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NEW CLASSES OF PHOSPHORUS-CONTAINING DYES

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IN the course of a research program for photographic sensitizing dyes, a new class of dyes containing a $C{=}P\!\!<$ auxochrome has been discovered. It may be subdivised into several subclasses.[1] It is our intention, in this preliminary communication, to bring a short record of the principal routes by which the new dyes may be obtained.

A first class of new phosphorus-containing dyes, which we propose to call "phosphinines", by analogy with the structurally related cyanine dyes, is characterized by the auxochromophoric system:

$$\rangle P{=}\overset{|}{C}\text{-}(CH{=}CH)_n - CH{=}\overset{|}{C}\text{-}\overset{+}{P}\!\!< \longleftrightarrow \rangle \overset{+}{P}\text{-}\overset{|}{C}{=}(CH\text{-}CH)_n = CH\text{-}\overset{|}{C}{=}P\!\!<$$

These new dyes may be synthesized in a variety of ways. Starting with cyclopentadienylene-triphenylphosphorane (I), whose nucleophilic properties have been pointed out recently by Ramirez and Levy[2], the symmetrical dye II may be obtained, e.g. by refluxing with ethyl orthoformate or orthoacetate in acetic anhydride.

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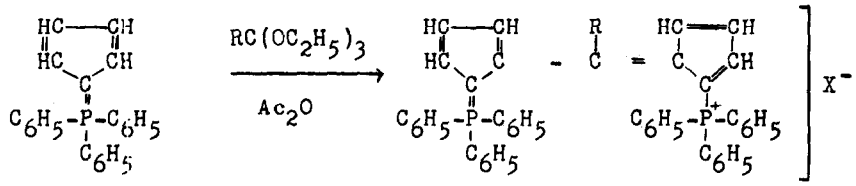
[1] Gevaert, Belg.Pat. 583.922 (prior. G.-B. 24.10.58) and A.Van Dormael, J.Nys and H. Depoorter, Sci. & Ind. Phot. (2) 31, 389 (1960)

[2] F. Ramirez and S. Levy, J.Amer.Chem. Soc. 79, 6167 (1957)



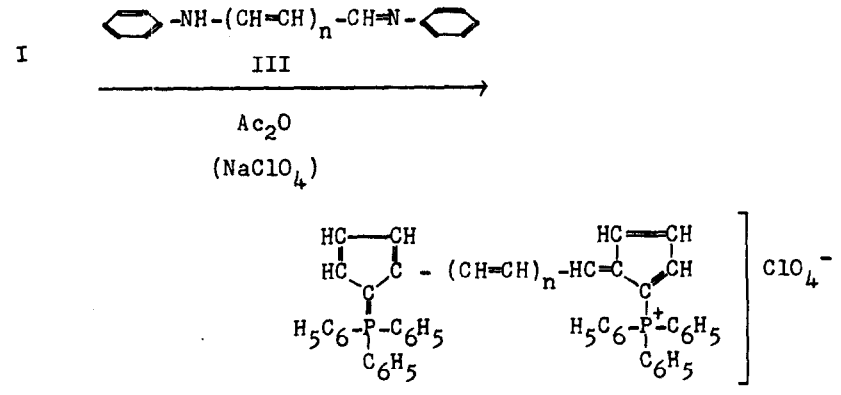
I II

II : R = H; $X^- = I^-$; λ_{max} = 477 mμ *

II : R = CH_3; $X^- = ClO_4^-$; λ_{max} = 488 mμ

It will be noticed that the introduction of a methyl-group in the methine link results in a bathochromic shift, analogously to the shift which was observed by Brunings and Corwin[3] in the same conditions with dipyrrylmethene dyes.

The same cyclopentadienylene-phosphorane I condensed with β-anilino acrolein anil (III, n = 1) leads to the corresponding dye IV (n = 1) with a trimethine link between both nuclei.



IV

* All optical data were determined in ethanolic solution.

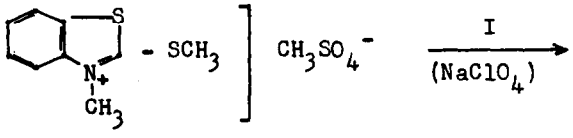
[3] K.J. Brunings and A.H. Corwin, J. Amer. Chem. Soc. 64, 593 (1942)

The phosphorane I yields the corresponding pentamethine homologue IV (n = 2) by reaction with the anil of 1-anilino-pentadien(1,3)-al(5) (III, n = 2). The absorption data are : dye IV (n = 1), λ_{max} = 597 mμ and dye IV (n = 2), λ_{max} = 695 mμ.

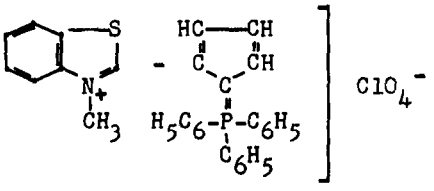
Furthermore, the cyclopentadienylene-phosphorane I, when allowed to react with various electrophilic reagents ordinarily used in the chemistry of cyanine and merocyanine dyes, yields asymmetrical dyes which we might call "phosphocyanines", characterized by the following auxochromophoric system :

$$\geq P=\overset{|}{C}-(CH=CH)_n-CH=\overset{|}{\underset{+}{N}}- \longleftrightarrow \geq P-\overset{|}{\underset{+}{C}}=(CH-CH)_n=CH-\overset{|}{N}-$$

As an example, I reacts with 2-methylmercapto-3-methyl-benzothiazolium methylsulphate (V) in ethanol to produce the dye VI (λ_{max} = 398 mμ). The reaction is catalyzed by triethylamine.

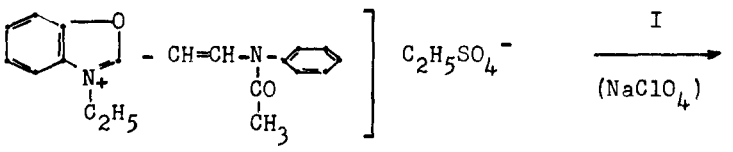


V

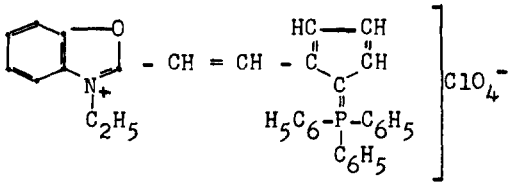


VI

Similarly, the reaction of (I) with 2-(β-acetanilido-vinyl)-3-ethyl-benzoxazolium ethylsulphate (VII) yields the dye VIII (λ_{max} = 480 mμ).

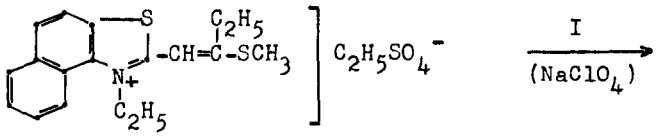


VII

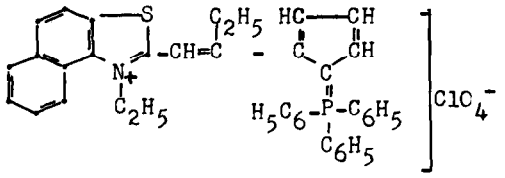


VIII

Chain-substituted phospho-cyanine dyes may be obtained by using β-alkyl-β-methylmercaptovinyl derivatives such as IX whereby dye X (λ_{max} = 542 mμ) is obtained.



IX

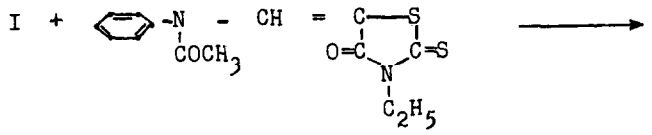


X

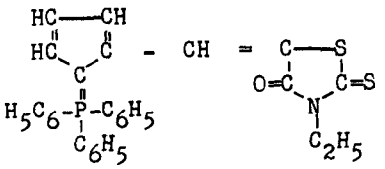
The cyclopentadienylene-phosphorane I also reacts with acetanilidomethylene derivatives of ketomethylene nuclei in the presence of acetic anhydride, whereby merocyanine-like systems are obtained, for which the name "merophosphinines" is proposed.

These dyes, too, display a new characteristic auxochromophoric pattern, namely :

Thus, reaction of I with the rhodanine-intermediate XI yields the new dye XII (λ_{max} = 486 mμ).

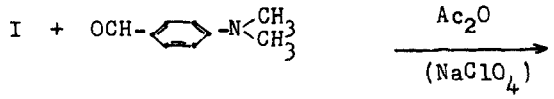


XI

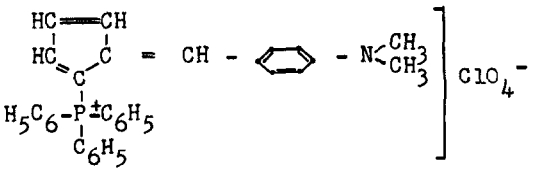


XII

Aromatic aldehydes react with I in appropriate conditions (refluxing in acetic anhydride) to yield another new series of polymethine dyes. With p -dimethylaminobenzaldehyde (XIII), e.g. dye XIV is obtained (λ_{max} = 495 mμ).

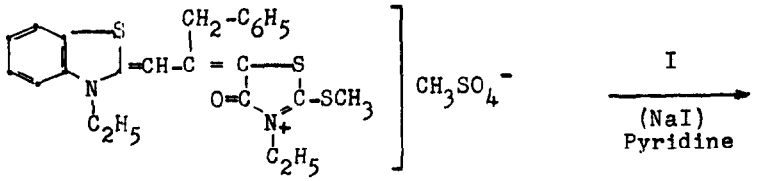


XIII

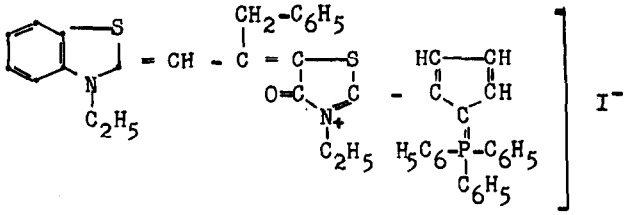


XIV

Still more complex dye-systems may be synthesized. As an example, starting from the quaternized merocyanine dye XV, the complex dye XVI (λ_{max} = 606 mμ) is obtained by reaction with I in pyridine.

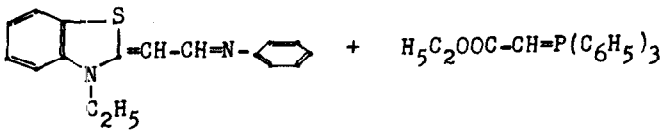


XV



XVI

Finally, instead of cyclopentadienylene-triphenyl-phosphorane (I), other phosphoranes such as carbethoxymethylene-triphenyl-phosphorane[4] (XVII) may be used. By reaction with the anil of 2-formylmethylene-3-ethyl-benzothiazoline (XVIII) in acetic anhydride, dye XIX is obtained (λ_{max} = 446 mμ).



XVIII XVII

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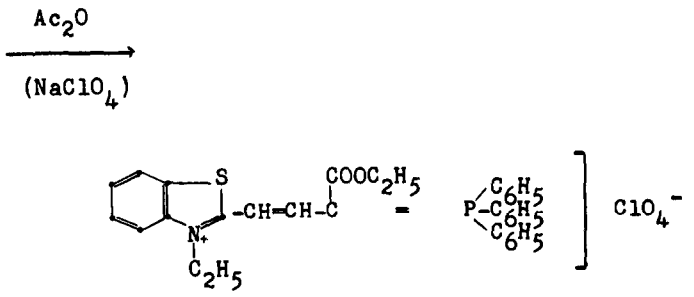
[4] O. Isler, H. Guttmann, M. Montavon, R.Ruegg, G. Ryser and P.Zeller, Helv. Chim. Acta 40, 1242 (1957).



XIX

A detailed description of the synthesis and the properties of the new dyes will be published elsewhere,[5] whilst the optical data of some of these dyes have been discussed recently.[6]

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[5] H. Depoorter, J. Nys and A. Van Dormael, Bull.Soc.Chim.Belg. in preparation.

[6] A. Van Dormael, Chimia 15, 67 (1961).