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NOVEL METHODS OF SYNTHESIS OF DITHIZONATE TYPE PHOTOCHROMIC DYES & POLYMERS

By

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Abstract

A method is described for the preparation of photochromic dyes wherein a diazotized p-aminophenyl mercuric acetate is coupled with various compounds such as bis-N,N-acetoxyethylaniline and 1-phenyl-3-methylpyrazolone. This method opens the feasibility of altering the nature of the photochromic dye just by changing the coupling compounds. Dyes prepared by this method have been characterized and found to be superior in many respects. Acrylic type monomers with chromophoric substituents have been synthesized and subjected to polymerization and copolymerization with other monomers. Films cast from solution of these polymers are found to be superior to polymers coated or imbibed with photochromic solutions.

Introduction

Metal dithizonate dyes are one of the earliest organic dyes that were found to exhibit photochromism. In spite of the fact that several modern day dyes have dominated the world of photochromism, the interest in metal dithizonate is still alive. This is because this family of dyes exhibit the best fatigue resistance properties.

Although the relative ease of preparation of dithizonate dyes has been recognized, the diversity of dyes that can be prepared by the hitherto known schemes of synthesis is limited to change in the metal atom in the molecule. Some modifications in the substituents are also possible. Several heavy metals have been successfully incorporated in these photochromic dyes by Meriwether and others. But it was Meriwether[1,2] who drew the conclusion that the photochromism was a general phenomenon of the heavy metal dithizonates. The most popular heavy metals used in the synthesis of photochromic metal dithizonates are mercury, palladium, silver, platinum, zinc, bismuth, lead, and cadmium.

Known Methods of Synthesis

The best known methods of preparation of metal dithizonates are by Kazan[3] and by Meriwether[4].

Kazan's Method[3,5]

In Kazan's method, the basic dye, (p-Aminophenyl) Mercuric Dithizonate) was obtained by the reaction between p-amino phenylmercuric

acetate and diphenyl thiocarbazone. Desired substituents were attached in the second step by the reaction between the amino group with the halogen of the reactant such as cyanuric chloride.

Meriwether's Methods

1. Aqueous solution of the suitable metal salt (nitrate, chloride, sulfate or acetate) was extracted with a solution of dithizone dissolved in chloroform or carbon tetrachloride, thus giving the primary complex, metal dithizonate.

2. The chloride salt of the desired metal was dissolved in absolute ethanol; to this suspension benzene solution of dithizone was added. The mixture was refluxed for several hours.

The primary metal dithizonate formed by these methods was subjected to a second step to attachd desired substituents.

The known mechanism of photochromism of metal dithizonates:

Meriwether, Breitner, and Colthrup[2] found that the photochromism of metal dithizonates involves a hydrogen transfer process as well as a geometrical isomerism as illustrated in the following reaction mechanism on irradiations. The photochemical reaction is postulated to involve a trans-cis isomerization about the C=N bond and nitrogen-to-nitrogen hydrogen transfer. Thus, an entirely altered chromophone containing a thiocarbonyl group is produced.

Performance of Metal Dithizonates

Although the metal dithizonates do not result in high quantum yield, high optical densities can be realized with adequate light intensity. They show good photochemical stability in the visible region of the electromagnetic spectrum, but they gradually decompose when exposed to shorter wavelengths below 340 nm.

New Approaches to The Synthesis of Metal Dithizonates

In order to provide diversity in the shades of color of the final product within the same metal dithizonate, substituents need to be changed. For this purpose, two systems are employed in this scheme of synthesis. They are the acid system and the alkaline system. In both systems, the diazotized metal compound is first made and then coupled with an appropriate coupling compound, leading to the desired substituent in the final dye. In the final step, the coupled product is reacted with diphenyl thiocarbozone, giving the metal dithizonate dye.

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Diazotization

In the first step, a 2000 ml beaker was charged with 400 parts of water, 35 parts of concentrated hydrochloric acid, and 35.1 parts (0.1 mole) of p-aminophenyl mercuric acetate. The beaker with its contents was cooled to 0°C. in an ice bath. A solution of 6.9 parts of sodium nitrite in 50 parts of water was then added to the mixture in the beaker slowly during a period of one hour. When the addition of sodium nitrite solution was complete, the mass was stirred for one hour, maintaining the temperature between 0°C. and 5°C. The excess nitrous acid was destroyed with sulfamic acid.

In the second step, a coupling solution was prepared as follows:

Acid coupling compounds.

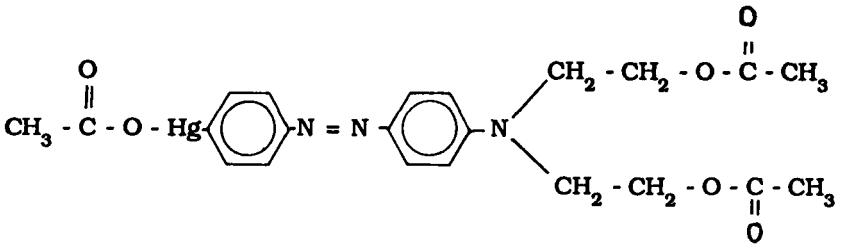
A 500 ml three necked flask was charged with 25 parts of glacial acetic acid and 18.3 parts of 2,2'-(phenyl imino) diethanol (0.11 mole). The mixture was heated to 95°C. and then at 95°C. to 100°C. Then 23 parts of acetic anhydride was added to it drop by drop. When the addition of acetic anhydride was complete, the reaction mass was held at 98°C. - 100°C. for one hour. Then the reaction product was poured into a mixture of 13 parts of concentrated hydrochloric acid, 250 parts of water, and 250 parts of ice.

Coupling.

In the third step, the materials of steps 1 and 2 above were coupled as follows:

The coupler solution was iced to 0°C. and the diazo solution from step 1 was added to it slowly during a period of one hour, maintaining the temperature at 0°C. - 5°C. When the addition of the diazo solution was complete, a solution of 250 parts of water and 50 parts of anhydrous sodium acetate was added to the coupling mixture at 0°C - 5°C. during a period of one hour. The reaction mass should be slightly acidic to congo red paper. The mixture was stirred for five hours, filtered, and the residue in the filter paper was washed with 500 parts of cold water and dried. The dye was recrystallized from acetone solution.

This diazotization of p-aminophenylmercuric acetate and coupling provided the following compound (structural formula).



Yield - 62.3 parts (99.3%)

Molecular formula- $C_{22}H_{25}HgN_3O_6$

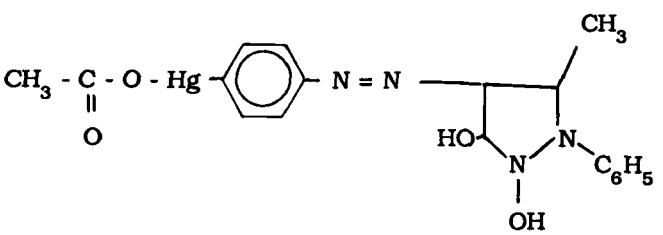
Percentages of elements:

	Calculated	Found
Carbon, C	42.1	41.8
Hydrogen, H	4.0	3.9
Mercury, Hg	31.9	31.2
Nitrogen, N	6.7	6.5

Similarly, the following coupling compounds were used to prepare other new dyes: N,N-Diethyl aniline; N-ethyl-N-acetoxy ethyl aniline; N,N-bisacetoxy ethyl-m-toluidine; N-ethyl-N-cyano ethyl aniline; N,N-biscyano ethyl aniline; N,N-biscyano ethyl-m-toluidine.

Alkaline coupling compounds:

A coupler solution containing 17.4 parts of N-phenyl-3-methyl pyrazolone in 75 parts of water and 4.1 parts of sodium hydroxide was prepared at 25°C. To this coupler solution was added a solution of 15 parts of anhydrous sodium carbonate in 150 parts of water. The entire solution was cooled to 8° to 10°C. The diazo solutionfrom step one was added to this coupler solution maintaining the temperature at 8° to 15°C. The slurry was stirred overnight, then filtered, washed, and dried. The dye was recrystallized from chloroform solution.



Yield - 53.4 parts (99.6%)

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Molecular formula - $C_{18}H_{16}HgN_4O_3$

Percentage of elements:

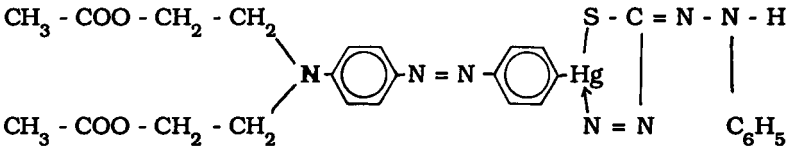
	Calculated	Found
Carbon, C	40.3	39.9
Hydrogen, H	3.0	2.9
Mercury, Hg	37.3	36.8
Nitrogen, N	10.4	10.1

Similarly, the following coupling compounds were coupled with the diazo compound.

1-p-chlorophenyl-3-methyl pyrazolone; 1-m-chlorophenyl-3-methyl pyrazolone; 1-p-sulfophenyl-3-methyl pyrazone; 7-hydroxy-4-methyl coumarin; 8-hydroxy quinoline; p-cresol; naphthol AS; naphthol ASSG.

Chromophore Formation Step.

To a vigorously stirred mixture of 150 parts of chloroform and 100 parts of water were added 8.9 parts (0.0142 mole) of product from example 1, i.e. 4-mercuric acetate - 4 - (N,N - bis aceloxy ethyl) amino -1, 1' - azobenzene, 3.78 parts (0.045 mole) of sodium bicarbonate and 3.33 parts (0.013 mole) of diphenyl thio carbozone in small portions. The mixture changed color from purple to reddish or orange. After stirring for 15 minutes, the chloroform was evaporated under reduced pressure and the product was isolated by filtration. Recrystallization from acetone solution gave reddish needles of the photochromic dye:



Yield - 11.3 parts (98.1%)

Molecular Formula - $C_{33}H_{33}HgN_7O_4S$

Percentage of elements:

Table 2

	Calculated	Found
Carbon, C	48.1	47.9
Hydrogen, H	4.0	3.9
Mercury, Hg	11.9	11.8
Nitrogen, N	3.9	3.7
Sulfur, S.	3.9	3.7

Monomer

Preparation of P-acrylamidophenylazophenyl mercuric acetate

The following were dissolved in 20ml of anhydrous N-N-dimethylacetamide: 4.56 g (0.01 mol) of p-aminophenylazophenyl mercuric acetate, 0.3 g of hydroquinone, and 1.5 ml of anhydrous ethylamine. To this solution was added dropwise under ice cooling 10 ml of N,N-dimethylacetamide solution containing 1.35 ml acryloylchloride followed by stirring for 5 hours. Acetic acid (20 ml) was then added to the reaction mixture, and the resulting solution was poured into a large quantity of water to afford yellowish brown precipitates. Recrystallization from dimethylformamide (DMF) - water combination gave 3.5g (78.1) brown powder of mp 7320°C.

Polymer

Preparation of p-acrylamidophenylazophenyl mercuric acetate - Methylmethacrylate copolymer

A solution of 0.1 g of p-acrylamidophenylazo-phenyl mercuric acetate, 0.9 g of methylmethacrylate, 2 ml of dimethylformamide, and 0.01 g of α,α'1-azobisisobutyronitrile were charged into a pyrex glass ampoule. Then it was frozen under vacuum and sealed off. The reaction ampoule was heated at 80°C. in a thermostat bath for 48 hours. The viscous solution resulted was poured into 10 ml benzene followed by centrifugation to remove the unpolymerized monomer. After evaporation of the solution in vacuo, the solid obtained was dissolved in 20 ml carbon tetrachloride, followed by filtration to separate the copolymer. The solution was poured into a large amount of methanol. Solid orange colored product obtained was filtered, dried, and analyzed by azo group estimation.

Photochromic Polymer

Preparation of p-acrylamidophenylazophenyl mercury (II) dithizonate copolymer

A 5.0 g copolymer was dissolved in 200 ml methylethylketone. To this stirred solution, a mixture of 0.023 g dithizone and 0.0261 g sodium bicarbonate was added in small proportions at room temperature. The mixture was stirred vigorously for five hours and was kept overnight in the dark. The resulting red colored solution was filtered. The filtrate was evaporated under vacuum. The solid (red color) obtained indicates formation of photochromic function in the side chains of the copolymer.

Rate Measurements

The copolymer (0.5 g) was dissolved in 5 ml of toluene. Film of thickness ca. 0.05 mm was prepared from this solution by spreading it over

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a glass plate followed by evaporation of the solvent at room temperature. The film was elapsed for at least a week before measurement of photochromism. The film was exposed to sunlight for 30 to 1200 sec. and immediately placed in Beckman DK-2A, ratio recording spectrophotometer. The change of absorbance was recorded by scanning a spectra at various time intervals. Absorption spectra of infinite time was taken after several days.

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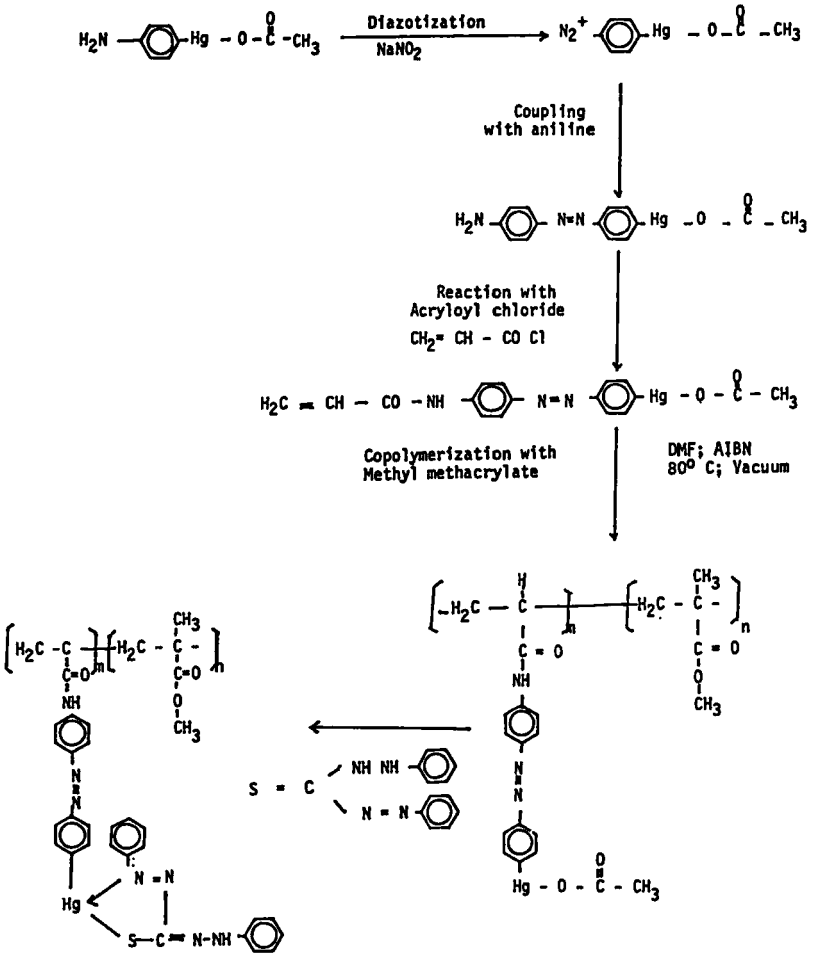
Reaction Scheme



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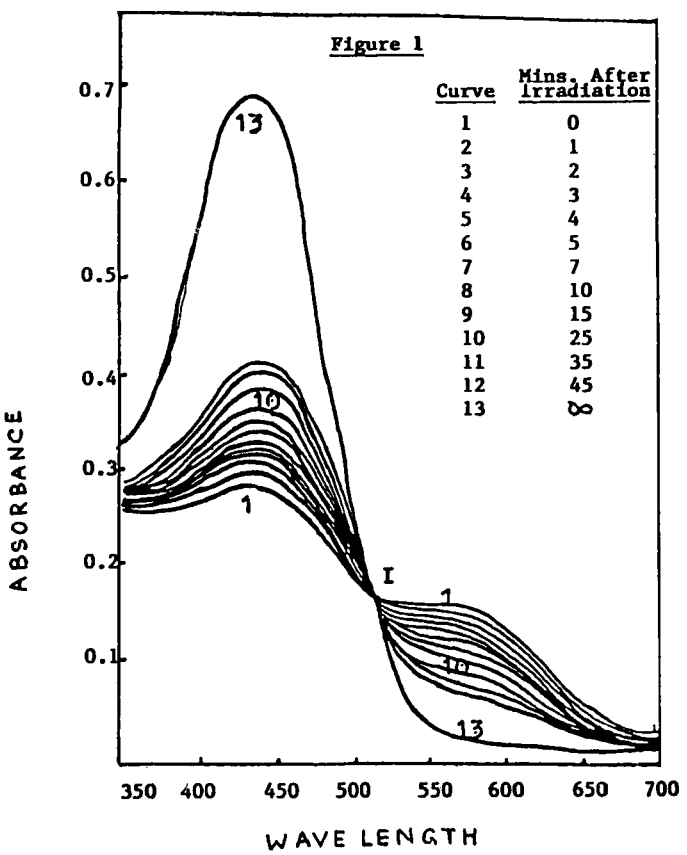

Visible spectrum of return reaction of copolymer film exposed to sunlight for 10 min: (α) infinite time; (I) Isobestic point

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