

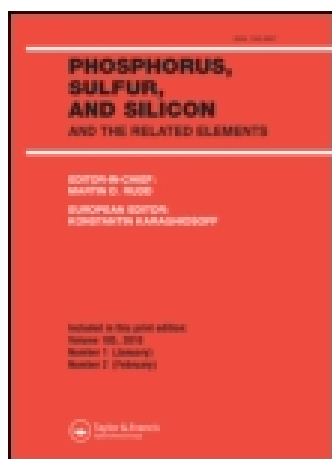
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The Synthetic Potential of C-Halophosphaalkenes

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THE SYNTHETIC POTENTIAL OF C-HALOPHOSPHAALKENES

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Abstract. Methodologies for the functionalization of phosphalkenes $\text{Mes}^*\text{P}=\text{CHal}_2$ were developed. Lithiation with *n*-butyllithium yielded carbenoids $\text{Mes}^*\text{P}=\text{CLiHal}$ which were reacted with various electrophiles such as acid chlorides, carbonyl compounds, and metal halides. The dihalophosphaalkenes were also converted to monohalophosphaalkenes; the latter proved to be suitable for Stille-type cross coupling reaction with Grignard reagents. New phosphalkenes of the type (*E*)- $\text{Mes}^*\text{P}=\text{C}(\text{H})\text{Ar}$ with a variety of functionalities were obtained in high yield and isomeric purity.

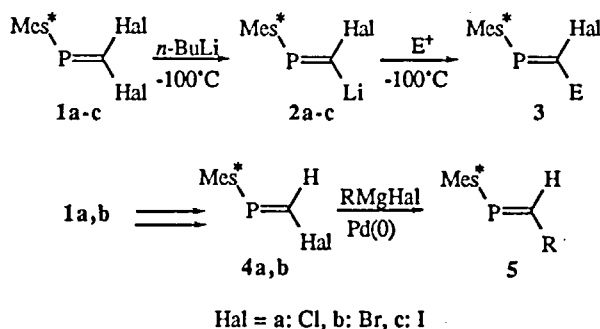
INTRODUCTION

Since 1981 halogen substituted phosphalkenes have been reported.¹ Phosphalkenes of the type $\text{Mes}^*\text{P}=\text{CHal}_2$ ($\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$; **1a**: Hal = Cl; **1b**: Br; **1c**: I) can easily be converted to phosphavinylidene carbenoids of the type $\text{Mes}^*\text{P}=\text{CLiHal}$ by halogen-lithium exchange with *n*-butyllithium. Although these species should have a large synthetic potential, only few applications are known.^{2,3} Challenged by the potentially rich chemistry of these carbenoids, we investigated their reactions with various electrophiles such as acid chlorides,⁴ carbonyl compounds, and metal halides.

Recently, several groups have been reporting on the coordination of phosphalkenes, incorporated in bidentate ligand systems. In order to develop a convenient method for the preparation of a variety of bidentate ligand systems, we investigated the reactivity of monohalophosphaalkenes with Grignard reagents in Stille-type cross coupling reactions. By this method (substituted) aryl groups were introduced.

SYNTHESIS

Halophosphaalkenes **1a-c** can easily be converted into (*Z*)-phosphavinylidene carbenoids **2a-c** by low temperature halogen-lithium exchange (-100 to -130°C). Addition of an electrophile to a solution of the carbenoid results in the formation of *trans*-functionalized phosphoalkenes **3** with retention of configuration.³ More interesting, e.g. for the synthesis of phosphoalkene based bidentate ligand systems, are *trans*-functionalized phosphoalkenes with aromatic substituents. However, these cannot be introduced via a Stille-type coupling reaction with the dihalophosphaalkenes **1a-c** or the carbenoids **2a-c**.⁵ Therefore convenient new procedures for the synthesis of (*E*)-halophosphaalkenes **4a,b** were developed.⁶ **4a,b** were subjected to a Pd(0) catalyzed cross coupling reaction with Grignard reagents furnishing **5** as shown in SCHEME 1.

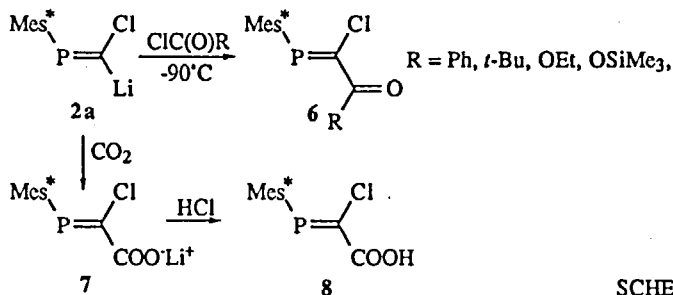


SCHEME 1

REACTIONS

 β -Phosphaenones

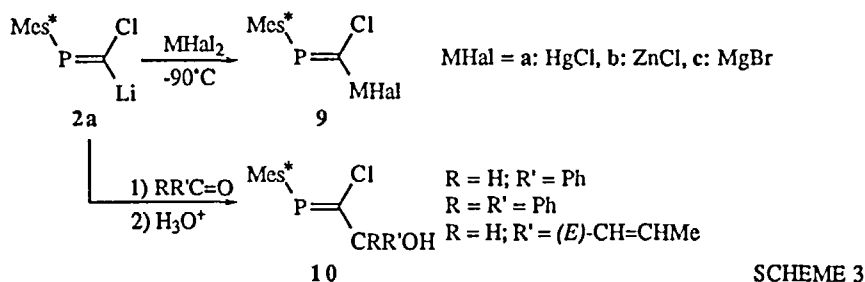
The chlorophosphavinylidene carbenoid **2a** was reacted at -100°C with acid chlorides furnishing β -phosphaenones **6** in high yield (SCHEME 2). Another method for the formation of β -phosphaenones is the reaction with CO₂ furnishing the unexpectedly stable carboxylate **7**. Acidification of **7** with hydrochloric acid furnished the first β -phosphaacrylic acid **8**. Because of the high stability of the products, the enones could be isolated, purified, and fully characterized by NMR, UV and IR spectroscopy.⁴



SCHEME 2

Transmetallation reactions

In general, the stability of carbenoids mainly depends on the halogen (Cl>Br>I) and the metal (Hg>Mg>Zn>Li).⁷ Phosphavinylidene carbenoids decompose at temperatures below -50 °C. In order to determine their stability and reactivity with different metals, we transmetallated **2a** with HgCl₂, MgBr₂, and ZnCl₂. The mercury carbenoid **9a** was isolated as air stable crystals. The formation of the zinc (**9b**) and magnesium (**9c**) carbenoids could be proved indirectly by addition of D₂O at 15 °C and at RT, respectively. The deuterated product was isolated in high yield and isomeric purity in both cases, which demonstrates the thermal and configurational stability of these carbenoids. **9a** and **9b** were unreactive towards benzaldehyde. However, **2a** reacted with carbonyl compounds furnishing 3-phosphaallylic alcohols **10** (SCHEME 3).

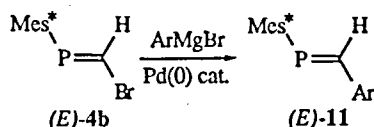


SCHEME 3

In spite of the increased stability of the **9c** (decomposition at 15°C), it did react with acetophenone to give 75% of the corresponding phosphoallylic alcohol; in contrast, **2a** reacted exclusively by deprotonation.

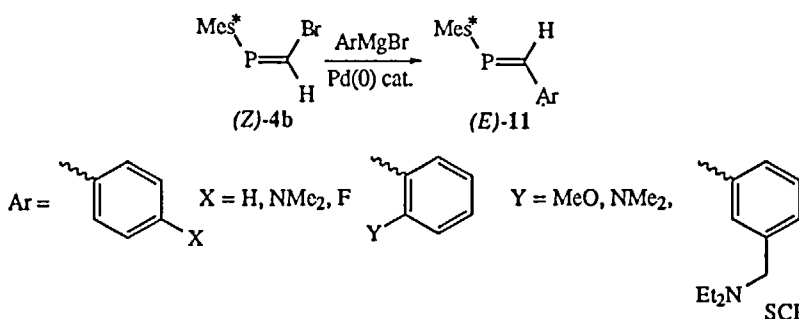
Coupling with Grignard reagents

The functionalization of phosphoalkenes via the carbenoid route is limited to nucleophilic reactions with reactive electrophiles. Recent developments in phosphoalkene chemistry show that there is interest in phosphoalkene based bidentate ligand systems.⁸ For this reason, methodologies for the synthesis of *trans*-(aromatically)substituted phosphoalkenes were investigated. With dihalophosphoalkenes, Pd(0) catalyzed coupling with organometallic compounds could not be achieved.⁵ Therefore, we developed new, convenient synthetic procedures for the preparation of (*E*)-halophosphoalkenes wherein the halogen is chlorine or bromine (**4a,b**; SCHEME 1).⁶ (*E*)-Chlorophosphoalkene **4a** was reacted with Grignard reagents in the presence of a catalytic amount of Pd(PPh₃)₄ at room temperature. Only phenylmagnesium chloride proved to be reactive under these conditions; the *trans*-phenylphosphoalkene **11** (Ar = Ph) was isolated in 76% yield. (*E*)-Bromophosphoalkene **4b** turned out to be much more reactive. A large variety of aromatic Grignard reagents could be coupled, furnishing the products **11** in high yield (80-90%), and isomeric purity (100% (*E*)-isomer) (SCHEME 4).



SCHEME 4

In an attempt to synthesize the (*Z*)-isomers of **11**, we used (*Z*)-**4b** in analogous experiments. To our surprise, only the corresponding (*E*)-**11** were obtained in all cases (SCHEME 5). Apparently, a rapid rearrangement occurs after the oxidative addition of palladium(0) into the C-Br bond. The products were isolated in 80-90% yield, with 100% isomeric purity. In the case of *para*-substituted aromatics, the reaction takes 5 hours stirring at room temperature. When the aryl-Grignard reagent contains an *ortho*-substituent, heating to 50 °C during 5 hours is needed, probably because of steric hindrance. Electron-withdrawing or electron-donating substituents on the aromatic ring seemed to have no effect on the rate of the reaction.



SCHEME 5

REFERENCES

1. A. A. PRISHCHENKO and I. F. LUTSENKO, *Zh. Obshch. Khim.*, **51**, 2630 (1981).
2. R. APPEL, C. CASSER, and M. IMMENKEPPEL, *Tetrahedron. Lett.*, **26**, 3551 (1985).
3. M. YOSHIFUJI, T. NIITSU, and N. INAMOTO, *Chem. Lett.*, 1733 (1988).
4. M. VAN DER SLUIS, F. BICKELHAUPT, N. VELDMAN, H. KOOLJMAN, A. L. SPEK, W. EISFELD, and M. REGITZ, *Chem. Ber.*, **128**, 465 (1995).
5. V. D. ROMANENKO, M. SANCHEZ, T. V. SARINA, M-R. MAZIÈRES, and R. WOLF, *Tetrahedron. Lett.*, **33**, 2981 (1992).
6. J. B. M. WIT, M. VAN DER SLUIS, and F. BICKELHAUPT, see further in this issue.
7. O. M. NEFEDOV, A. I. D'YACHENKO, and A. K. PROKOF'EV, *Russ. Chem. Rev.* **46**, 941 (1977).
8. A. JOUAI, M. GEOFFROY, F. TERRON, and G. BERNARDINELLI, *J. Chem. Soc. Chem. Commun.*, 155 (1992).