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## TRIARYLMETHANE COMPOUND

Joseph B. Dickey and James G. McNally, Roch-ester, N. Y., assignors to Eastman Kodak Com-pany, Rochester, N. Y., a corporation of New Jarcow Jersey

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## 1 Claim. (Cl. 260-391)

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This invention relates to polyarylmethane compounds. More particularly, the polyarylmethane compounds of our invention are characterized by containing as a nuclear substituent in para position to the methane carbon atom 5 the group having the general formula:



or the group having the general formula:



wherein in the above formulas n represents zero or the numeral 1, X represents an acidic radical,  $X_1$  represents an atom of oxygen, or an atom of 25sulphur, R represents an alkylene group, R1 represents an alkyl group, R<sub>x</sub> represents an alkyl group, an allyl group, a phenyl group, a furyl group, or the group



 $\mathbf{R}_{y}$  represents an alkyl group, an allyl group, a 35 phenyl group, a furyl group or the group



and  $Z_1$  and  $Z_2$  each represents hydrogen or an alkali-forming metal.

Specifically, the polyarylmethane compounds of our invention are diarylmethane or triarylmethane compounds of the benzene and naphthalene series, the nuclei of the said compounds containing, if desired, besides one of the above described phosphorus groups, one or more monovalent substituents selected from the group consisting of alkyl groups such as methyl, ethyl, propyl, butyl, cetyl, allyl, alkoxy groups such as methoxy, ethoxy, propoxy, butoxy, halogen 55 atoms such as chlorine, bromine, fluorine, sulphonamide groups such as sulphonethylamide, sulphonfurfurylamide, sulphondimethylamide, carboxylic acid groups and their alkyl esters, a sulphonic acid group, amino groups such as di- 60

methylamino, acetamino, furfurylamino, and the like, and groups such as

2,304,890



wherein n,  $X_1$ , R,  $R_1$ ,  $R_x$ ,  $R_y$ ,  $Z_1$  and  $Z_2$  have the same meanings as previously defined. In connection with the definitions of the foregoing symbols, X can be an atom of chlorine or bromine, a 15 group such as perchlorate, alkylsulfate, p-toluenesulfonate, and the like R, can be methylene, ethylene, propylene, butylene for example, R1 can be methyl, ethyl, propyl, butyl, cetyl, Rx and  $\mathbf{R}_{y}$  can be methyl, ethyl, propyl, butyl, cetyl, allyl, phenyl, tolyl, chlorophenyl, phenylsulfonic acid, 20 furyl, furfuryl, and a phosphorus group of the kind previously indicated, and  $Z_1$  and  $Z_2$  can be hydrogen, an atom of sodium, potassium, calcium, and the like, or an ammonium radical.

We have found that the above described polyarylmethane compounds of our invention are particularly valuable as dyes for antihalation backings, antihalation underlayers or screening layers, and antihalation overlayers for photo-30 graphic plates, films, and in some cases for photographic papers. In the latter case, the antihalation layer would be an underlayer being located between the paper surface and the lightsensitive emulsion. Our new dyes are blue to greenish-blue in color and have the property of becoming and remaining soluble and capable of diffusing away from the support during the usual photographic operations of developing, fixing and washing. Besides, they are quite stable to hard water and easily dischargeable with sodium bisulfite.

It is an object of the invention, therefore, to prepare the polyarylmethane compounds described. A further object is to provide a lightsensitive photographic element having an antihalation layer containing one or more polyarylmethane dyes of the kind described, the said layer being readily decolorized and easily diffused from the support.

The polyarylmethane compounds of the invention may be prepared by a number of methods. For example, the diarylmethane compounds containing the phosphatoalkyl group



can be prepared by condensing two molar equivalents of a disodium phosphatoalkylamino derivative of an aryl compound of the benzene or

naphthalene series with one molar equivalent of carbonyl chloride, reducing the product to the hydrocarbon, and then oxidizing to the dye compound. Another process is to condense an omega-hydroxyalkylamino derivative of a benzene or naphthalene compound with an aroyl chloride of the benzene or naphthalene series, reduce the ketone produced to the hydrocarbon, oxidize the latter to the color compound, and then phosphate the product with an equivalent 10 quantity of phosphorus oxychloride. It will be understood that in place of the phosphatoalkyl group there may be introduced by known methods a thiophosphatoalkyl group or a phosphitoalkyl group. The diarylmethane compounds 15containing the hydroxyalkylphosphonic acid group



can be prepared by condensing the chloro deriva-25 tive of the above group with an aromatic amine of the benzene or naphthalene series, condensing the product obtained with an aroyl chloride of the benzene or naphthalene series, reducing the ketone obtained to the hydrocarbon, and then 30 oxidizing to the dye compound. Another process is to condense an aminobenzene or an aminonaphthalene with a chloro derivative of an aliphatic ketone, treat the product with phosphorus trichloride and acetic acid following the general 35 procedure described by J. B. Conant and A. D. MacDonald in the Journal of the American Chemical Society 42, 2337 (1920), hydrolyze with water to the free acid, further condense the product with carbonyl chloride, reduce the product to the methane compound, and then oxidize to the color compound. The triarylmethane compounds containing the above hydroxyalkylphosphonic acid group can be prepared from a triarylmethane carbinol having one or more 45 alkylamino groups as nuclear substituents in para position to the methane carbon atom by condensing with the chloro derivative of a hydroxyalkylphosphonic acid obtained as described.

The invention is further illustrated by the 50following examples which indicate the methods of preparation and the application of the dye compounds in antihalation photographic elements.

#### Example 1

1 mole of ethylaniline is condensed with 1 mole of  $\alpha$ -chloro- $\beta$ -hydroxy- $\beta$ -phosphopropane and the product obtained further condensed with benzoyl chloride to yield the diarylketone, which is then reduced with zinc and hydrochloric acid to the diarylmethane compound, and the latter then oxidized in the presence of hydrochloric acid to the color compound having the formula:



In place of ethylaniline in the above process,

pounds such as methylaniline, propylaniline, butylaniline, cetylaniline and their various halogen, alkyl, alkoxy, sulfonamide derivatives, including ethyl-m-toluidine, propyl-m-toluidine, butyl-m-toluidine, m - chloro - ethylaniline, mbromo-propylaniline, methyl cresidine, ethyl cresidine, butyl cresidine and similar kind of compounds. In place of benzoyl chloride, there can be employed benzoyl chlorides substituted by one or more monovalent substituents selected from the group consisting of chlorine and bromine atoms, methyl, ethyl, propyl, butyl, methoxy, alkoxy, sulfonamide, sulfonethylamide groups, and the corresponding naphthoyl chloride and its derivatives. Likewise the  $\alpha$ -chloro- $\beta$ -hydroxy- $\beta$ phosphopropane can be substituted by other  $\alpha$ chloro- $\beta$ , $\beta$ -hydroxy phosphoalkanes such as for example  $\alpha$ -chloro- $\beta$ -hydroxy- $\beta$ -phosphobutane. The diarylmethane compounds above mentioned 20 are water-soluble, quite stable to hard water, and dyes for antihalation layers.

#### Example 2

1 mole of methylaniline is condensed with 1 mole of  $\alpha$ -chloroacetone and the product obtained further condensed with phosphorus trichloride in the presence of acetic anhydride, followed by hydrolysis with water to obtain the free acid. This product is then condensed with an equivalent amount of carbonyl chloride and the resultant diarylketone reduced to the corresponding diarylmethane compound with zinc dust and hydrochloric acid. The dye obtained by oxidation with lead peroxide has the formula:



The above compound can be converted to a salt by treatment with a basic compound of sodium, potassium, calcium, ammonium, or an organic base such as dimethylamine.

#### Example 3

A dye compound of the type:

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wherein the amino groups are in positions para to the methane carbon atom, and wherein n rep-60 resents a whole number not greater than 10. each R represents a member selected from the group consisting of a benzene nucleus, and a naphthalene nucleus, R1 represents a member se-<sup>65</sup> lected from the group consisting of hydrogen, an alkyl group, such as methyl, ethyl, propyl, butyl, cetyl, an alkylene group such as allyl, an aryl group such as phenyl, a heterocyclic group such as furyl, and the group 70

(CH2),-

R<sub>2</sub> represents an alkyl group such as methyl, there may be employed other alkylaniline com- 75 ethyl, cetyl, R3 and R4 are the same or different  $\mathbf{5}$ 

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groups selected from the group consisting of an alkyl group such as methyl, ethyl, cetyl, an allyl group, a phenyl group, a furyl group, and the group

$$-(CH_2)_n - C - R_2$$

X represents an acidic radical such as chlorine, bromine, iodine, alkylsulfate, perchlorate, and the like, is phosphonated with a mixture of phos- 10 phorus trichloride and acetic acid, and the product obtained hydrolyzed to the free phospho acid derivative.

### Example 4

A leuco base of the triarylmethane series such as 4,4',4''-trimethylamino-triphenylcarbinol is treated with two equivalents of  $\alpha$ -chloro- $\beta$ -hydroxy- $\beta$ -phosphopropane and the product oxidized with lead peroxide in the presence of hydrochloric acid to the dye having the formula:



1 mole of the compound having the formula:

$$HSO_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{3}$$

is heated on a water bath with approximately 4.4 molar equivalents of phosphorus trichloride in a large excess of acetic acid. The reaction prod-45 uct is slowly poured into water and then oxidized with lead peroxide thereby producing a greenblue solution from which the acetic acid is removed by distillation and any desired salt prepared. The compound obtained has the formula: 50



By employing the general methods of the preceding examples, there may be prepared other closely related compounds which can be represented by the following structural examples:







 mole of anhydro-[4,4'-bis(di-β-hydroxyethyl) aminol-diphenylcarbinol chloride is dissolved in pyridine and treated at room temperature with 650 grams of phosphorus oxychloride. After standing for a short time, the reaction mix-70 ture is heated to 70° C. for 4 hours, cooled, and then treated with 1 liter of water and sufficient sodium carbonate to neutralize all the hydrogen chloride formed in the reaction and to convert the product to the sodium salt of the phosphato
75 acid. The pyridine and water are removed under

3

reduced pressure: The dye obtained has the formula:



The above dye compound can also be prepared by starting with 2 moles of di-disodium phosphatoethyl-aminobenzene and condensing with 1 mole of carbonyl chloride, reducing the diarylketone formed to the diarylmethane compound, and then oxidizing to the dye.

Similarly we can prepare by any of the methods just indicated in the preceding, a number of closely related diarylmethane compounds of which the following are only illustrative:

#### Example 7

1 mole of the compound having the formula:



is treated in pyridine with approximately 2.5 molar equivalents of phosphorus oxychloride and the reaction completed by warming. The resulting chloroester is hydrolyzed to the phosphate with an aqueous solution of potassium bicarbonate. The pyridine and water are removed under reduced pressure, the product oxidized with lead peroxide in the presence of hydrochloric acid and then treated with potassium bicarbonate. The dye obtained has the formula:



The above compounds are water-soluble, easily the exposure to light is usually made through discharged with agents such as sodium bisulfite, 75 the support. While the invention is illustrated

and valuable as backing dyes for antihalation layers for photographic materials.



In the application of our water-soluble dyes for antihalation layers on photographic materials, the particular dyes or mixture of dyes is ordinarily applied as a composition comprising the dye and a binding agent selected from the group of substances such as gelatin, gum arabic, dextrin, polyvinyl alcohol and similar kind of substances. A satisfactory composition, for example, is an aqueous gelatin solution of a dye or a combination of the dyes disclosed in Examples Nos. 1 to 5. Approximately 75 grams of gelatin, and up to about 10 grams of dye may be employed per 1000 ccs. of water. Alcohol or other 20 water-miscible organic solvents may be added in appropriate amount to the solution, as desired, in order to promote the adherence of the composition to the support and to facilitate its drying. In some cases, it may be desirable to add to the composition a small amount of a watermiscible high boiling compound such as glycerine, an alkylene glycol, or a higher alcohol sulfate such as sodium oleyl sulfate. As a photographic support there can be employed a transparent sheet comprising an organic derivative of cellulose including cellulose nitrate, cellulose acetate, cellulose propionate, cellulose butyrate, celacetate-propionate, cellulose acetatelulose butyrate, methyl cellulose, ethyl cellulose, benzyl 35 cellulose, polyvinyl acetals, viscose and the like, as well as transparent or translucent glass plates. The composition is customarily applied as a coating on the rear surface of the support, but can also be applied on the front surface as an interlayer over which the light-sensitive emulsion is coated, or, it can be applied as an overlayer coated upon the emulsion layer, in which case

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2,304,890

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more particularly in connection with antihalation layers on transparent supports, it will be understood that such antihalation layers can also be employed as interlayers on opaque materials such as pigmented sheets or photographic papers. We claim:

The polyarylmethane compound having the formula:



5