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Abstract

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SYNTHESIS OF PHOSPHOCYANINE DYES

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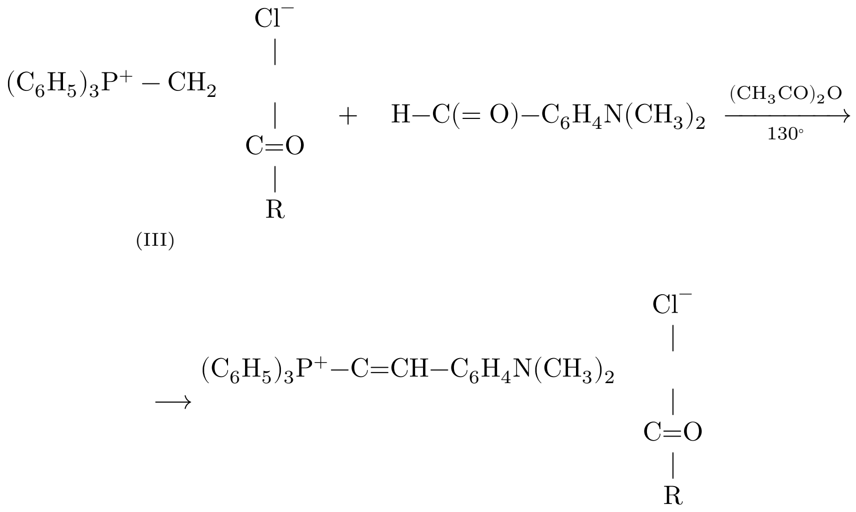
Cyanine dyes, whose chromophoric system consists of a conjugated chain of carbon atoms bounded by nitrogen atoms (I), have now been studied fairly extensively (^{1}). Dyes of this type are widely used as optical sensitizers for silver halide emulsions. It seemed of interest to us to study routes for the synthesis of analogous dyes whose conjugated system is bounded by nitrogen and phosphorus atoms (II), or by two phosphorus atoms (III):

$$>\ddot{N}-(C=C)_n-C=\overset{+}{N}< \qquad \text{(I)}$$

$$\equiv\ddot{P}=C-(CH=CH)_n-C=\overset{+}{N}< \qquad \text{(II)}$$

$$\equiv\ddot{P}=C-CH=CH-CH=C-\overset{+}{P}< \qquad \text{(IIa)}$$

We have established that phosphonium salts of type III, containing an active methylene group, are able rather readily to enter into reaction with *p*-dimethylaminobenzaldehyde, forming dyes analogous to styryl dyes:



$$\underset{\text{(III)}}{(C_6H_5)_3P^+-\overset{\overset{Cl^-}{|}}{\underset{\underset{R}{|}}{\underset{C=O}{|}}}{CH_2}} + H-C(=O)-C_6H_4N(CH_3)_2 \xrightarrow[130^\circ]{(CH_3CO)_2O}$$

$$\longrightarrow \underset{\text{(IV)}}{(C_6H_5)_3P^+-C=CH-C_6H_4N(CH_3)_2\ \overset{\overset{Cl^-}{|}}{\underset{\underset{R}{|}}{\underset{C=O}{|}}}}$$

Thus, for example, triphenylphenacylphosphonium chloride (III, $R = C_6H_5$), when heated in acetic anhydride, readily forms a phosphostyryl dye (IV, $R = C_6H_5$), having an absorption maximum in alcoholic solution at 450 mμ. Table 1 gives the optical and analytical data of the phosphostyryl dyes obtained.

Further, we found that 2-(β-methylmercapto)-vinyl derivatives of heterocyclic bases (V) also form dyes fairly readily on interaction with triphenylphenacylphosphonium chloride.

The reactions for the formation of phosphocyanine dyes (VI) proceed readily on heating the starting products in pyridine with the addition of triethylamine and acetic anhydride. The reaction is accompanied by the formation of a by-product dye as a consequence of the great tendency toward self-condensation of the initial β-methylmercaptovinyl derivatives of heterocyclic bases (V). Purification from the by-product was carried out by chromatography or by repeated recrystallization from alcohol. Similar-

$$(C_6H_5)_3\overset{+}{P}{-}CH_2{-}C(=O){-}C_6H_5\ \ \overset{-}{Cl} + CH_3{-}S{-}CH{=}CH{-}\overset{+}{N}(R){-}Z\ \ CH_3SO_4^-$$

$$\text{(V)}\quad \xrightarrow[\text{Ac}_2\text{O}]{\text{pyridine}}$$

$$(C_6H_5)_3\overset{+}{P}{-}C(=CH{-}CH{=}\overset{+}{N}(R){-}Z){-}C(=O){-}C_6H_5\ \ \overset{-}{Cl} \qquad \text{(VI)}$$

Table 1

Phosphostyryl dyes

Compound	Maxima, mμ abs., mμ	P content, %, found	P content, %, calc.	N content, %, found	N content, %, calc.	Yield, %
$\overset{-}{ClO_4}$ $(C_6H_5)_3\overset{+}{P}$–C(=CH–C_6H_4–N$(CH_3)_2$, with C(= O)C_6H_5 substituent	450	4.91	5.06	2.28	2.28	44.0
$\overset{-}{ClO_4}$ $(C_6H_5)_3\overset{+}{P}$–C(=CH–C_6H_4–N$(CH_3)_2$, with C(= O)CH_3 substituent	442	5.87	5.64	2.28	2.54	25.0

dyes of the same kind are formed in the condensation of 2-(β-methylmercapto)-vinyl derivatives of heterocyclic bases (V) with salts of triphenylcarbethoxymethyland triphenylacetonylphosphonium (III, $R = OC_2H_5$; $R = CH_3$). An attempt to use 2-formylmethylbenzselenazoline for the synthesis of phosphocyanines was not successful; on heating it with triphenylacetonylphosphonium chloride in acetic anhydride, only a self-condensation product is formed—symmetrical selenacarbocyanine, as evidenced by the appearance of only one absorption maximum (560 mμ) on the absorption curve of the reaction mixture.

Fig. 1. Absorption curves of alcoholic solutions: *I*—phosphostyryl (IV, $R = C_6H_5$), phosphocyanine (V, Z—residue of N-ethyl-5-methoxy-6-methylmercapto-benzthiazole)

Table 2 gives some data on the phosphocyanine dyes obtained by us.

A study of the optical properties of the synthesized dyes showed that they absorb in the near visible part of the spectrum, with absorption maxima in the region 460–488 mμ. The absorption curve of an alcoholic solution of phosphostyryl (IV, $R = C_6H_5$) has a somewhat diffuse character, with a poorly expressed maximum at 450 mμ (Fig. 1). The absorption curve

Table 2

Compound	Absorption maximum, mμ	P, % found	P, % calc.	N, % found	N, % calc.	S, % found	S, % calc.	Yield, %
$\left[(C_6H_5)_3\overset{+}{P}-C(=O)(C_6H_5)=CH-CH=\text{thiazoline ring with } N-C_2H_5\right] ClO_4^-$	460	–	–	–	–	4.77	4.86	30.0
$\left[(C_6H_5)_3\overset{+}{P}-C(=O)(OC_2H_5)=CH-CH=\text{thiazoline ring with } N-C_2H_5\right] ClO_4^-$	420	4.84	4.94	2.68	2.26	–	–	36.6
$\left[(C_6H_5)_3\overset{+}{P}-C(=O)(CH_3)=CH-CH=\text{thiazoline ring with } N-C_2H_5\right] ClO_4^-$	450	5.17	5.33	–	–	4.98	5.32	31.0
$\left[(C_6H_5)_3\overset{+}{P}-C(=O)(C_6H_5)=CH-CH=\text{selenazoline ring with } N-C_2H_5\right] ClO_4^-$	466	–	–	2.10	1.95	–	–	35.2
$\left[(C_6H_5)_3\overset{+}{P}-C(=O)(C_6H_{11})=CH-CH=\text{thiazoline ring with } N-C_2H_5, SCH_3, OCH_3\right] ClO_4^-$	488	4.43	4.55	2.50	2.08	–	–	32.7
$(C_6H_5)_3\overset{+}{P}-C(=O)(OC_2H_5)=CH-CH=CH-C(=O)(OC_2H_5)=P(C_6H_5)_3, ClO_4^-$	446	7.65	7.44	–	–	–	–	36.5

The alcoholic solution of phosphocyanine has a more sharply expressed absorption maximum with steeply descending branches in the long-wave and short-wave regions of the spectrum (Fig. 1).

We have also synthesized one representative of the class of phosphinine dyes, whose conjugation system is bounded by phosphorus atoms. On interaction of chlorotriphenylcarbethoxymethylphosphonium with 1,1′,

$$
\begin{aligned}
&(C_6H_5)_3 \overset{+}{\equiv} P(Cl^-)–CH_2–C(=O)–OC_2H_5 \\
&\quad + \ (C_2H_5O)_2CH–CH_2–CH(OC_2H_5)_2 \\
&\quad + \ H_2C–\overset{+}{P}(Cl^-)(C_6H_5)_3–C(=O)–OC_2H_5 \ \xrightarrow{\text{paraffin}} \\
&\longrightarrow \ (C_6H_5)_3 \overset{+}{\equiv} P(Cl^-)–C(=O)(OC_2H_5)=CH–CH=CH–C(=O)(OC_2H_5)=P \equiv (C_6H_5)_3 \qquad (VII)
\end{aligned}
$$

with 3,3′-tetraethoxypropane in pyridine medium, a dye is formed in good yield with an absorption maximum at 446 mμ, to which, on the basis of analytical data, the structure (VII) may be assigned.

As a result of the investigations carried out, we have developed several routes for the synthesis of new classes of polymethine dyes—phosphostyryls, phosphocyanines, phosphinines—and have obtained individual representatives of these classes of dyes. In the future, it will be of great interest to study the question of the localization of the positive charge in the conjugation system of phosphocyanines. In contrast to cyanine dyes, whose conjugation system is bounded by identical atoms, which leads to a more or less uniform delocalization of the charge along the conjugation chain, phosphocyanines have different atoms at the ends of the conjugated system, which should lead to localization of the charge predominantly on one of these two atoms:

$$
> P–C=CH–(\underset{|}{\overset{+}{C}}H=CH)_4–N < \rightleftarrows > P=C–(CH=\underset{|}{C}H)_4–CH=\overset{+}{N} <
$$

It should be noted that recently Van Dormael reported the preparation of cyanine dyes whose conjugated system is bounded by a triphenylphosphonincyclopentadienylide residue, but the synthetic procedure was not given ([2]).

Below are examples of the synthesis of phosphocyanine dyes.

Experimental Part

Condensation of triphenylphenacylphosphonium chloride (IIIa) with methyl sulfate of *N*-ethyl-2-(β-methylmercapto)vinyl-5-methoxy-6-methylmercaptobenzothiazole (Va). 0.2 g (0.0005 mole) of IIIa was dissolved with heating in 5 ml of pyridine; 0.21 g of Va and 3 drops of triethylamine were added. The reaction mixture was heated for 6 hr at 100–120°. The course of the reaction was monitored spectrometrically, using SF-2. After completion of the reaction, dry ether was added to the reaction mass.

The precipitated dye crystals were separated and recrystallized from alcohol and washed with hot benzene. Obtained: 0.09 g of bright-orange crystals. Yield: 30.0%, m.p. 253°. After purification by recrystallization or chromatography, the absorption curve of the resulting dye has only one maximum, 488 mμ.

Condensation of triphenylcarbethoxymethylphosphonium chloride (IIIb) with 1,1′,3,3′-tetraethoxypropane. 0.38 g of IIIb was dissolved with heating in 2 ml of pyridine; 0.25 ml of 1,1,3,3-tetraethoxypropane was added. The reaction mixture was heated for 8 hr at 130° and precipitated with ether; the resinous residue was dissolved in 1 ml of alcohol, and 5 ml of a 20% $NaClO_4$ solution was added. Yellow crystals separated. After recrystallization from alcohol, 0.15 g (36.5% of theory) of light-yellow crystals with m.p. 142° was obtained. Absorption maximum in ethanol: 446 mμ.

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Note: Figure translations are in progress. See original paper for figures.

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