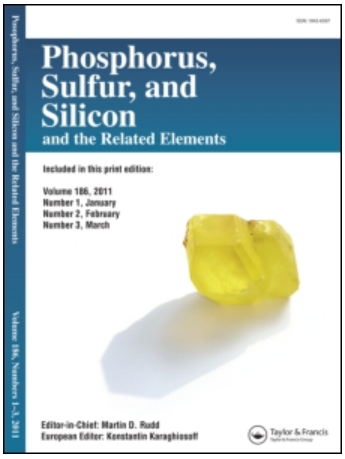

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APPROACHING *P*-INDOXYLE, *P*-INDIGO AND *P*-VINYLCHALCOGENIDES

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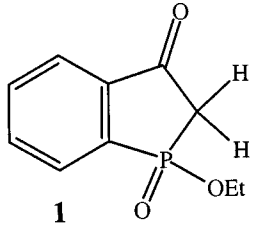
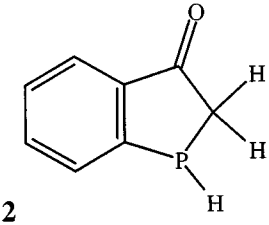
A great challenge in the chemistry of π-conjugated organophosphorus compounds and dyestuffs remains the preparation of *phosphoindigo*, in which the nitrogen atoms of indigo are replaced by phosphorus. Indole-related benzophosphole (*phosphindole*) derivatives are well known, but only scattered information is available on their 3-oxo derivatives,[1] which would be related to precursors of indigo or thioindigo. On the way to phosphoindigo, we studied a number of reactions to find suitable reagents and conditions for the oxidative coupling of known 1-ethoxy-1-oxophosphindoline-3-one (**1**)[1,2] or new phosphindoline-3-one (**2**) [*phosphoindoxyle*] leading to the first 1,1′-*diphosphaindigo derivatives*.



1



2

Bromination of **1** led not to C=C coupling but instead to the formation of mono- and dibromonation products and—in the absence of bases—to products from P–OEt ester cleavage like 1-hydroxy-1-oxo-2,2-dibromophosphindoline-3-one (**3**).[2] In solid **3**, molecules of

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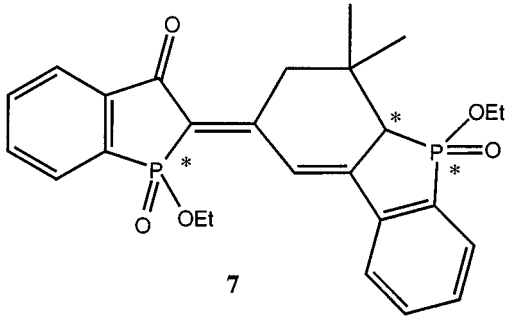
the phosphinic acid are connected by intermolecular P=O···H–O–P bridges and by Br···Br "soft-soft" van der Waals contacts.[2] Attempted debromination of **3**, of its trimethylsilyl derivative **4** and of the mono- and dibromide of **1** (**5**, **6**) did not allow C, C coupling.[2]

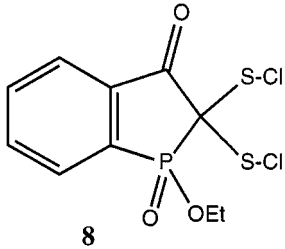
In the presence of bases, formation of a surprising colored 2:2 condensation product of **1** with acetone was observed. Protonation of the red anion led to a yellow bis-phosphinic ester **7** that is remarkably C, H-acidic.



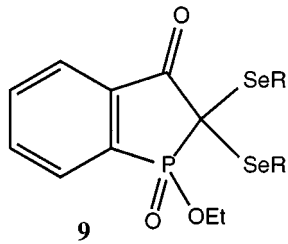
7

Following this observation, a number of new phosphindole-related dyes were synthesised by deliberate Knoevenagel-type reactions of **1** with aromatic aldehydes. Cyanomethylation (of the CO functions) of these derivatives furnished several *P*-functionalized dyes.

Further experiments were directed to induce C, C coupling by chalcogenation/dechalcogenation of **1**. Reactions of **1** with sulfur dichloride and 2,4,6-triisopropylbenzene selenenyl bromide furnished compounds **8** and **9**.



8

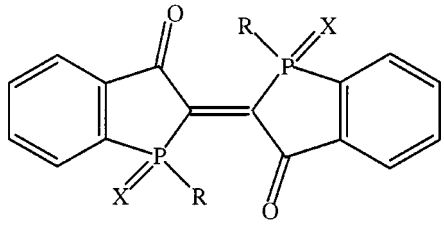


9

R = 2,4,6-(i-C_3H_7)$_3$$C_6H_2$-

Attempted dechalcogenation of 2-S- and 2-Se-derivatives **8** and **9** of **1** did not allow the intended C=C coupling. Decomposition of **9** occured with formation of the diaryldiselenide; however, compound **10** was not observed. Successful C, C coupling was achieved only by

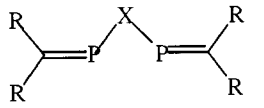
treating **1** with SeO_2 as dehydrogenating agent. From a mixture of isomers, pure *trans*-**10** was isolated.



10: R = O-Et, X = O; **11**: R = OH, X = O
12: R= Cl, X = O

Heating of the bis-phosphinic chloride **12** with phenylsilane leads to the reduction of the P(=O)Cl functions (MS evidence), but isolation pure 1,1′-diphospha($\sigma^3\lambda^3$)-indigo was not yet accomplished.

Reduction of the starting material **1**, however, allowed to isolate pure liquid phosphindoline-3-one (**2**) (*phosphoindoxyle*), that could subsequently be stabilized by coordination with $W(CO)_5$. As part of our study on new bis-phoshorus compounds with potential π-interactions, properties of new *di(phosphavinyl)-chalcogenides* **13–16** are also being investigated.



R = $SiMe_3$

13: X = O, **14:** X = S,
15: X = Se, **16:** X = Te

Structures of several derivatives of **1** were determined (P. G. Jones, F. Ruthe, TUBS), among them those of **3**,[2] of hydrated **7**, of the 2,2-di-SCl-derivative **8**, a 3-dicyanomethylene derivative of **1**, the first 1,1′-diphospha($\sigma^4\lambda^5$)indigo **10**, a salt of the related bis-phosphinic acid **11**, and the $W(CO)_5$ complex of *phosphoindoxyle*.

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[2] S. Vollbrecht, W. Grahn, F. Ruthe, P. G. Jones, and W.-W. du Mont, *Chem. Ber./Recueil*, **130,** 1765 (1997).