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 α-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 (tannined) 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.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 453]

RESEARCHES ON UNSATURATED KETONIC ACIDS. I. THE CONSTITUTION OF THE SO-CALLED "PECHMANN DYES" AND THE MECHANISM OF THEIR FORMATION FROM BETA-BENZOYLACRYLIC ACID[1,2]

BY MARSTON TAYLOR BOGERT AND JOHN J. RITTER

RECEIVED SEPTEMBER 12, 1924 PUBLISHED DECEMBER 13, 1924

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.

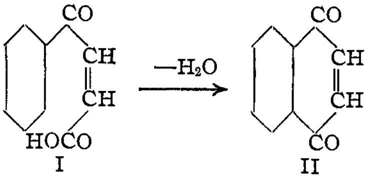
Von Pechmann,[3] who was the first to attempt the production of alpha-

[1] Presented before the Division of Dye Chemistry, American Chemical Society, April 23, 1924.

[2] 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.

[3] Von Pechmann, *Ber.*, **15,** 885 (1882).

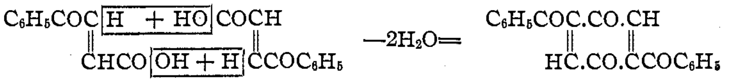
naphthaquinones (II) by dehydration of β-benzoylacrylic acid (I) or its homologs,



I II

obtained instead highly colored compounds which, although of the same percentage composition as the expected naphthaquinones, were totally different and whose nature was not ascertained. These have since been known generally as "Pechmann Dyes." They are characterized by brilliant colors and striking color changes, as well as by other interesting physical and chemical properties. Their absorption spectra and certain of their color reactions resemble those of pigments related to chlorophyll; and by the study of their behavior with ammonia and other amines, we hope to throw some additional light upon the question of the structure of the coloring matters of the hemopyrrole and phyllopyrrole group, possibly involving also their immediate progenitors, such as hemin, hematoporphyrin, bilirubin and others.

Kozniewski and Marchlewski,[4] 24 years later, repeated von Pechmann's work and extended it. Incidentally, they mentioned in a footnote the significant fact that the dye from mesitoylacrylic acid was obtained always in two different forms, one red and the other yellow. They came to the conclusion that these dyes were diaroylquinones, formed by a dehydration involving the beta hydrogen atom,



$$\begin{matrix} C_6H_5COC\boxed{H\ +HO}COCH \\ \| \qquad\qquad\qquad\quad \| \\ CHCO\boxed{OH+H}CCOC_6H_5 \end{matrix} \quad -2H_2O= \quad \begin{matrix} C_6H_5COC.CO.CH \\ \| \qquad \| \\ HC.CO.CCOC_6H_5 \end{matrix}$$

III

basing this assumption upon the deep color of the compounds, the ease with which they yielded di-anils with aniline and benzoic acid on oxidation.

We have found, however, that the α-methyl derivative of β-benzoylacrylic acid does not give a Pechmann dye. Nor does the quinone formula provide any simple answer to the question as to how it yields diphenacylfumaric acid by the action of alkali. It offers no explanation for the *cis-trans* isomerism observed by us, nor for the production of the dibromide obtained by Kozniewski and Marchlewski.

Von Pechmann stated that the action of alcoholic potassium hydroxide upon the dye gave a yellowish product, which regenerated a red substance when boiled with acetic anhydride. Investigation of this yellow product has now shown it to be a mixture of a bright yellow acid, diphenacylfumaric (XI), with a colorless one, diphenacylmaleic acid (X).

By the oxidation of phenylcrotolactone (VII) with ferric chloride,

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[4] Kozniewski and Marchlewski, *Bull. acad. sci. Cracow*, **1906**, 81.

Kugel[5] obtained a red, crystalline compound, whose percentage composition and molecular weight corresponded to the formula $C_{20}H_{12}O_4$, and to which he assigned as a tentative structure that represented by Formula VIII. Action of alcoholic potassium hydroxide upon the dilactone gave an acid, $C_{20}H_{16}O_6$, which he suggested was probably diphenacylfumaric. When this acid was heated with glacial acetic acid, there was formed an isomer of the original dilactone, which he thought was probably a stereoisomer, and which he described as crystallizing in fine, yellow prisms that appeared bright red in superimposed masses.

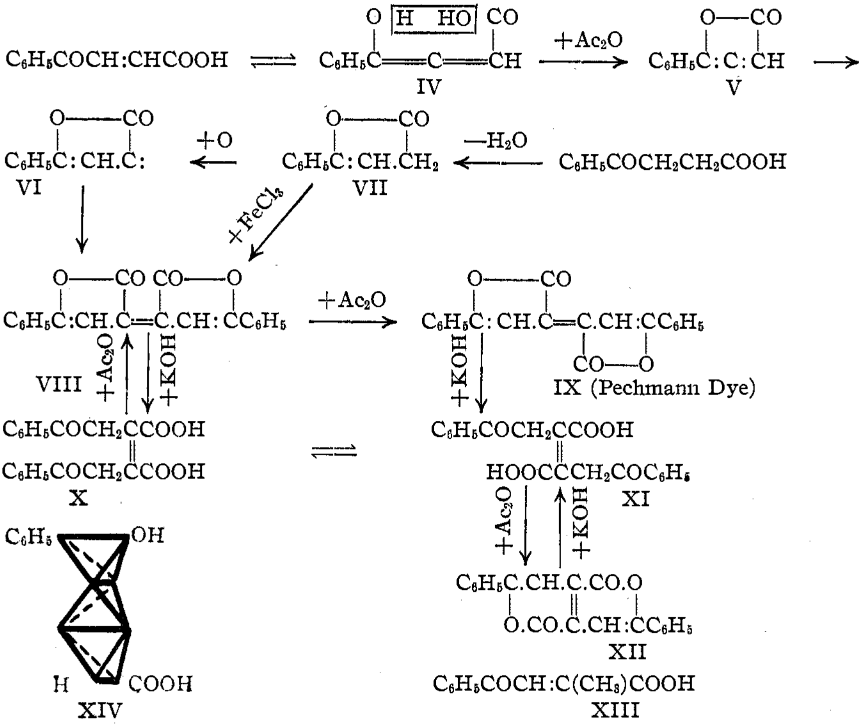
Kugel's dilactone is the diphenacylmaleic dilactone (VIII), and results from the simultaneous oxidation and union of two molecules of the phenylcrotolactone (VII). What he suggested might be diphenacylfumaric acid is actually that acid and is identical with the yellow acid obtained by us from the Pechmann dye and alcoholic potassium hydroxide. Its origin from a *cis*-dilactone is due to the ease with which this dilactone rearranges to the *trans* isomer. Dehydration of this acid, instead of yielding a dilactone (IX), gives the dilactide (XII), that is, it closes to the 6- instead of to the 5-membered cycle. On the other hand, the diphenacylmaleic acid (X), which should not form a dilactide, does not do so, but reverts directly to the Kugel dilactone (VIII) when it is treated with dehydrating agents.

This same *cis*-dilactone can be obtained by heating β-benzoylacrylic acid for a short time with acetic anhydride. On longer heating of the benzoylacrylic acid with acetic anhydride, or on heating the *cis*-dilactone with the same reagent, it rearranges to the *trans* isomer, which is the Pechmann dye. Depending upon the duration of the heating with acetic anhydride, therefore, the product will contain varying amounts of the two stereoisomers and hydrolysis of such a mixture by alcoholic potassium hydroxide will give corresponding quantities of diphenacylmaleic and diphenacylfumaric acids. Further, the proportion of *cis* and *trans* acids thus liberated may be changed by transition of one form into the other under the conditions of the experiment.

Upon the foundation erected by the facts presented in the foregoing, we have constructed the following hypothesis to explain the mechanism of the formation of the Pechmann dye from β-benzoylacrylic acid. The first step consists in the transition of the acid to the enolic form (IV), with subsequent loss of water and transient production of the highly unsaturated lactone (V) of allene type, which promptly undergoes a bimolecular condensation to the Kugel dilactone (VIII), possibly through an unstable intermediate stage (VI) identical with what might be expected also in the production of this dilactone by Kugel's method of oxidizing the phenylcrotolactone (VII).

[5] Kugel, *Ann.*, **299**, 50 (1898).

These different steps are exhibited in the following flow-sheet.



It will be seen that both of these deeply colored dilactones (VIII and IX) contain the indigo chromophore, $-\mathrm{CO.\overset{|}{C}:\overset{|}{C}.CO}-$, united on both sides with unsaturated cyclic systems, and it is believed that their color is due to this configuration.

Another point of interest concerns the stereoconfiguration of β-benzoylacrylic acid itself. The work of Mrs. Rice[6] and others makes it appear probable that benzoylacrylic acid, in its keto form, possesses the fumaroid configuration, and this has been advanced by some as the reason for the failure of the efforts to condense it to α-naphthaquinone. But it will be noted that the change to the enolic form immediately eliminates any *cis-trans* distinction with development of a symmetrical structure (XIV), in which the C_6H_5 and OH groups of the upper tetrahedron are equidistant from the H and COOH of the lower one; and since the COOH is united to the lower tetrahedron by a single bond there is no reason why the tetrahedral carbon of this COOH should not rotate until its OH and the OH of the upper one mutually assume a position favorable to the

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[6] Rice, THIS JOURNAL, **45**, 222 (1923); **46**, 214 (1924).

elimination of a molecule of water and the temporary formation of the unstable allene lactone (V). In further support of this explanation of the course of the reaction is the fact that β-benzoylpropionic acid when treated with dehydrating agents yields the phenyl-γ-crotolactone (VII) and no dihydronaphthaquinone $\rightleftharpoons$ 1,4-dihydroxynaphthalene.

The assumption that both diphenacylfumaric and diphenacylmaleic acids easily pass into the enolic configuration is supported by the color changes they exhibit. Both dissolve instantly in cold dil. aqueous potassium hydroxide to give a deep blood-red solution, which changes to pale yellow or colorless when warmed. From the red, pale yellow or colorless solution, mineral acid precipitates the original acid unaltered.

In the case of the diphenacylfumaric acid, for example, the keto form is pale yellow in solution, the enol deep red. A strong aqueous solution of its potassium salt is also deep red, but this color gradually fades following dilution, as enol changes to keto. Assuming that the enolic hydrogen is but slightly ionized, but that its potassium salt in very dilute solution is very largely ionized and that the hydrolysis equilibrium adjusts itself practically instantaneously, the lag in decoloration may be taken as a measure of the time necessary for the transformation of enol to keto. The temporary red color of dil. aqueous solutions of the potassium salt, therefore, is probably to be ascribed to the free enolic acid. It should be possible to follow this change by measuring the decreasing conductivity of the salt solution, although a solution containing both carboxylic and enolic salts presents a rather complex system, in which the degree of hydrolysis of either salt group will be affected by the extent of the hydrolysis of the other, due to alteration of hydroxyl-ion concentration as a result of such hydrolysis.

The behavior of the keto acid with alcoholic ferric chloride likewise discloses an interesting time factor in the rearrangement of keto to enol, for the characteristic red-brown color appears very tardily and reaches its maximum depth of shade only after 15 or 20 minutes.

Wolff[7] noted that β-acetylacrylic acid dissolved in cold aqueous barium hydroxide forming a yellow solution, the color of which vanished when the solution was warmed, and interpreted this as indicating the formation of the enolic salt at the lower temperature and rearrangement to the colorless keto form at the higher one.

New members of the Pechmann Dye group have been prepared from the naphthoylacrylic acids. They are beautiful, deeply colored, crystalline solids, that from the α-naphthoylacrylic acid possessing a remarkably brilliant blue luster.

Other articles are in press and the investigation is being continued actively in various directions.

[7] Wolff, *Ann.*, **264**, 252 (1891).

Experimental Part

Diphenacylmaleic Dilactone (VIII).—When a solution of 100 g. of β-benzoylacrylic acid in 150 g. of acetic anhydride was refluxed for an hour and the resulting deep red solution was then allowed to cool, 20 g. of diphenacylmaleic dilactone separated.

The same product was obtained by boiling diphenacylmaleic acid for ten minutes with an excess of acetic anhydride. The crude product was washed successively with acetic anhydride, glacial acetic acid, alcohol and ether. It crystallized from xylene in dark red needles or plates with a beautiful deep blue luster, was insoluble in the ordinary neutral solvents and sublimed when strongly heated. It dissolved slowly in concd. sulfuric acid to form a greenish-blue solution the color of which soon changed to a clear deep blue. Dilution of this solution reprecipitated the original substance unaltered.

Anal. Calc. for $C_{20}H_{12}O_4$: C, 75.95; H, 3.80. Found: C, 75.44; H, 4.02.

This compound was identical with the product which Kugel obtained when he oxidized γ-phenylcrotolactone (VII) with ferric chloride. This fact was established by repeating his work and comparing the products of the two methods. Kugel obtained his benzoylpropionic acid from succinic anhydride and benzene, but we found it more satisfactory to prepare it by reduction of benzoylacrylic acid with zinc dust and acetic acid, a method which gives a yield approximately equal to that calculated. A single crystallization from water of this crude product gave the pure compound, m. p. 116°, in agreement with the melting point recorded by Kugel. The lactone prepared from this by the action of acetic anhydride melted at 92°. Kugel gives the melting point as 92–93°. Oxidation of this lactone by alcoholic ferric chloride gave a compound whose physical and chemical properties coincided with those recorded by Kugel for his product.

When this *cis*-dilactone was boiled for two hours with an excess of acetic anhydride, it changed into the *trans* isomer, which is the Pechmann Dye. The same change occurred more slowly when the *cis*-dilactone was warmed or was crystallized repeatedly from xylene.

Diphenacylfumaric Dilactone (IX), "Pechmann Dye."—This is the product generally obtained by the action of dehydrating agents upon β-benzoylacrylic acid. It is prepared most satisfactorily by the original method of von Pechmann, namely, by boiling a solution of one part of benzoylacrylic acid in 1.5 parts of acetic anhydride for two to three hours. Von Pechmann reported yields as high as 45%; but Kozniewski and Marchlewski on repeating the work obtained yields of only 10–25%, and our experience was similar.

The product agreed in all its physical and chemical properties with his description. In benzene solution, it exhibited a golden-yellow fluorescence, which was intensified by the addition of ligroin. It crystallized from xylene in deep red plates of bronze luster, which were sparingly soluble in the ordinary neutral solvents and sublimed when heated strongly. The solution in concd. sulfuric acid was pure cobalt blue; the original material was precipitated unaltered from this solution on dilution. After 24 hours or longer, the blue solution changed to red.

Anal. Calc. for $C_{20}H_{12}O_4$: C, 75.95; H, 3.80. Found: C, 75.91; H, 4.03.

Benzoylacrylic acid gave this dye when heated alone or above its melting point, or when treated with acetic anhydride, acetyl chloride, stannic chloride, phosphorus tri-, penta- or oxychloride, phosphorus pentoxide, sulfuric acid (dil. or fuming), or aluminum chloride. None of the methods which convert benzoylbenzoic acid into anthraquinone produced any naphthaquinone whatever from benzoylacrylic acid.

Ruhemann and Stapleton[8] found that phenoxyfumaric acid could be condensed to a chromone carboxylic acid by the action of sulfuric acid,

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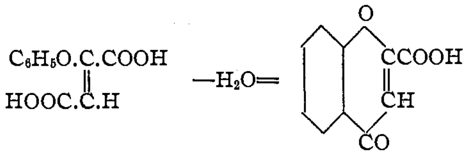
[8] Ruhemann and Stapleton, *J. Chem. Soc.*, 77, 1179 (1900).



but benzoylacrylic acid under similar conditions gave no naphthaquinone.

By-product in the Preparation of Pechmann Dye.—Previous workers make no mention of the formation of large amounts of another product in this preparation, yet the elucidation of its character is sure to give a clearer insight into the mechanism of this interesting reaction.

In a typical experiment, a solution of 75 g. of benzoylacrylic acid in 115 g. of acetic anhydride was refluxed for two hours. After the solution had cooled thoroughly, 17 g. of Pechmann dye precipitated and was removed. The filtrate was diluted with 500 cc. of 95% alcohol and 32 g. of by-product separated. From the alcoholic filtrate, 10 g. more was recovered by the addition of water. As thus separated, it formed a bulky light red, finely divided solid, very easily soluble in acetic anhydride, chloroform or ethylene bromide; readily soluble also in glacial acetic acid; less readily in ethyl acetate, benzene or toluene; and practically insoluble in water or alcohol. Attempts to obtain it in crystalline form failed. The Pechmann dye is not attacked by dil. aqueous alkalies, but when this by-product was boiled with 10% aqueous sodium hydroxide solution it dissolved readily with formation of tarry products and acetophenone.

Diphenacylfumaric Acid (XI).—A solution of two parts of Pechmann dye in a 10% alcoholic potassium hydroxide solution containing 1.2 parts of potassium hydroxide was refluxed for 30 minutes and then cooled thoroughly. A mass of bright red crystals separated from the red liquid. These crystals were removed, washed with alcohol, dissolved in water and mineral acid was added until the precipitation of the yellowish solid was complete. The precipitate was collected and dried; yield, about equal to the weight of initial dilactone.

This product was a mixture consisting mainly of diphenacylfumaric with some diphenacylmaleic acid. The two were separated through the greater solubility of the former in hot 95% alcohol. By repeated crystallization from small volumes of alcohol, it was obtained in bright yellow, minute, short needles which did not melt but lost water at 130–140° with the formation of the dilactide. It may be crystallized also from dil. acetic acid, as Kugel found, but some dilactide often is formed simultaneously and this renders the purification more troublesome. Yellow prisms, obtained by crystallization from ethyl acetate, were analyzed.

Anal. Calc. for $C_{20}H_{16}O_6$: C, 68.18; H, 4.55. Found: C, 68.11; H, 4.80.

It was soluble in alcohol, acetic acid, benzene, ether, ethyl acetate or chloroform, and practically insoluble in water. The solution in aqueous alkalies was deep red. When the acid was boiled for a few minutes with acetic anhydride, the dilactide resulted.

Diphenacylmaleic Acid (X).—The crude product obtained by the action of alcoholic potassium hydroxide upon the Pechmann dye, after extraction of the diphenacylfumaric acid with hot alcohol was treated with dil. (3–5%) aqueous alkali, to remove the diphenacylmaleic acid from dark colored impurities. The filtered alkaline solution was precipitated by mineral acid, the precipitate collected, dried and crystallized from benzene, in which it is but sparingly soluble even at the boiling-point. Colorless, minute, silky scales were thus obtained, soluble in ethyl acetate or acetic acid, but insoluble or difficultly soluble in most neutral solvents. The substance did not melt, but gradually darkened at temperatures above 120°. Boiled with acetic anhydride, it yielded the dilactone, as already noted. Its solution in aqueous alkalies was deep red.

Anal. Calc. for $C_{20}H_{16}O_6$: C, 68.18; H, 4.55. Found: C, 67.84; H, 4.77.

The acid was obtained also, and in good yield, by the action of alcoholic potassium hydroxide solution upon its dilactone.

Diphenacylfumaric Dilactide (XII).—Diphenacylfumaric acid was boiled with excess of acetic anhydride for an hour. As observed by Kugel, glacial acetic acid has a similar effect, but its action is much slower. The crude product crystallized from xylene in minute, orange needles, identical with the compound obtained by Kugel. The diphenacylfumaric acid used must be freed carefully of all diphenacylmaleic acid, or the product will be red from the presence of the dilactone of the latter, which is not easily removed by recrystallization from xylene. This is probably the explanation of Kugel's statement that at temperatures of 130° and over the diphenacylfumaric acid lost water with formation of the red oxidation product (the *cis*-dilactone). The compound does not melt, but sublimes partly on strong heating. Its solution in concd. sulfuric acid was brownish-red, in alcoholic potassium hydroxide, bright red.

Anal. Calc. for $C_{20}H_{14}O_4$: C, 75.95; H, 3.80. Found: C, 75.10, 75.59; H, 3.82, 3.85.

β-Benzoyl-α-methylacrylic Acid (XIII) and Acetic Anhydride.—When 0.4 g. of this acid (m. p. 153°, corr.) was boiled with 2 g. of acetic anhydride for 30 minutes, a pale yellow solution resulted, in striking contrast to the deep red color which betokens the formation of the Pechmann dye and which usually appears very quickly. Nothing separated from this yellow solution as it cooled. Dilution with water precipitated 0.7 g. of a pale yellow solid, insoluble in the ordinary neutral solvents, excepting chloroform, and which dissolved in hot dil. (10%) aqueous sodium hydroxide solution to form a brown liquid. Its purification and identification have not been completed, but the great increase in weight indicates an addition reaction of some kind.

Di-α-naphthacylfumaric Dilactone, from β(α-naphthoyl)acrylic acid and acetic anhydride, crystallized from xylene in nearly black needles with a brilliant, rich blue luster, which melted with decomposition at a high temperature; yield, 15–20%. In concd. sulfuric acid, it dissolved slowly to form a deep blue solution.

Anal. Calc. for $C_{28}H_{16}O_4$: C, 80.77; H, 3.85. Found: C, 80.16; H, 3.94.

Di-β-naphthacylfumaric Dilactone, prepared similarly from β(β-naphthoyl)acrylic acid and acetic anhydride, formed minute, dark red, glistening needles without the brilliant blue luster of the α-naphthacyl isomer.

Anal. Calc. for $C_{28}H_{16}O_4$: C, 80.77; H, 3.85. Found: C, 80.37; H, 4.10.

Summary

1. Evidence is submitted that the so-called "Pechmann Dye" is the *trans*-dilactone of diphenacylmaleic acid and that the *cis* isomer is identical with the dilactone which Kugel obtained when he oxidized γ-phenylcrotolactone. The other anhydride obtained by Kugel from diphenacylfumaric acid is probably the dilactide of that acid.

2. An explanation of the mechanism of the reaction is offered, showing why Pechmann dyes, and not *alpha*-naphthaquinones, result when β-benzoylacrylic acids are treated with dehydrating agents.

3. A number of new compounds have been synthesized and studied.

New York, N. Y.