THE CHEMISTRY OF THE PECHMANN DYES

ERWIN KLINGSBERG

American Cyanamid Company, Research Division, Bound Brook, New Jersey

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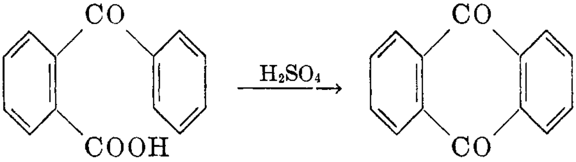
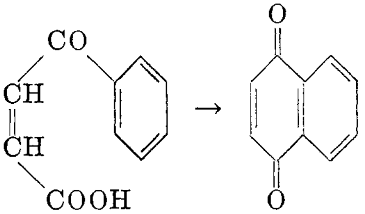
I. INTRODUCTION

The well-known cyclization of *o*-benzoylbenzoic acid to anthraquinone



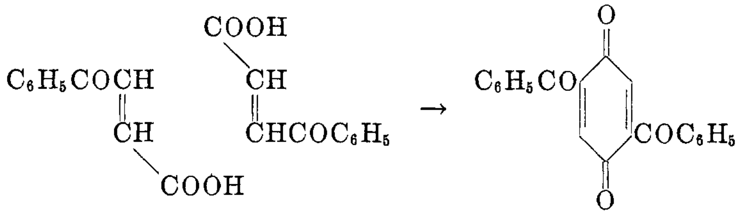
o-Benzoylbenzoic acid — Anthraquinone

prompted von Pechmann in 1882 to attempt the preparation of 1,4-naphthoquinone from β-benzoylacrylic acid:



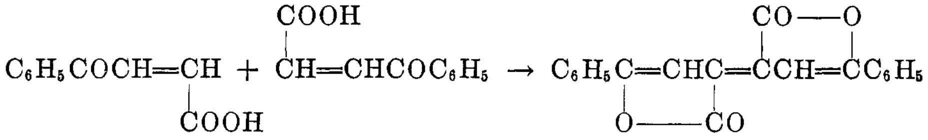
β-Benzoylacrylic acid — 1,4-Naphthoquinone

Instead of the desired product, a red pigment with the same empirical formula as naphthoquinone was obtained; the elimination of water had occurred in some unexpected direction (36). von Pechmann gave a careful description of the product but did not propose a structure for it. Twenty-four years later, in the course of some interesting observations of the properties of this red compound, Kozniewski and Marchlewski (33) suggested that the pigment was 2,5-dibenzoylbenzoquinone:



2,5-Dibenzoylbenzoquinone

This quinone was subsequently synthesized and shown to be entirely different from the Pechmann dye (38), but even earlier the structure had been rejected by Bogert and coworkers, who showed that the dye behaved, not like a quinone (5), but like a bifunctional lactone (6):



$$C_6H_5COCH{=}\underset{\displaystyle COOH}{CH} + \overset{\displaystyle COOH}{CH}{=}CHCOC_6H_5 \rightarrow C_6H_5\underset{\displaystyle O}{C}{=}CH\underset{\displaystyle CO}{C}{=}\overset{\displaystyle CO}{C}CH{=}\overset{\displaystyle O}{C}C_6H_5$$

After long opposition, Chovin, who is responsible for much of the subsequent work on the Pechmann dye, has now accepted this formula (24).

Because of the long-standing differences of opinion as to the structure of the Pechmann dye and the related compounds, the literature is rather confusing, although most of the reactions are now well understood. It will be seen, however, that more than one interesting question has remained unanswered, or even unnoticed.

II. PREPARATION OF PECHMANN DYES

A. *Dehydration of β-aroylacrylic acids*

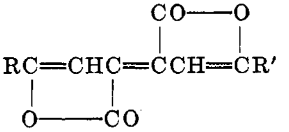
von Pechmann's preferred dehydrating agent for benzoylacrylic acid was acetic anhydride, under reflux or at 150–160°C. in a sealed tube. Yields occasionally reached 45 per cent of theory, but were often much lower (36). The benzoylacrylic acid may be replaced by its hydration product, β-benzoyllactic acid, $C_6H_5COCH_2CHOHCOOH$ (33).

Mesitoylacrylic acid gives exceptionally high yields (33). The reaction also succeeds with numerous other aroylacrylic acids (see table 1), but not with α-methyl-β-benzoylacrylic acid, anthroylacrylic acid, or β-acetylacrylic acid (4).

Since the time of von Pechmann, the yields in these reactions have been generally poor and erratic (6, 33), reaching as low as 5–7 per cent (28), until the discovery by Bergmann and Fang of the powerful catalytic action of copper or its salts in the presence of ammonium salts (3, 31) or boric acid (2). This work now makes it possible to prepare the Pechmann dyes, conveniently and reproducibly, in yields of 70–80 per cent of theoretical.

TABLE 1

Table of known Pechmann dyes



$$\begin{array}{l} \qquad\qquad\qquad\;\; \mathrm{CO{-}{-}O} \\ \qquad\qquad\qquad\;\; |\qquad\;\, | \\ \mathrm{RC{=}CHC{=}CCH{=}CR'} \\ |\qquad\quad\;\; | \\ \mathrm{O{-}{-}{-}CO} \end{array}$$

Symmetrical

R = R′ =	METHOD OF PREPARATION*	MELTING POINT	REFERENCES
		°C.	
C_6H_5	A	317	(6, 28, 33, 36)
	B		(34, 39)
	C	317	(26, 27)
	D	317	(13, 31)
p-$CH_3C_6H_4$	A		(2, 3, 33, 36)
	D	357	(8, 13)
2,4-$(CH_3)_2C_6H_3$	A		(33)
2,4,5-$(CH_3)_3C_6H_2$	A		(33)
2,4,6-$(CH_3)_3C_6H_2$	A	278	(33)
	B(?)	288–290	(1)
p-$C_6H_5C_6H_4$	A	297	(2, 3, 4, 31)
p-BrC_6H_4	D	432	(2, 8, 13)
p-$CH_3OC_6H_4$	A		(2, 3)
p-$C_2H_5OC_6H_4$	A		(33)
m-$NO_2C_6H_4$	A	361	(3, 31)
$C_6H_5CH{=}CH$	D	324	(31)
α-$C_{10}H_7$	A		(6)
β-$C_{10}H_7$	A		(6)
	D	361	(3, 31)

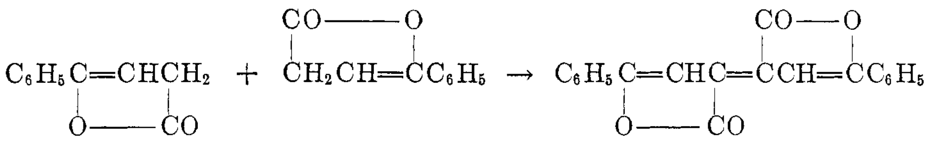
Unsymmetrical

R	R′	METHOD OF PREPARATION	MELTING POINT	REFERENCES
C_6H_5	p-$CH_3C_6H_4$	D	307	(7, 13)
C_6H_5	p-BrC_6H_4	D	347	(8, 13)
p-$CH_3C_6H_4$	p-BrC_6H_4	D	397	(8, 13)
C_6H_5	β-$C_{10}H_7$	D	297	(8, 13)
p-$CH_3C_6H_4$	β-$C_{10}H_7$	D	316	(8, 13)
p-BrC_6H_4	β-$C_{10}H_7$	D	377	(8, 13)
C_6H_5	$C_6H_5CH{=}CH$	D	324	(31)

* See Section II.

B. Oxidation of γ-phenyl-Δ^{β}-butenolactone

This lactone, which can be prepared by the action of acetic anhydride on β-benzoylpropionic acid, was oxidized by Kugel to a dark red dyestuff with the aid of alcoholic ferric chloride (34). The yield of product was 0.22 g. from 2 g. of lactone, 35 per cent of the starting material being recovered unchanged. Kugel suggested the following structure:

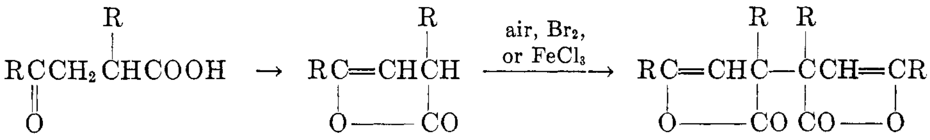


The yield is "better by far" if the lactone is oxidized with permanganate in the presence of magnesium sulfate (39).

The earlier workers (before 1920) did not notice any relationship between this compound and the Pechmann dye. Bogert and Ritter (6) believed them to be *cis–trans* isomers, but Chovin (10, 15) demonstrated their identity.

Mesitoylpropionic acid is apparently oxidized (and dehydrated) to the corresponding Pechmann dye simply by refluxing in acetyl chloride (1).

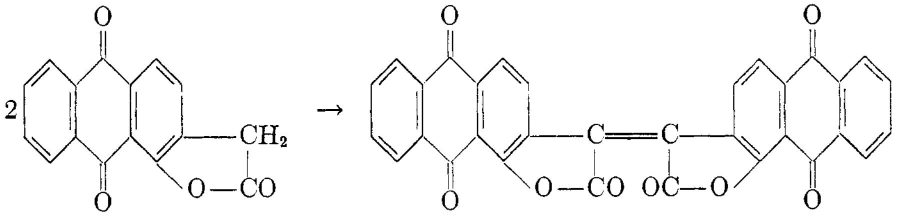
An analogous bimolecular dehydrogenation is undergone by α-aryl-β-aroylpropionic acids, or their lactones, under mild oxidizing conditions (37):



R = C_6H_5 or p-$CH_3C_6H_4$.

(These dilactones are colorless; in solution above 100°C. they appear to dissociate into green free radicals by cleavage of the central bond.)

A fused-ring anthraquinone analog of the Pechmann dye has been prepared by oxidation of the lactone of 1-hydroxy-2-anthraquinoneacetic acid (35):



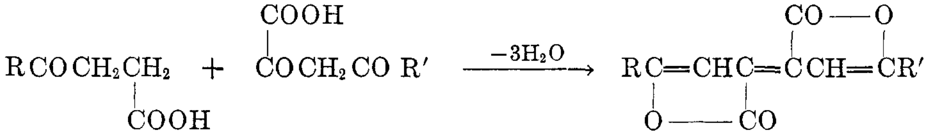
C. Self-condensation of ethyl benzoylpyruvate

Under the influence of phosphorus pentachloride, ethyl benzoylpyruvate gives the Pechmann dye in yields of the order of 3 per cent of theoretical (26). In order to formulate a mechanism for the reaction, a reduction or disproportionation of the starting material must be postulated (27).

From both theoretical and practical standpoints, this is the least important method which has been reported.

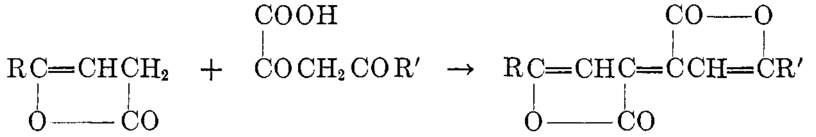
D. Condensation of γ-keto and α,γ-diketo acids

This is the only method permitting the synthesis of unsymmetrically substituted Pechmann dyes (7, 11):



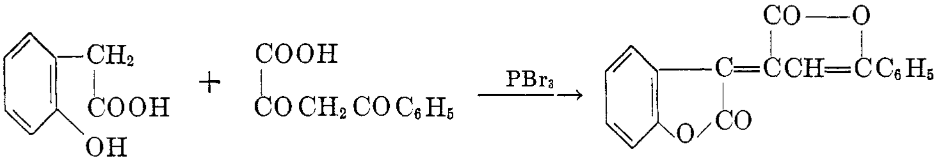
Phosphorus tribromide is the dehydrating agent of choice, giving yields of 20–35 per cent under optimum conditions. Phosphorus trichloride is somewhat less successful, while a wide variety of other acidic and basic condensing agents give little or no product.

While it was first reported that poorer yields are obtained when the starting materials are used in the form of their esters or lactones (12), yields of 60–80 per cent have recently been realized by condensing the γ-lactone with the α,γ-diketo acid in acetic anhydride (31):

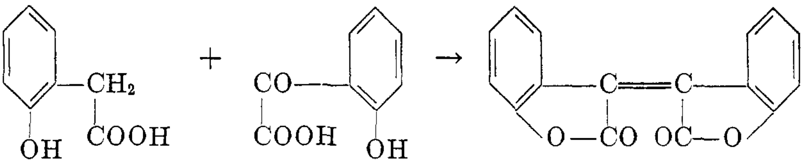


This general method has been used to prepare a number of symmetrically and unsymmetrically substituted dyes. In the latter case it has been shown that identical products are obtained when R and R′ are interchanged in the reactants; in other words, that the chromophore of the Pechmann dye is symmetrical (7, 13).

The reaction has also been extended to fused-ring analogs of the Pechmann dye, in which one or both hydroxyl groups are phenolic rather than enolic:



Orange-red crystals,
m.p. 269°C. (21)



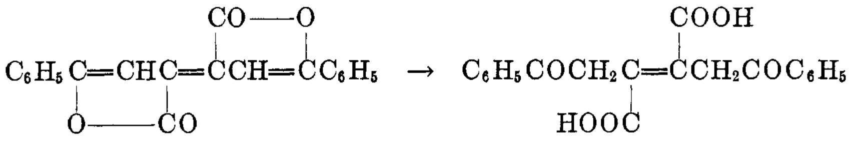
Orange crystals,
m.p. 283°C. (23, 24, 25)

The hypsochromic effect of the successive ring fusions is noteworthy.

III. STRUCTURE OF PECHMANN DYES

The elementary composition and molecular weight of the Pechmann dye (34), and its oxidative degradation to more than one mole of benzoic acid (33), indicate a structure $C_6H_5C_8H_2O_4C_6H_5$, and a corresponding structure $RC_8H_2O_4R$ for its substitution products. The symmetry of the chromophore —$C_8H_2O_4$— is established by the demonstration that a given pair of dissimilar substituents, R and R′, can give rise to one Pechmann dye only, and not two (13).

Hydrolysis in alcoholic potassium hydroxide results in the addition of two molecules of water, to give a product which was assigned the structure diphenacylfumaric acid by Kugel (34) and Bogert and Ritter (6):



$$C_6H_5\underset{O}{C}{=}CH\underset{CO}{C}{=}\overset{CO}{C}CH{=}\overset{O}{C}C_6H_5 \rightarrow C_6H_5COCH_2\underset{HOOC}{C}{=}\overset{COOH}{C}CH_2COC_6H_5$$

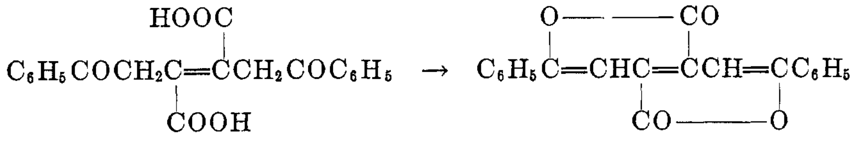
Although an independent synthesis of this acid has never been reported, no one has since questioned that the Pechmann dye is, in fact, its dilactone. Two objections have, however, been lodged against the conclusions of Bogert and Ritter:

(*1*) It was thought that Kugel's dye (prepared by the oxidation of γ-phenyl-Δ^{β}-butenolactone) (34) was the maleoid isomer of the Pechmann dye, and also was formed *initially* from benzoylacrylic acid and acetic anhydride but gradually isomerized on continued boiling, so that the product actually obtained consisted of a mixture of *cis* and *trans* isomers, in proportions dependent on the duration of boiling.

According to the rather convincing argument of Chovin (10, 15), no such isomerism exists; the supposed isomers are identical in melting point and absorption spectrum, and Bogert and Ritter were deceived by superficial differences in crystalline appearance.

Isomerism apart, there seems to be no published evidence indicating whether the Pechmann dye has, in fact, the *cis* or the *trans* structure. In the present survey, the formulas have been written in the form (generally *trans*) which more clearly illuminates the reaction under discussion.

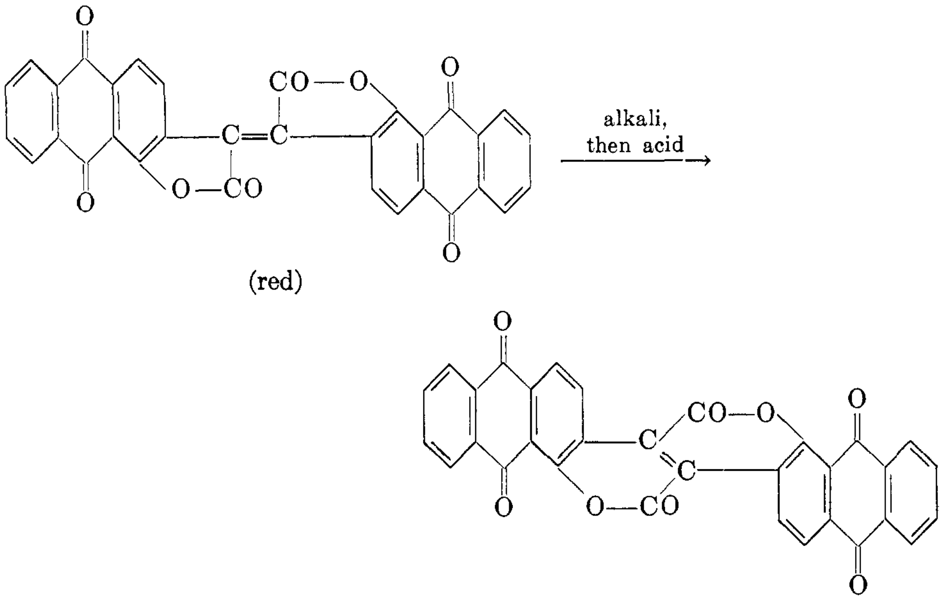
(*2*) *Two* dilactones of diphenacylfumaric acid are known, the Pechmann dye itself and an isomeric yellow lactone which was obtained by Bogert and Ritter (6) by dehydration of the acid (prepared from the dye). They called the yellow isomer the "dilactide" and assigned to it the following structure, embodying *six*-membered rings:



$$C_6H_5COCH_2\overset{HOOC}{C}{=}\underset{COOH}{C}CH_2COC_6H_5 \rightarrow C_6H_5\overset{O}{C}{=}CH\underset{CO}{C}{=}\overset{CO}{C}CH{=}\underset{O}{C}C_6H_5$$

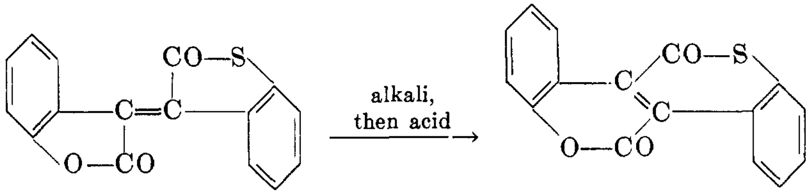
While it is not obvious which ring structure corresponds to the red dilactone, and which to the yellow, it is certainly significant that the Pechmann dye can be formed from pentacyclic intermediates under conditions which hardly favor ring-opening (methods B and D, above).

Nevertheless, Bogert's assignment of structure was at first rejected by Dufraisse and Chovin (30). Arguing by analogy from stability, color, and fluorescence, they ascribed the *six*-membered ring structure to the Pechmann dye, and the five-membered structure to the yellow isomer. Ten years later, however, further evidence convinced Chovin that Bogert had been right (24). This evidence consisted of the properties of five pairs of isomeric compounds. Three of the pairs are related to each other like the two lactones of diphenacylfumaric acid:



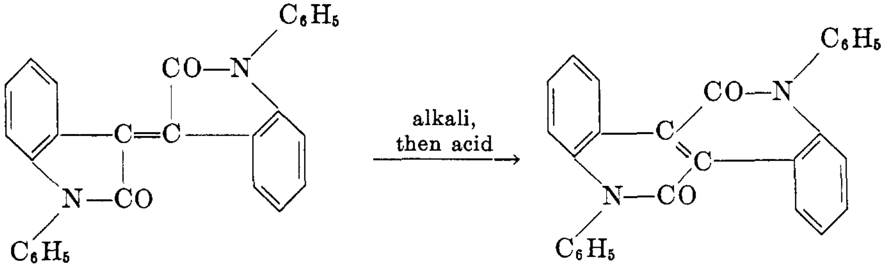
(red)

(yellow)



(orange)

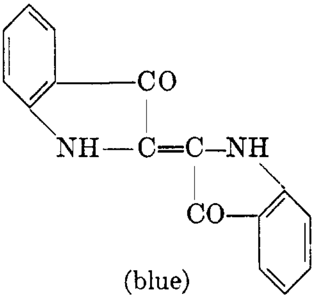
(yellow)



(red)

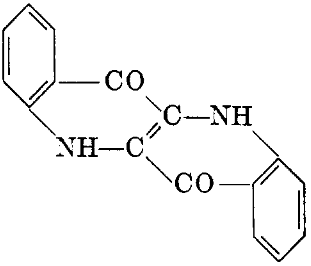
(yellow)

The other two pairs of compounds also display an isomerism of five- and six-membered rings, but the functional groups are in the gamma, rather than the alpha, relationship (in these cases the direct ring-enlargement reaction is not possible).

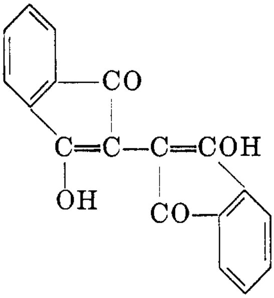


(blue)

and

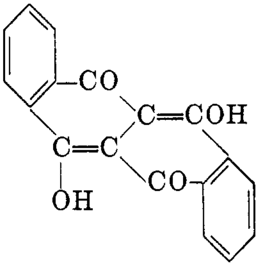


(yellow)



(brown-violet)

and



(orange-red)

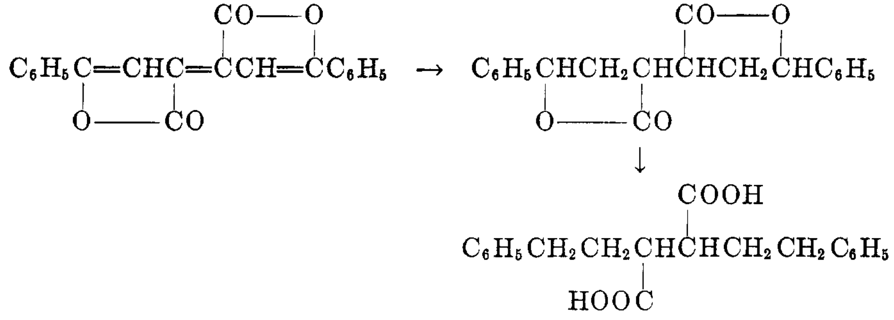
The chemical and color relationships of these compounds support Bogert's choice of structures for the Pechmann dye and its yellow isomer. This choice has now been further strengthened by infrared absorption studies (see Section IV).

IV. PROPERTIES OF PECHMANN DYES

The original Pechmann dye forms lustrous deep red plates or needles, which begin to sublime at 270°C. and melt at 317°C. (6, 31, 36). It is insoluble in water, alcohol, and ligroin, sparingly soluble in acetone, ether, and chloroform, and soluble in boiling acetic acid, benzene, xylene, and ethylene dibromide (27, 34). It can be recrystallized from benzene, toluene, or xylene. In benzene it gives beautiful red solutions with a golden-yellow fluorescence which is intensified by the addition of ligroin. The solution in concentrated sulfuric acid is green to blue, and precipitates the dyestuff unchanged on dilution. On heating (or on standing for 24 hr.), however, the solution turns red; dilution then gives a reddish solution with an intense green fluorescence (6, 34, 36). The dyestuff is insoluble in cold aqueous alkali but dissolves on heating; it is readily soluble in cold alcoholic potassium hydroxide, giving a red solution which turns a dirty brown on heating (34, 36). Zinc and alkali give a colorless solution, and zinc and acetic acid a colorless crystalline reduction product which regains the red color on exposure to air or ferric chloride (36).

According to the original publication of von Pechmann (36), distillation with zinc converts the dye into a hydrocarbon; no analytical data are reported. If insufficient zinc is used, the product appears to be an isomer of the dye. These reactions have never been studied further.

Catalytic hydrogenation gives first the saturated dilactone, which is then hydrogenolyzed to α,β-di(β-phenethyl)succinic acid (31):



$$C_6H_5C{=}CHC{=}CCH{=}CC_6H_5 \;(\text{CO—O},\ \text{O—CO}) \rightarrow C_6H_5CHCH_2CHCHCH_2CHC_6H_5 \;(\text{CO—O},\ \text{O—CO}) \downarrow C_6H_5CH_2CH_2CH(COOH)CH(COOH)CH_2CH_2C_6H_5$$

Oxidation with dilute nitric acid converts the Pechmann dye ($C_{20}H_{12}O_4$) into a colorless dibasic acid $C_{20}H_{14}O_6$, m.p. 224°C., which re-forms the dye on pyrolysis and is reduced by iron and acetic acid to a neutral substance, $C_{20}H_{14}O_4$, m.p. 333°C., which gives yellow solutions with "magnificent green fluorescence" (27).

The Pechmann dye has been applied to wool by soaking the fabric in a dilute alkaline solution of benzoylacrylic acid, acidifying, and boiling in acetic anhydride. The resulting deep brownish-red dyeing proved fast to washing, milling, acid, and alkali, but not to light. The color was discharged to a very pale yellow by sodium hydrosulfite and largely restored by hydrogen peroxide (4).

The substitution products of the Pechmann dye (see table 1) resemble the parent compound closely in their properties. The product prepared from mesitoylacrylic acid, is, however, unusual; it is obtained in the very high yield of 50 per cent, and shows high solubility and an unexpected absorption spectrum consisting of a single band in the blue. (Further spectral details are not given.) It exists in two forms, a red and a yellow. Its solutions in chloroform and xylene are reddish yellow rather than red. These anomalous properties are apparently not shown by the isomeric 2,4,5-trimethyl derivative (33).

Although little attention has been paid to the possible significance of these observations, any mechanism for the conversion of aroylacrylic acids to Pechmann dyes requires some sort of enolization step, and it is, therefore, tempting to ascribe the high yields of the mesityl dyestuff to the enhanced enolization of mesityl ketones (32); this implies that the rate or degree of enolization is a limiting factor in the synthesis.

Absorption spectra have been reported for the Pechmann dye and a number of its derivatives (14, 26, 29, 31, 33).

For the present review, samples of the Pechmann dye and its p,p'-dimethoxy and p,p'-diphenyl derivatives, prepared in this laboratory by Drs. J. E. Pretka and S. E. Ulrich, have been subjected to absorption spectra measurements.

The visual and ultraviolet absorption spectra in toluene solution (cell length, 1.00 cm.) were determined by S. P. Kodama and are presented in figures 1–6, plotted on an ordinate linear with the logarithm of absorbancy, to give a curve shape which is independent of concentration.

Infrared studies were made by Dr. D. N. Kendall, who reported his findings as follows:

> "Rock salt region infrared spectra of the Pechmann dye, figure 7, the dimethoxy derivative, figure 8, and the diphenyl derivative, figure 9, were run in the solid state as Nujol mulls on a Perkin and Elmer Model 21 infrared spectrophotometer.

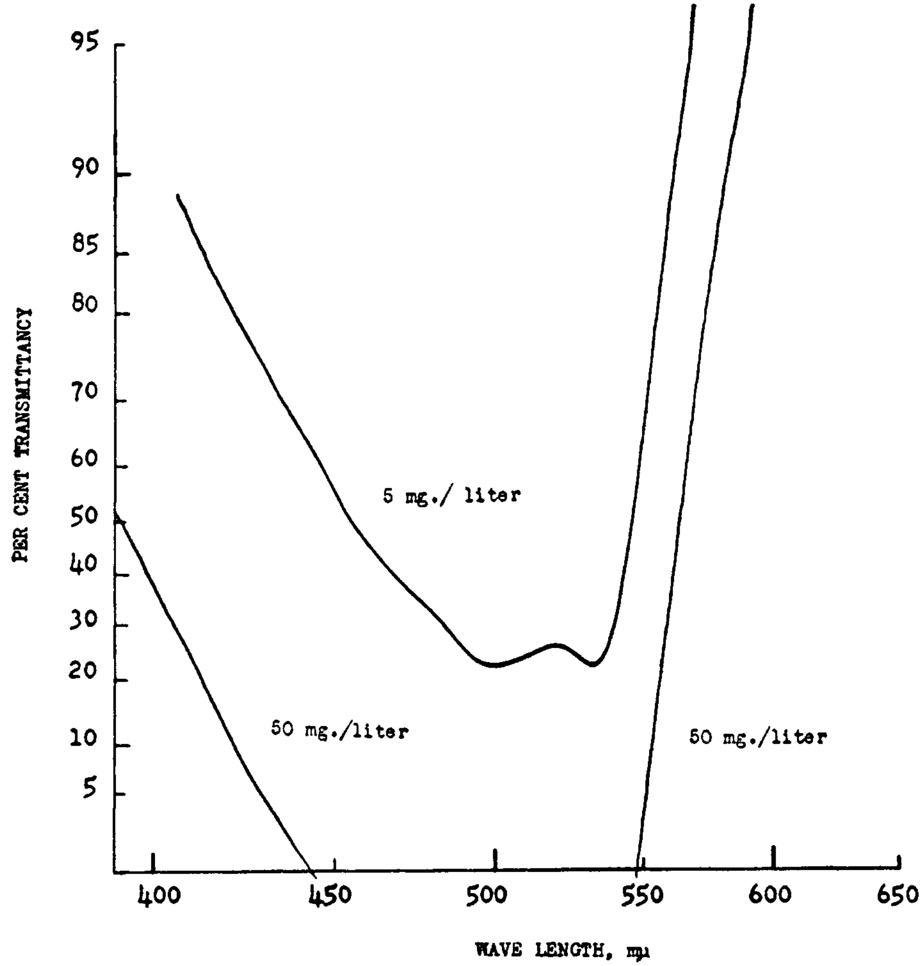


FIG. 1. Visual absorption spectrum of the Pechmann dye in toluene

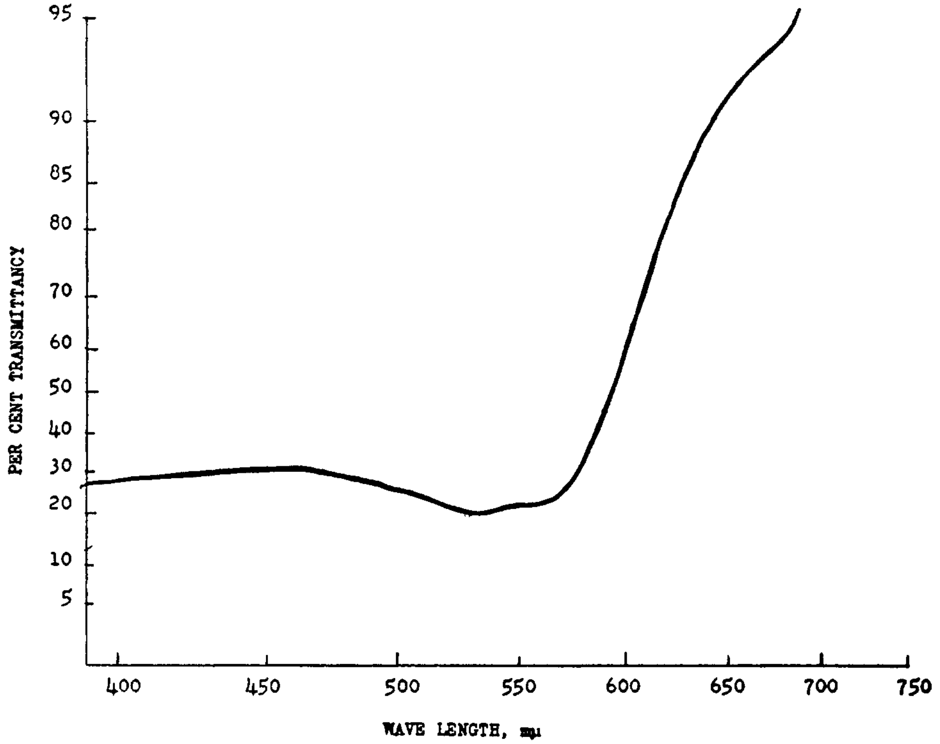
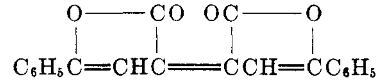


FIG. 2. Visual absorption spectrum of the p,p'-dimethoxy derivative of the Pechmann dye at a concentration of 50 mg. per liter in toluene.

"The Pechmann dye, figure 7, on a basis of infrared structural study, is probably a five-membered carbonyl ring existing as the *cis* isomer with the following structure:



$$\begin{array}{llll} \mathrm{O} \text{———} & \mathrm{CO} & \mathrm{OC} \text{———} & \mathrm{O} \\ | & | & | & | \\ \mathrm{C_6H_5C{=}} & \mathrm{CHC{=\!=}} & \mathrm{CCH{=}} & \mathrm{CC_6H_5} \end{array}$$

The Pechmann dye infrared spectrum showed a strong carbonyl absorption at 1752 $cm.^{-1}$, indicating a strained ring. It showed ring C—O—C, monosubstituted benzene, and *cis*-isomer bands. The five-membered ring is more likely than a six-membered one because of carbonyl strain.

"The diphenyl derivative also showed a strong carbonyl absorption at 1752 $cm.^{-1}$, indicating a strained ring. Its spectrum in the carbonyl stretching region was practically identical to that shown by the Pechmann dye itself.

"The dimethoxy derivative showed a strong carbonyl absorption at 1768 $cm.^{-1}$ and a medium strong absorption at 1742 $cm.^{-1}$ Its spectrum in the carbonyl stretching region is in sharp contrast to that shown by the Pechmann dye and the diphenyl derivative of the Pechmann dye. Randall, Fowler, Fuson, and Dangl (*Infrared Determination of Organic Structures*, D. Van Nostrand Company, Inc. (1949)) reported on the spectrum of dehydracetic acid (p. 231). They observed a strong carbonyl absorption at 1721 $cm.^{-1}$ By analogy, although a somewhat poor one, between the dehydracetic acid, the Pechmann dye, the diphenyl derivative, and the dimethoxy derivative, it would probably be concluded that the Pechmann dye and the diphenyl derivative thereof are five-membered ring lactones, whereas the dimethoxy derivative is probably a six-membered ring lactone or possibly a mixture of structural isomers."

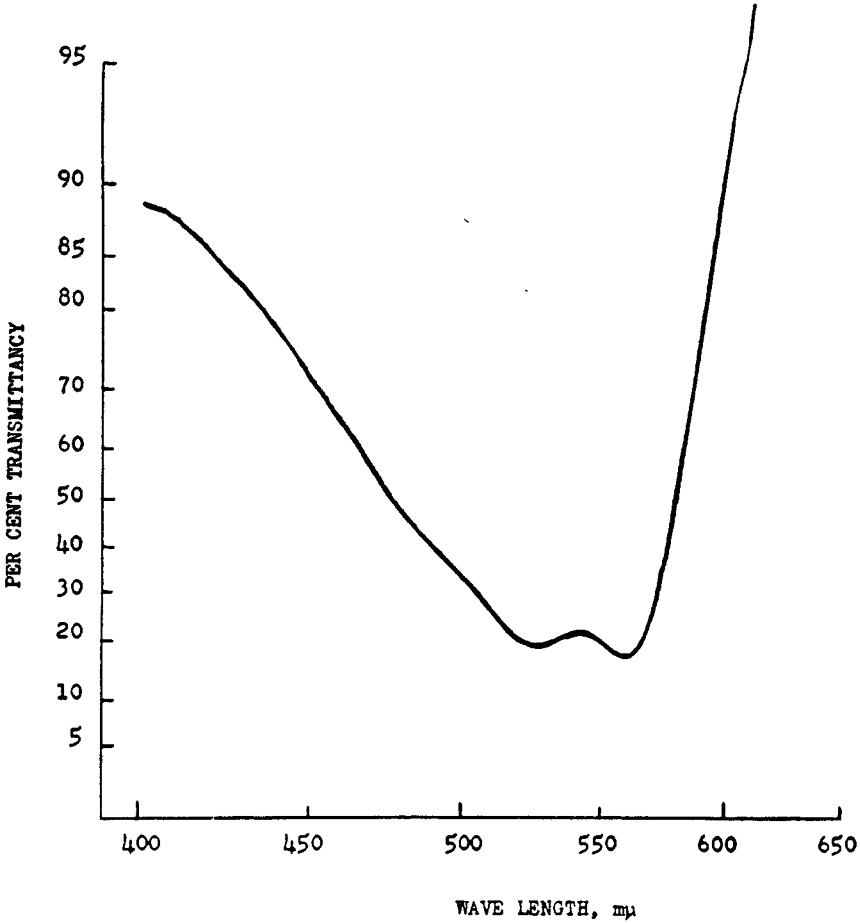


FIG. 3. Visual absorption spectrum of the p,p'-diphenyl derivative of the Pechmann dye at a concentration of about 20 mg. per liter in toluene.

V. HYDROLYSIS

Alcoholic potassium hydroxide hydrolyzes the lactone groupings of the Pechmann dye; the product can be isolated as the stable dipotassium salt of diphenacylfumaric acid, which is deep red and evidently exists in the enolic form. If this salt is treated with acid, or if it is dissolved in water and the resulting red solution immediately acidified, diphenacylfumaric acid is *not* obtained. Instead lactonization occurs; the nature of the product depends on the strength of the acid used. Treatment with a weak acid gives diphenacylfumaric monolactone (called the "monohydrated acid" in the literature); the ring must be five-mem-

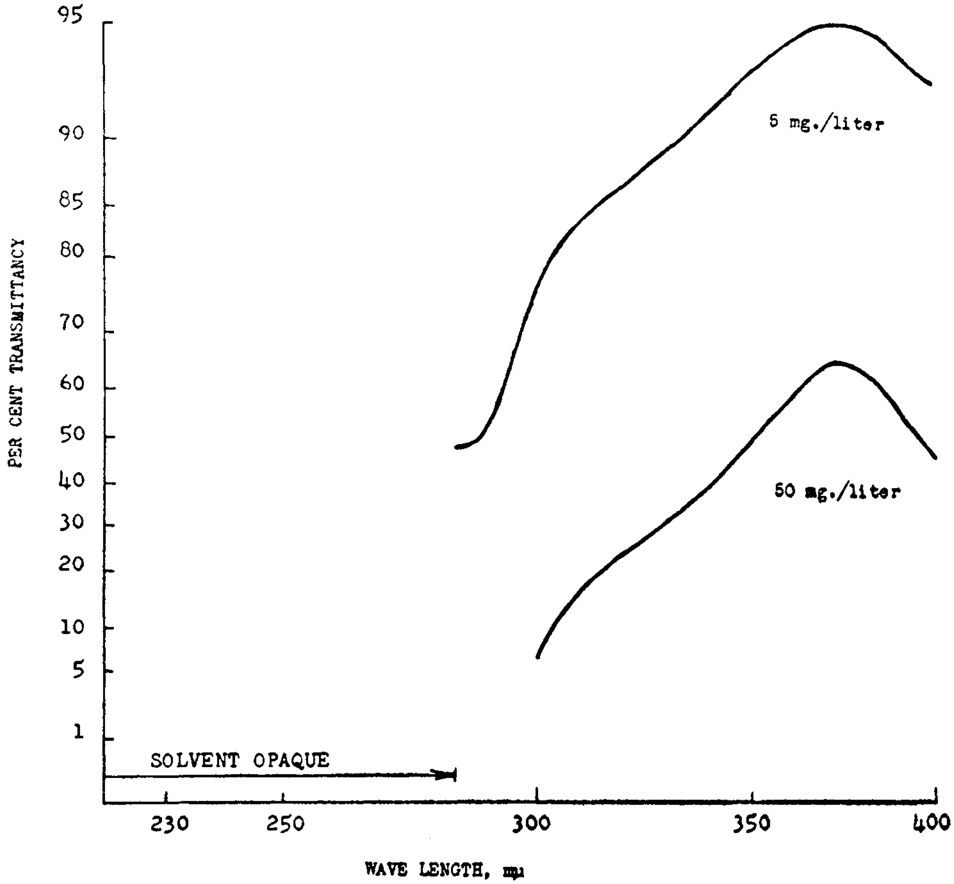


FIG. 4. Ultraviolet absorption spectrum of the Pechmann dye in toluene

bered, since the compound can be converted to the Pechmann red dilactone by heat or acetic anhydride. Strong acid gives the same monolactone, mixed with the two *di*lactones (the red Pechmann dye and its yellow isomer). Evidently strong acid catalyzes lactonization. The dilactones can be separated by chromatographic adsorption; fractional crystallization is ineffectual.

If, on the other hand, the dipotassium salt solution is allowed to stand, even a short time, it gradually turns yellow as it undergoes ketonization. On acidification, the monolactone obtained is mixed with diphenacylfumaric acid itself (called the "yellow dihydrated" acid). If the alkaline solution stands until ketonization is complete (1–3 hr. at room temperature), diphenacylfumaric acid is obtained free of lactone; in this case the strength of the acid used has no effect on the results. Acetic anhydride converts this acid to the yellow dilactone (9, 16). Esterification with diazomethane gives a diester which loses one molecule of methanol to give a monoester lactone; inasmuch as this compound gives the yellow dilactone on heating, it probably has the six-membered lactone ring (20).

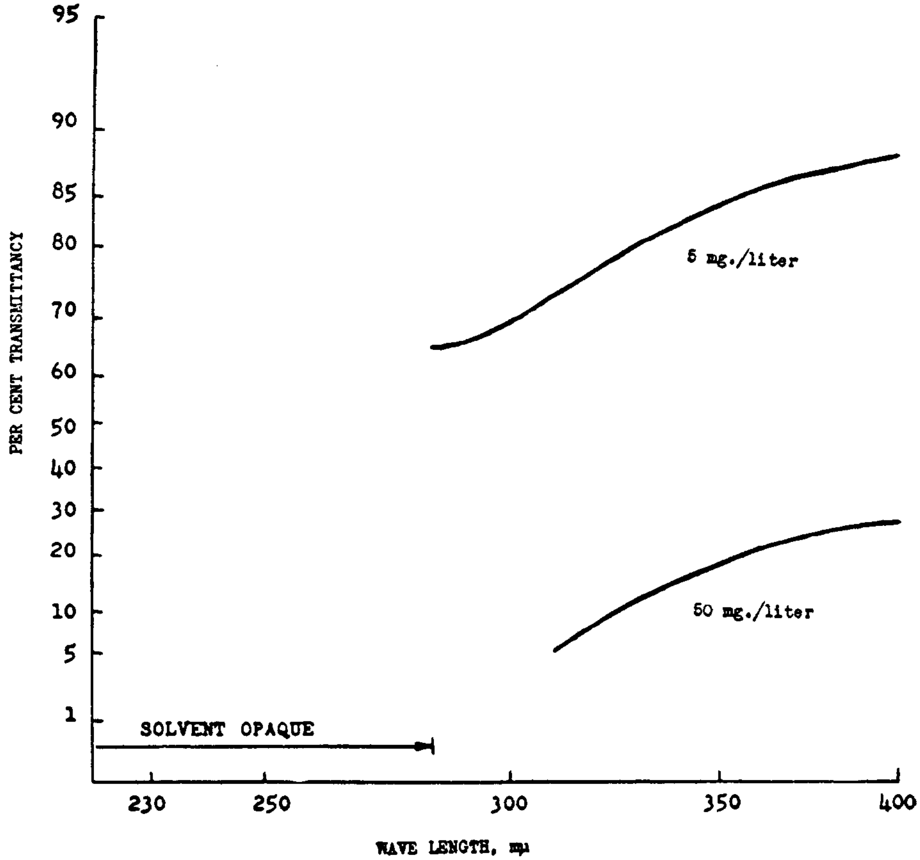


FIG. 5. Ultraviolet absorption spectrum of the p,p'-dimethoxy derivative of the Pechmann dye in toluene.

A further change occurs if the dipotassium salt stands in solution for a considerably longer time, 24–48 hr.; acidification now precipitates, not diphenacylfumaric acid, but a colorless isomer of it (called "white dihydrated acid"), possibly the *cis* form, diphenacylmaleic acid. Here also the strength of the precipitating acid is immaterial. This compound is probably the same as the diphenacylmaleic acid of Bogert and Ritter (6); acetic anhydride converts it to the Pechmann dye.

The enol form of diphenacylfumaric acid thus shows a strong tendency to undergo lactonization, especially in the presence of mineral acid. If ketonization occurs, however, the tendency becomes much weaker, and lactone formation then requires rather severe conditions, such as concentrated sulfuric acid or boiling acetic anhydride.

The most important of these transformations are diagrammed on page 75. (In consulting the original papers it must be remembered that Chovin has since interchanged his formulas for the Pechmann dye and its yellow isomer (24).

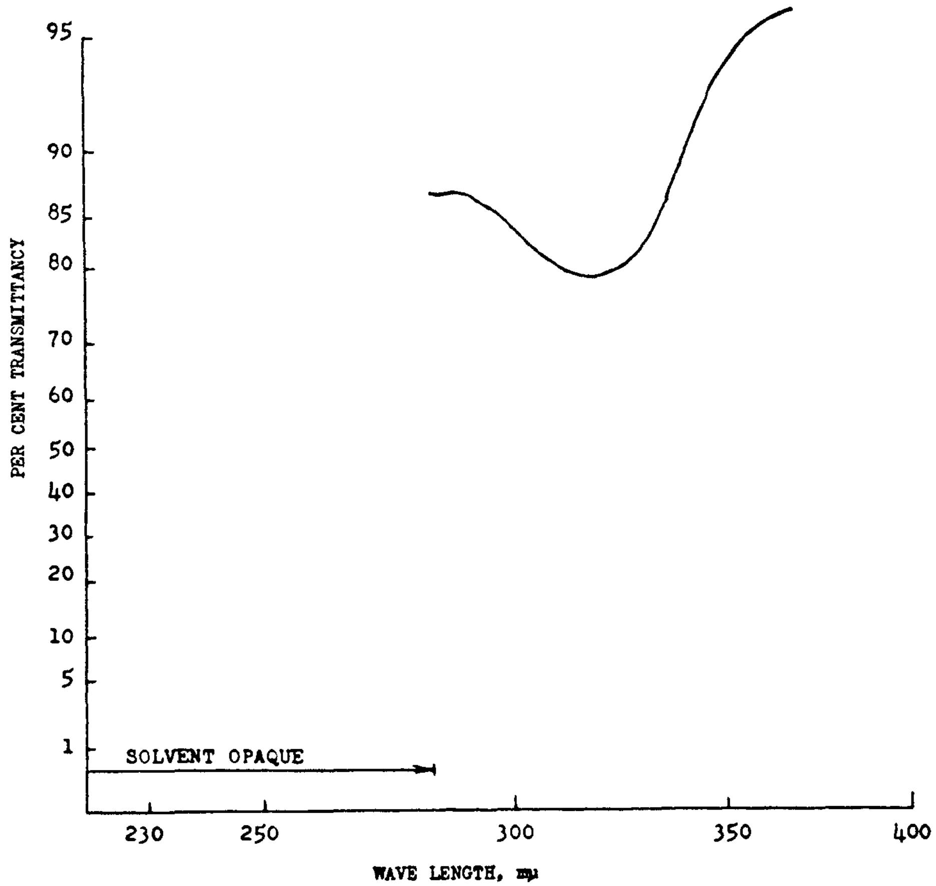


Fig. 6. Ultraviolet absorption spectrum of the p,p'-diphenyl derivative of the Pechmann dye at a concentration of about 2 mg. per liter in toluene.

The earlier work (6, 34) on the hydrolysis is incomplete; not all of the important experimental variables were recognized.)

Some of these reactions have also been carried out with homologs (17) and benzologs (18) of the Pechmann dye. If the dye is unsymmetrically substituted, the possibilities of isomerism are of course increased. However, in the hydrolysis of the phenyl β-naphthyl dye, only one "monohydrated" acid was obtained (19).

VI. AMINOLYSIS OF PECHMANN DYES

Kozniewski and Marchlewski (33) found that the Pechmann dye, when heated with aniline in glacial acetic acid, is converted to a dark green crystalline product which is easily sublimed. Bogert and Greenberg (4) describe maleoid–fumaroid isomers of this substance, but these isomers are not very sharply characterized, and their existence must be considered doubtful, since they are derived from the

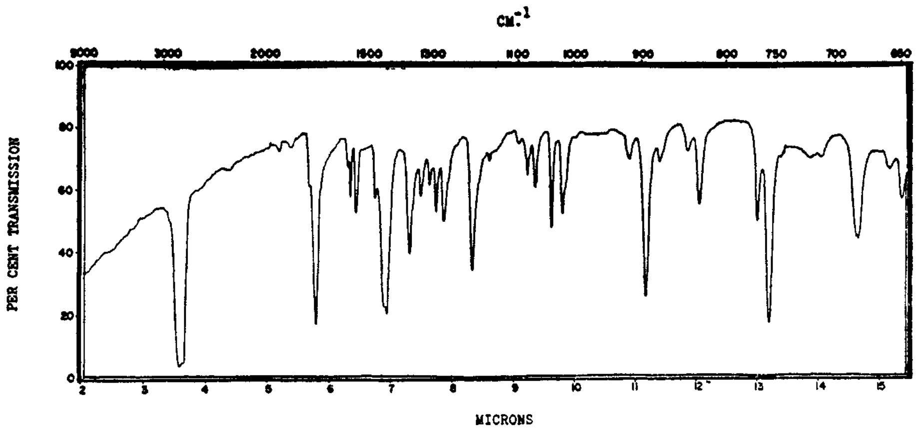


FIG. 7. Infrared absorption spectrum of the Pechmann dye

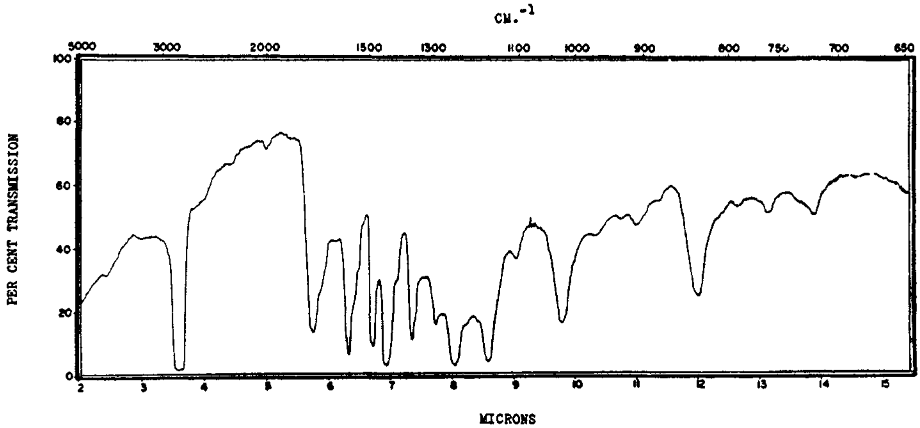


FIG. 8. Infrared absorption spectrum of the p,p'-dimethoxy derivative of the Pechmann dye.

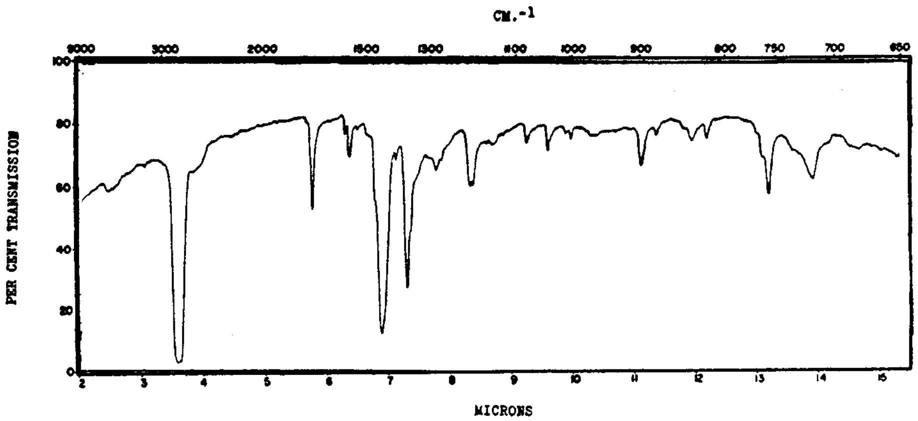
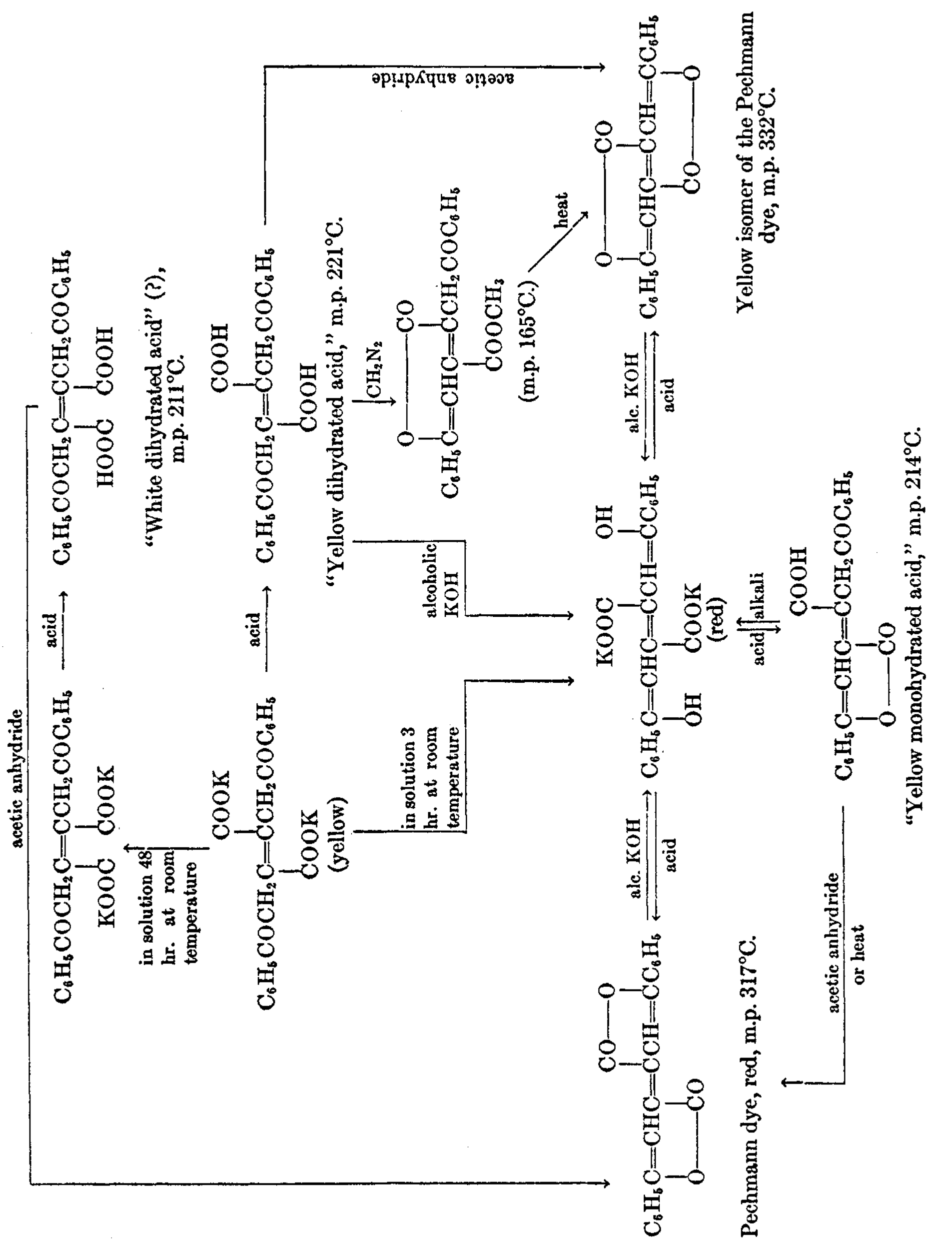


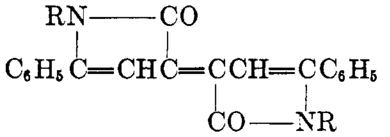
FIG. 9. Infrared absorption spectrum of the p,p'-diphenyl derivative of the Pechmann dye.



supposed stereoisomers of the Pechmann dye, which Chovin (15) has shown to be non-existent.

The aminolysis reaction was greatly extended by Bogert and Greenberg (4), who obtained the analogous reaction products from ammonia and fifty-nine amines, including various aniline derivatives, the naphthylamines, benzylamine, a number of aliphatic and aromatic amino acids, urea, sodium sulfanilate, arsanilic acid, phenylhydrazine, and *p*-aminoazobenzene. (However, a number of amines gave no product. Apart from the fact that simple aliphatic amines fail to react, there seems to be no general rule governing the success of the reaction.) The reaction was also successful with diamines such as benzidine and the phenylenediamines; in these cases only one amino group reacted. The yields were excellent. The products varied in color from bright or dark green to violet and purple; the compound obtained from aniline fluoresced violet or other shades in xylene solution. Light-fast violet or purple dyeings on wool or silk were given by the reaction products from *m*-aminophenol, glycine, alanine, leucine, sodium sulfanilate, and *p*-arsanilic acid. However, no dyeing resulted when wool was boiled with the Pechmann dye in aniline and glacial acetic acid.

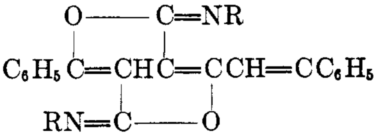
The analytical data indicate that these compounds are formed by the elimination of two molecules of water from two molecules of amine and one of dyestuff. Bogert and Greenberg proposed the following possible structures



$$\begin{array}{l} \quad RN\text{——}CO \\ C_6H_5C{=}CHC{=}CCH{=}CC_6H_5 \\ \qquad\qquad CO\text{——}NR \end{array}$$

Dilactam

or

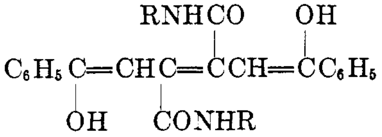


$$\begin{array}{l} \qquad O\text{——}C{=}NR \\ C_6H_5C{=}CHC{=}CCH{=}CC_6H_5 \\ \quad RN{=}C\text{——}O \end{array}$$

Diimido ether

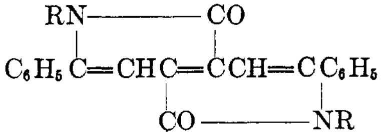
and preferred the latter, because the compounds are readily hydrolyzed by alcoholic potassium hydroxide, with liberation of the amine and the formation of diphenacylfumaric acid.

However, it is quite plausible that, in the formation of these compounds, the first step should be a simple aminolysis of the lactone ring, leading to a diamide:



$$\begin{array}{l} \qquad\qquad RNHCO \quad OH \\ C_6H_5C{=}CHC{=}CCH{=}CC_6H_5 \\ \qquad OH \quad CONHR \end{array}$$

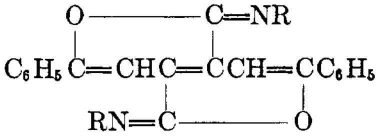
When this intermediate loses two molecules of water, it could give six-membered rings just as easily as five-membered rings:



$$\begin{array}{l} \quad RN\text{————}CO \\ C_6H_5C{=}CHC{=}CCH{=}CC_6H_5 \\ \qquad\quad CO\text{————}NR \end{array}$$

Dilactam

and



$$\begin{array}{l} \qquad O\text{————}C{=}NR \\ C_6H_5C{=}CHC{=}CCH{=}CC_6H_5 \\ \qquad RN{=}C\text{————}O \end{array}$$

Diimido ether

These possibilities were, however, never entertained by Bogert and Greenberg, and a choice does not appear to be possible on the basis of the available evidence.

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Ulrich, S. P. Kodama, D. N. Kendall, and Ray Krammes in the preparation of Pechmann dye compounds and in the study of their absorption spectra presented in the present review.

VII. REFERENCES

(1) ALLEN, C. F. H., NORMINGTON, J. B., AND WILSON, C. V.: Can. J. Research **11,** 382–94 (1934).
(2) BERGMANN, W.: U. S. patent 2,640,836 (June 2, 1953).
(3) BERGMANN, W., AND FANG, C. S.: U. S. patent 2,640,837 (June 2, 1953).
(4) BOGERT, M. T., AND GREENBERG, I. W.: Collection Czechoslov. Chem. Communs. **2,** 83–94 (1930).
(5) BOGERT, M. T., AND HOWELLS, H. P.: J. Am. Chem. Soc. **52,** 837–50 (1930).
(6) BOGERT, M. T., AND RITTER, J. J.: J. Am. Chem. Soc. **46,** 2871–8 (1924).
(7) CHOVIN, P.: Compt. rend. **204,** 360–3 (1937).
(8) CHOVIN, P.: Compt. rend. **204,** 1073–5 (1937).
(9) CHOVIN, P.: Compt. rend. **205,** 565–7 (1937).
(10) CHOVIN, P.: Compt. rend. **205,** 677–80 (1937).
(11) CHOVIN, P.: Ann. chim. (Paris) **9,** 447–553 (1938).
(12) CHOVIN, P.: Ann. chim. **9,** 480 ff. (1938).
(13) CHOVIN, P.: Ann. chim. **9,** 486 ff. (1938).
(14) CHOVIN, P.: Ann. chim. **9,** 476, 551 ff. (1938).
(15) CHOVIN, P.: Ann. chim. **9,** 495 (1938).
(16) CHOVIN, P.: Ann. chim. **9,** 500 ff., 545 ff. (1938).
(17) CHOVIN, P.: Ann. chim. **9,** 504, 522 (1938).
(18) CHOVIN, P.: Compt. rend. **207,** 1418–20 (1938).
(19) CHOVIN, P.: Compt. rend. **208,** 1228–30 (1939).
(20) CHOVIN, P.: Compt. rend. **209,** 169–71 (1939).
(21) CHOVIN, P.: Compt. rend. **211,** 474–6 (1940).
(22) CHOVIN, P.: Compt. rend. **212,** 549–51 (1941).
(23) CHOVIN, P.: Bull. soc. chim. France **11,** 82–90 (1944).
(24) CHOVIN, P.: Bull. soc. chim. France **11,** 91–6 (1944).
(25) CHOVIN, P., AND GUNTHART, J.: Bull. soc. chim. France **12,** 105–11 (1945).
(26) DUFRAISSE, C., AND CHOVIN, P.: Compt. rend. **197,** 1127–9 (1933).
(27) DUFRAISSE, C., AND CHOVIN, P.: Bull. soc. chim. France **1,** 771–89 (1934).
(28) DUFRAISSE, C., AND CHOVIN, P.: Bull. soc. chim. France **1,** 781 (1934).
(29) DUFRAISSE, C., AND CHOVIN, P.: Bull. soc. chim. France **1,** 782 (1934).
(30) DUFRAISSE, C., AND CHOVIN, P.: Bull. soc. chim. France **1,** 790–6 (1934).
(31) FANG, C. S., AND BERGMANN, W.: J. Org. Chem. **16,** 1231–7 (1951).
(32) KOHLER, E. P., AND THOMPSON, R. B.: J. Am. Chem. Soc. **59,** 887–93 (1937).
(33) KOZNIEWSKI, T., AND MARCHLEWSKI, L.: Bull. acad. sci. Cracow **1906,** 81–95 (in German); Chem. Zentr. **1906, II,** 1189.
(34) KUGEL, M.: Ann. **299,** 50–66 (1898).
(35) MARSCHALK, C.: Bull. soc. chim. France **9,** 826–32 (1942).
(36) PECHMANN, H. VON: Ber. **15,** 881–92 (1882).
(37) PUMMERER, R., AND BUCHTA, E.: Ber. **69,** 1005–17 (1936).
(38) PUMMERER, R., AND BUCHTA, E.: Ber. **69,** 1018–21 (1936).
(39) THIELE, J., AND SULZBERGER, N.: Ann. **319,** 196–211 (1901).