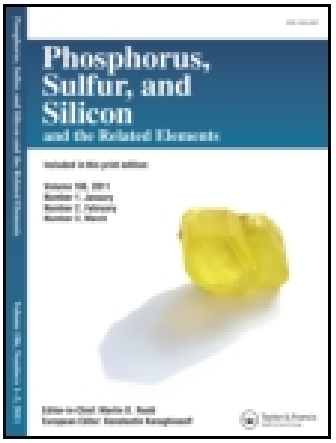

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

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Accepted author version posted online: 15 Nov 2012.Published online: 08 May 2013.

To cite this article: Elisabet Öberg & Sascha Ott (2013) Alternative Synthesis of A C,C-Diacetylenic Phosphaalkene, Phosphorus, Sulfur, and Silicon and the Related Elements, 188:1-3, 164-167, DOI: 10.1080/10426507.2012.743146

To link to this article: http://dx.doi.org/10.1080/10426507.2012.743146

Phosphorus, Sulfur, and Silicon, 188:164–167, 2013

ISSN: 1042-6507 print / 1563-5325 online
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ALTERNATIVE SYNTHESIS OF A C,C-DIACETYLENIC PHOSPHAALKENE

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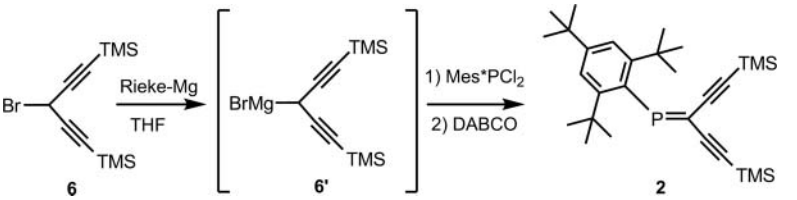
GRAPHICAL ABSTRACT



Abstract *Bis(trimethylsilyl)-terminated C,C-diacetylenic phosphaalkene was prepared from Mes*PCl$_2$ and a propargylic Grignard reagent that in turn was formed from 3-bromo-1,5-bis(trimethylsilyl)penta-1,4-diyne and Rieke-Mg.*

Keywords Phosphaalkene; alkyne; π-conjugation; Rieke magnesium

INTRODUCTION

Phosphaalkenes are one of many interesting classes of organophosphorus compounds.[1] By incorporating phosphaalkenes into π-conjugated systems, both we[2] and others[3] have shown that the phosphorus centers has a profound impact on the frontier molecular orbitals of the systems, thereby altering their optical and electronic properties. In order to expand the synthetic procedures to C,C-diacetylenic phosphaalkenes (C,C-A$_2$PAs), we have developed an alternative route to the bis(trimethylsilyl)-substituted C,C-A$_2$PA which constitutes an important building block for more elaborate oligomers.[2(e,f)] The new procedure omits an acetylenic chloroallene intermediate that has been used previously, but is sometimes available only in lower yields.

RESULTS AND DISCUSSION

We have recently shown that C,C-A$_2$PA **2** can be synthesized from an allenic chloride **1**, whereas propargylic chloride **3** gives rise to butadiyne-substituted phosphaalkene **4** (Scheme 1).[2(c)] Both chlorides were reacted with Mes*PCl$_2$ (Mes* = 2,4,6-(*tert*-Bu)$_3$Ph)

Received 12 September 2012; accepted 21 October 2012.
This work was supported by the Göran Gustafsson Foundation, COST action 0802 PhoSciNet and Uppsala University through the U^{3}MEC molecular electronics priority initiative.
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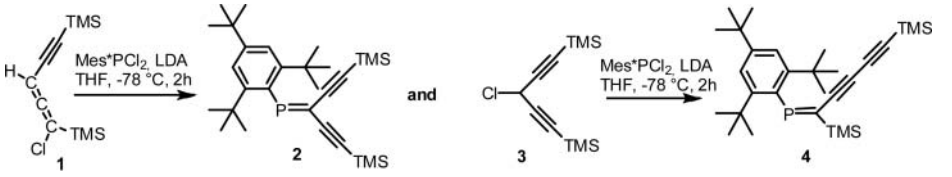

Scheme 1 Synthesis of C,C-diacetylenic phosphaalkene **2** and butadiyne-substituted phosphaalkene **4**.

and elimination of HCl and LiCl was achieved by LDA in order to form the P=C double bond.

In a different approach, we wanted to prepare a Grignard reagent from the propargylic chloride **3** in order to explore whether it was possible to access a different reactivity as compared to the LDA procedure, i.e., the reactivity at the central carbon atom and the formation of C,C-A_2PA **2**. In the first experiments, it was discovered that the activity of chloride **3** was not sufficient to allow for the formation of the Grignard reagent, even when freshly prepared Rieke magnesium was used. Having identified this shortcoming, propargylic alcohol **5** was reacted with Br_2 and PPh_3 in CH_2Cl_2 to afford bromide **6**, i.e., a more reactive starting material for the subsequent Grignard reaction (Scheme 2).[4] In analogy to the procedures reported for the formation of the allenic- and propargylic chlorides,[2(c)] the use of CH_2Cl_2 as solvent gives the propargylic bromide as the major product, which can be isolated after column chromatography in pentane in 71% yield. The occurrence of one signal for the TMS groups at $\delta = 0.20$ ppm in the ^{1}H-NMR and $\delta = -0.5$ ppm in the ^{13}C-NMR together with two signals for the acetylenic carbons at $\delta = 92.2$ and 98.9 ppm confirms the symmetric structure of **6**. Subsequently, bromide **6** was dissolved in THF and added dropwise to a suspension of commerically available Rieke Mg in the same solvent. The formed Grignard reagent 6' was transferred to a solution of Mes*PCl_2 in THF at 0°C. After stirring at room temperature, DABCO was added to facilitate dehydrochlorination and the formation of the P=C double bond.

Much to our satisfaction, this procedure yielded A_2PA **2** in 23% isolated yield, with diphosphene, Mes*P = PMes*, being the major side product due to the presence of unreacted Mg.[5] As stated above, the use of a Grignard reagent like **6′** favors a fairly different mechanistic pathway compared to our earlier described method.[2c] Firstly, the utilization of a Grignard reagent avoids a proton abstraction which is proposed to be the first step in the reaction of chlorides **1** and **3** upon treatment with LDA (Scheme 1). Whereas the lithiated **1** seems to react directly with Mes*PCl_2, the propargyllithium species of **3** is in an equilibrium with its allenyl lithium species and the reaction occurs at the carbon atom bonded to the TMS-group, yielding **4**.[2(c),6] However, this equilibrium does not seem to exist for the propargylic Grignard reagent **6′** in Scheme 2 or lies on the propargylic side, since no butadiyne-substituted phosphaalkene **4** that would stem from an allenic magnesiumbromide species could be detected.

CONCLUSIONS

In conclusion, we have explored an alternative synthetic route to a bis-TMS substituted C,C-diacetylenic phosphaalkene. The reaction of a propargylic Grignard reagent with Mes*PCl_2 and subsequent treatment with base gives the bis-TMS substituted C,C-diacetylenic phosphaalkene. The observed reactivity of **6′** is thus fundamentally different

to that of the previously used propargylic lithium reagents, which give rise to butadiyne-substituted phosphaalkenes.

EXPERIMENTAL

NMR Spectroscopy: ^{1}H-NMR spectra were recorded on a JEOL Eclipse + 400 MHz spectrometer (operating at 399.8 MHz). Chemical shifts are given in ppm and referenced internally to the residual solvent signal ($CHCl_3$, $\delta_H = 7.26$ ppm). ^{13}C-NMR spectra were recorded on the same instrument (operating at 100.5 MHz) and were also referenced internally to the residual solvent signal ($CHCl_3$, $\delta_c = 77$ ppm, central signal). ^{31}P-{^{1}H}-NMR spectra were also measured on JEOL Eclipse + 400 MHz spectrometer (operating at 161.8 MHz).

Compound **5** was prepared using known procedures.[2(c)]

1,5-Bis(trimethylsilyl)-3-bromopenta-1,4-diyne (6): To a solution of PPh_3 (2.07 g, 7.90 mmol) in 50 mL CH_2Cl_2, Br_2 (0.40 mL, 7.90 mmol) was added dropwise at 0°C. The solution was stirred for 30 min and 1,5-bis(trimethylsilyl)penta-1,4-diyne-3-ol (1.76 g, 7.85 mmol) was added in portions. The reaction mixture was stirred for 2 h. After addition of 10% $Na_2S_2O_3$ (aq) to neutralize unreacted Br_2, the phases were separated. The aqueous phase was extracted with pentane, and the combined organics dried with Na_2SO_4 and concentrated in vacuo. Purification by column chromatography (silica, pentane). Yield: 1.62 g (5.64 mmol, 71%). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 5.17$ (s, 1H, CH), 0.20 (s, 18H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 98.9, 92.2, 19.0, -0.5$

(Bis(trimethylsilylethynyl))(2,4,6-tri-*tert*-butylphenyl)phosphaethene (2): To a suspension of Rieke Mg (1.40 mL of a 25 mg/L Rieke Mg in THF, appr. 1.44 mmol) in THF (15 mL) at room temperature, 1,5-bis(trimethylsilyl)-3-bromopenta-1,4-diyne (0.139 M in THF, 1.39 mmol) was added drop wise during 45 minutes. The greenish brown suspension was stirred for 30 minutes and transferred to a solution of Mes^*PCl_2 (0.500 g, 1.44 mmol) at 0°C. After warming to room temperature and stirring for 3 h, 1,4-diazabicyclo[2.2.2]octane (0.314 g, 2.80 mmol) was added slowly. The reaction mixture was stirred for 14 h, filtered through celite, dried with Na_2SO_4 and concentrated in vacuo. Purification by column chromatography (1% EtOAc in pentane) and thereafter the two products (**2** and $Mes^*P = PMes^*$) were separated by preparative HPLC (Phenomenex® Gemini 110A C18, starting mixture methanol:THF = 95:5 and then a gradient, flow 2 mL/min). Yield: 0.154 g (0.329 mmol, 23%). Analytical data are in accordance to those reported earlier.[2c]

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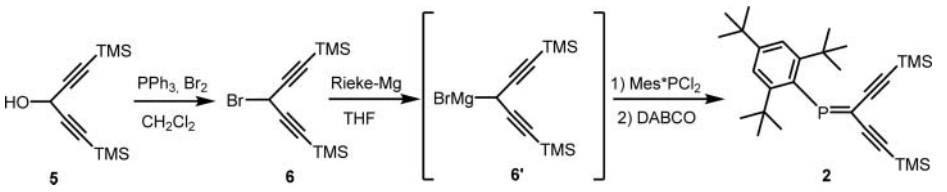

Scheme 2 Synthesis of C,C-diacetylenic phosphaalkene **2** via a Grignard route.

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