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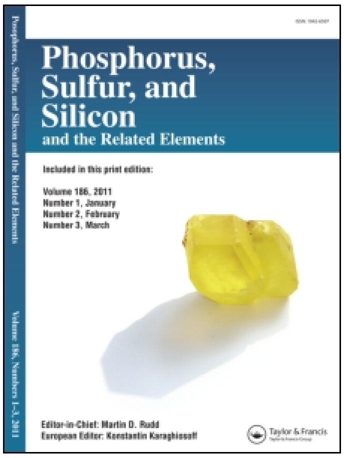

Phosphorus, Sulfur, and Silicon and the Related Elements

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PHOSPHOCYANINE DYES

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Abstract

The conjugated organic polymethine salts (cyanine dyes) are widely used in industry. Numerous applications in chemistry (dyes, photochemical sensitizers for photographic emulsions...) and physics (in optical devices, non linear optics and erasable laser disks) have been developed.
We present here a synthetic pathway towards previously unknown phosphocyanine dyes by condensation of N-silylated phosphinimines on carboxonium salts. As the synthesis of these dyes results in the enhancement of the conjugation path, new physical properties are expected. Furthermore their aza-Wittig reactivity allows the obtention of new series, i.e. the reaction with isocyanides lead to original α-aminopyridines.

Key Words : Phosphocyanine dyes, phosphaimines, aza-Wittig reactivity, isocyanides, substituted α-aminopyridines synthesis.

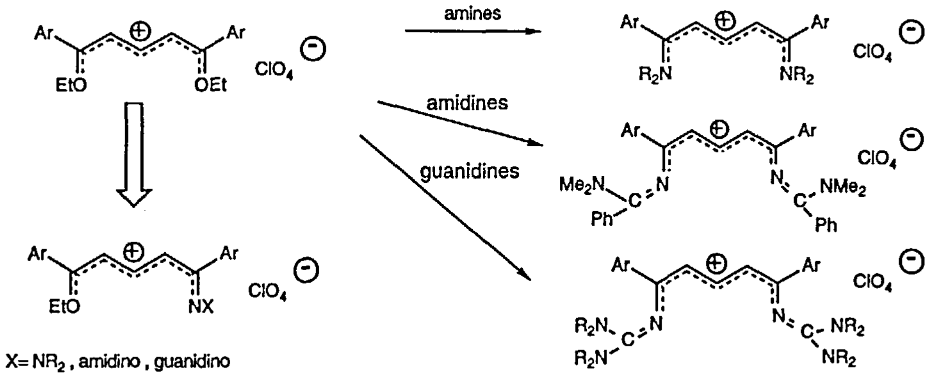
INTRODUCTION

The search of new synthetic methods leading to charged polyenic systems is currently developed in our laboratory. Our actual results are based on two different methods. First, the reaction of *tris*dialkylaminoarsanes or stibanes on pyrylium salts afford highly substituted and symmetrically aminated pentadienylium salts [1]. The second, the most general one, utilizes the selective reactivity of carboxonium salts, isolable cationic intermediates in the synthesis of pyrylium salts [2].

Owing to the large application pattern of the polyenylium salts in chemistry (dyes, sensitizers for color photography...), biology (fluorescence assays, DNA intercalation...), physics (non linear optics, optical data storage...) it seemed interesting to obtain new types of salts whith enhanced conjugation pathway either by delocalization beyond the nitrogen atoms (with imino nitrogen groups in amidino or guanidino environment) or by synthesis of polypentadienylium systems with active conjugated spacers. Other salts with passive or neutral spacers confering more degrees of freedom to the structure can be easily obtained. Furthermore, we try to replace the amino nitrogen terminal groups by other group 15 heteroelements.

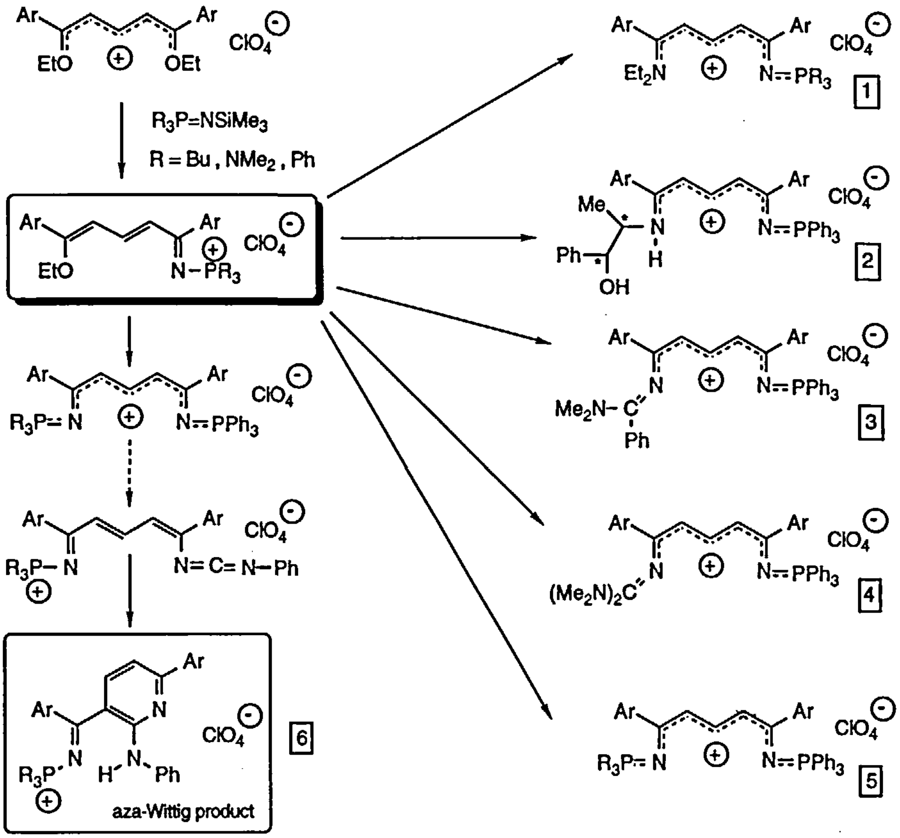
RESULTS AND DISCUSSION

The following scheme summarizes the general reactivity of carboxonium salts with amino and imino reactants; the possibility to obtain hemicarboxonium salts is to be emphasized for it opens the way to homo and hetero reactions leading to symmetrical and non-symmetrical compounds respectively [3].



The same reaction pathway was attempted with an other group 15 element, the phosphorus. Thus secondary phosphanes afford only traces of the expected products, the main part beeing formed of the ketodienether obtained by dealkylation of the carboxonium salt and formation of the phosphonium perchlorate. This was confirmed by the quantitative synthesis of the dealkylated product in presence of tertiary phosphanes. Nevertheless we decided to introduce the phosphorus heteroelement by the way of the reactivity of silaphosphaimines which revealed to be an important and extensive reaction.

Like in the reaction of amino and imino compounds, the formation of the monosubstituted phosphorus synthon has an outstanding importance for the obtention of a great variety of new non symmetrical pentadienylium salts [4]. The following scheme summarizes the main possibilities.



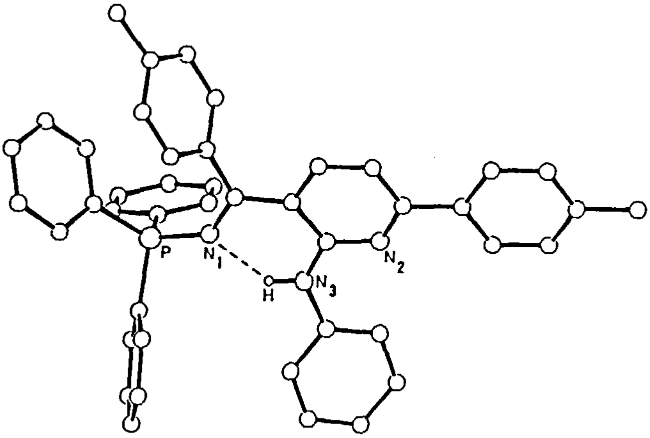
Compounds $\boxed{1}$ and $\boxed{2}$ are obtained by the action of amines with our "magical" building block. In the case of an optically active aminoalcohol like the (-)norephedrin,{α_D = -40} a striking change in rotatory power is observed (i.e. α = - 248 with Ar = $pMeOC_6H_4$ and R = Ph). Even larger effects on the optical rotation of cyanine dyes were recently described [5].

For examples $\boxed{3}$ and $\boxed{4}$ the amidino and guanidino groups permit the extension of the conjugation pathway over the nitrogen atom leading to a bathochromic and an hypochromic effect as compared to products of type $\boxed{1}$. Thus if Ar = $pMeOC_6H_4$ and R = Ph, we observed a red shift of 62 nm [475 ($\boxed{1}$) versus 537 (for $\boxed{3}$ and $\boxed{4}$)] whereas the molar extinction coefficients falls from 75000 to 54000 and 41000 for $\boxed{3}$ and $\boxed{4}$ respectively.The diphosphazenyl compounds like $\boxed{5}$ (R = NMe_2; $\delta\ ^{31}P$ = 28.9 and 13.5 ppm or R = Ph; $\delta\ ^{31}P$ = 13) offered the possibility of an azaWittig like reactivity [6] as it is demonstrated by the isolation of an aminopyridine phosphonium salt, cyclized end product of the reaction with phenylisocyanate. Moreover we obtained the solid state structure of $\boxed{6}$ with Ar = $pMeC_6H_4$ and R = Ph.

crystal data

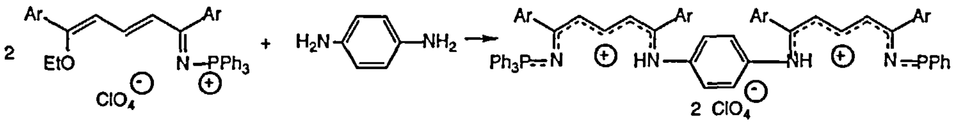
$C_{44}H_{38}ClN_3O_4P$, M = 739.2, monoclinic, a = 11.660(9) b = 20.388(7), c = 16.161(6) Å, V = 3771.9 Å^3, Z = 4, d_c = 1.30 g cm^{-3}, space group $P2_1/c$, F(000) = 1548.

Selected distances (Å)
$P\text{-}N_1$ = 1.634(4)
$N_1...H$ = 1.91(4)
$H\text{-}N_3$ = 0.89(4)
N_1 N_3 = 2.660(4)
and angle (°)
$N_1...H\text{-}N_3$ = 141(3)



CONCLUSION

The introduction of the phosphazenyl group at the end of charged polyenic system opens the way to an unlimited amont of new cyanine dyes. The new physical properties thus induced (i.e. solvatochromism) or their enhanced reaction pattern are currently studied. One example of these features is given hereafter with the synthesis of a dicationic entity with an active spacer. For Ar = $pMeC_6H_4$ we observed a large solvatochromic shift of $\Delta\lambda$ = 54 nm going from CH_3CN (λ = 503 nm) to toluene (λ = 557 nm).



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