to a pinkish, vitreous mass at about 148° (corr.), then darkened and finally melted at 203° (corr.) to a dark red liquid; yield, nearly that calculated.

*Anal.* Calc. for  $C_{26}H_{19}N_4S_2Cl$ : S, 13.47. Found: 13.34.

The substance was soluble in methyl or ethyl alcohol, or in acetone. Oxidized

by lead dioxide in acid solution, it gave the corresponding carbinol, the oxalate of which was a dark green powder that dyed wool a dull blue-green.

*Anal.* Calc. for  $2C_{25}H_{17}N_4S_2Cl_3C_2H_2O_4$ : S, 10.57. Found: 10.47.

**Di(4-phenyl-2-aminothiazyl-5)-*o*-nitrophenylmethane**, prepared similarly from the thiazole and *o*-nitrobenzaldehyde, was purified by crystallization from alcohol. Orange-yellow, small, prismatic needles were thus obtained, melting with decomposition at  $231.6^\circ$  (corr.); yield, nearly that calculated.

*Anal.* Calc. for  $C_{25}H_{19}O_2N_6S_2$ : C, 61.82; H, 3.96. Found: C, 61.66; H, 3.80.

The compound dissolved readily in benzene, toluene, xylene, methyl or ethyl alcohol, but was only slightly soluble in chloroform. Oxidized by lead dioxide in acid solution, a bright blue-green solution resulted, the color of which changed quickly to red.

**Di(4-phenyl-2-aminothiazyl-5)-*m*-nitrophenylmethane**, from the thiazole and *m*-nitrobenzaldehyde, was crystallized from a mixture of alcohol and benzene, and the crystals were dried in a vacuum desiccator over paraffin wax. The pure product consisted of pale yellow, lustrous rhombs, that sintered when heated and finally melted with decomposition at  $202.3^\circ$  (corr.); yield, 63%. These crystals proved to be the benzene addition product.

*Anal.* Calc. for  $C_{25}H_{19}O_2N_6S_2 \cdot C_6H_6$ : S, 11.36. Found: 11.26.

The crystals were heated at  $100^\circ$  for 24 hours and were then recrystallized from dil. alcohol. Dull yellow, short needles were obtained, which melted at the same point, but without any preliminary sintering.

*Anal.* Calc. for  $C_{25}H_{19}O_2N_6S_2$ : S, 13.18. Found: 13.05.

From this leuco base, the carbinol and dye (oxalate) were prepared as described in the analogous cases above. For analysis, the dye was crystallized from dil. acetone and then appeared as a green-black powder, that dyed wool a dull blue-green.

*Anal.* Calc. for  $2C_{25}H_{17}O_2N_6S_2 \cdot 3C_2H_2O_4$ : S, 10.35. Found: 10.49.

**Di(4-phenyl-2-aminothiazyl-5)-*p*-nitrophenylmethane**, from the thiazole and *p*-nitrobenzaldehyde, after recrystallization from methyl alcohol, appeared in pale greenish-yellow small needles that sintered when heated and finally melted with decomposition at  $238.5^\circ$  (corr.); yield, 35%.

*Anal.* Calc. for  $C_{25}H_{19}O_2N_6S_2$ : S, 13.18. Found: 13.21.

The compound dissolved readily in methyl or ethyl alcohol, or in acetone; less readily in benzene, toluene, xylene or chloroform, and was practically insoluble in water.

The dye (oxalate) from this leuco base was a green-black powder, whose tinctorial properties were similar to those of its *meta* isomer.

*Anal.* Calc. for  $2C_{25}H_{17}O_2N_6S_2 \cdot 3C_2H_2O_4$ : S, 10.35. Found: 10.22.

**Di(4-phenyl-2-aminothiazyl-5)-*p*-dimethylaminophenyl-methane**, from the thiazole and *p*-dimethylaminobenzaldehyde, after crystallization from dilute alcohol, formed small, colorless needles that sintered when heated and then melted sharply with decomposition at  $235.8^\circ$  (corr.); yield, 51%.

*Anal.* Calc. for  $C_{27}H_{26}N_6S_2$ : S, 12.94. Found: 13.02.

The crystals were more or less soluble in methyl or ethyl alcohol, acetone, benzene, xylene, dil. hydrochloric or glacial acetic acid.

The leuco base was oxidized to the carbinol by lead dioxide and hydrochloric acid, from which the dye (oxalate) was prepared. The latter was purified by crystallization from dil. alcohol and then appeared as a green-black powder, whose bluish-green

color in solution was changed to purple by the addition of an excess of concd. hydrochloric acid, the color returning to its original shade upon sufficient dilution with water.

*Anal.* Calc. for  $2C_{27}H_{28}N_5S_2 \cdot 3C_2H_2O_4$ : 10.23. Found: 10.05.

Wool immersed in a dilute alcoholic solution of the dye containing an amount of dye equal to 2% the weight of the fabric and 10% of sodium sulfate, was dyed a dull greenish-blue.

**Di(4-phenyl-2-aminothiazyl-5)-*o*-hydroxyphenylmethane**, from the thiazole and salicylaldehyde, crystallized from alcohol in colorless rhombs, which began to shrivel and turn yellow at about 148.5° and finally melted with decomposition at 222.5° (corr.); yield, 83%.

*Anal.* Calc. for  $C_{28}H_{20}ON_4S_2$ : C, 65.74; H, 4.43; S, 14.05. Found: C, 65.77; H, 4.48; S, 14.07.

The compound was freely soluble in boiling alcohol, also in methyl alcohol, acetone or ethyl acetate; in hot benzene, toluene or xylene, less readily cold; and was difficultly soluble in ether or chloroform.

When it was oxidized by lead dioxide and acid, a red solution resulted from which a pure carbinol could not be isolated.

**FUSION WITH POTASSIUM HYDROXIDE.**—For purposes of comparison, the analogous triphenylmethane derivative was prepared by the method of O. Fischer,<sup>15</sup> from salicylaldehyde and dimethylaniline. The product crystallized from alcohol in radiating clusters of colorless needles, *m. p.* 128° (corr.); yield, nearly that calculated.

This triphenylmethane derivative and its dithiazyl analog were fused separately with potassium hydroxide under identical conditions. A mixture of 1 part (by weight) of the *o*-hydroxy derivative with 4 parts of solid potassium hydroxide was heated at 145–150° for 15 minutes. Ammonia was given off by the thiazole melt, but not from the triphenylmethane derivative. In each case, the melt was extracted with boiling water, the filtered extracts were acidified with hydrochloric acid and extracted with ether. Evaporation of the ether left benzoic acid in the case of the thiazole melt, but no residue in the case of the triphenylmethane derivative, thus demonstrating the greater stability of the latter to hot caustic alkali.

**Di(4-phenyl-2-aminothiazyl-5)-*p*-hydroxyphenylmethane**, from the thiazole and *p*-hydroxybenzaldehyde, crystallized from dil. alcohol in minute, colorless needles that sintered and changed color at about 248° (corr.), and then melted with decomposition at 252.4° (corr.); yield, 50%.

*Anal.* Calc. for  $C_{28}H_{20}ON_4S_2$ : S, 14.05. Found: 14.14.

Oxidized by lead dioxide and hydrochloric acid, this leuco base gave a greenish-brown solution, from which the dye (oxalate) was obtained as a dull violet powder (from dil. alcohol).

***p*-Nitrobenzene-azo-(4-phenyl-2-aminothiazole)** (VI) was prepared by coupling the thiazole with diazotized *p*-nitro-aniline at 0°; yield, 80%. It crystallized from nitrobenzene in minute, green needles of metallic luster, *m. p.* 179.6° (corr.), which dyed wool a red.

*Anal.* Calc. for  $C_{15}H_{11}N_5S$ : S, 10.92. Found: 11.15.

The crystals dissolved easily in nitrobenzene or aniline; only slightly in methyl or ethyl alcohol, acetone, benzene or toluene. The stability of the compound to the action of concd. hydrochloric acid indicated that it was probably an amino-azo rather than a diazo-amino derivative. Since 2-aminothiazole itself also couples with diazotized *p*-nitro-aniline to an azo dye, the azo attachment to the thiazole nucleus is probably at Position 5, and not on the benzene group in Position 4.

<sup>15</sup> Fischer, *Ber*, **14**, 2522 (1881).

*p*-Sulfobenzene-azo-(4-phenyl-2-aminothiazole), from diazotized sulfanilic acid and the thiazole, was precipitated as the sodium salt by the usual salting-out process. Recrystallized from water and dried, it formed a dark red solid of bronze luster, which dissolved freely in water giving a crimson-red solution, that changed in color to pale yellow when acidified, and regained its original color when made alkaline again.

### Summary

1. 2-Aminothiazoles, prepared from  $\alpha$ -chloro derivatives of aldehydes or ketones and thio-urea, were condensed with aromatic aldehydes in the presence of hydrochloric acid, to di(aminothiazyl)phenylmethanes, which were then oxidized by lead dioxide in acid solution to the corresponding carbinols, whose mono-acid salts lost a molecule of water and formed di(aminothiazyl)phenylmethane dyes of Doebner Violet type, but which dyed silk, wool or mordanted (tanned) cotton, a dull blue-green. As dyes, they were inferior to Malachite Green.

2. The war "gases" used as initial materials were dichloro ether (for chloro-acetaldehyde), chloro-acetone and chloro-acetophenone; the thiazoles were the 4-methyl-, and 4-phenyl-2-aminothiazoles; and the aromatic aldehydes with which they were condensed were benzaldehyde, its *p*-chloro-, *o*-, *m*- and *p*-nitro-, *p*-dimethylamino-, *o*- and *p*-hydroxy- derivatives and piperonal.

3. The 2-aminothiazoles were used also as couplers for the production of new azo dyes.

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## RESEARCHES ON UNSATURATED KETONIC ACIDS. I. THE CONSTITUTION OF THE SO-CALLED "PECHMANN DYES" AND THE MECHANISM OF THEIR FORMATION FROM BETA-BENZOYLACRYLIC ACID<sup>1,2</sup>

BY MARSTON TAYLOR BOGERT AND JOHN J. RITTER

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### Introductory

For 42 years the constitution of the so-called "Pechmann Dyes" has remained an unsolved problem. The experimental data in the following pages and the conclusions drawn therefrom are submitted as a contribution to the solution of this problem.

Von Pechmann,<sup>3</sup> who was the first to attempt the production of alpha-

<sup>1</sup> Presented before the Division of Dye Chemistry, American Chemical Society, April 23, 1924.

<sup>2</sup> We welcome this opportunity to express publicly our appreciation of the courtesy of the Barrett Company, who generously provided us with the maleic acid necessary for this research.—M. T. B. and J. J. R.

<sup>3</sup> Von Pechmann, *Ber.*, **15**, 885 (1882).