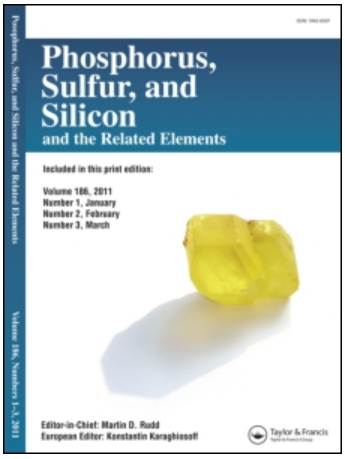



## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# The Synthesis of Hexaphenylcyclotriphosphazene in Improved Yield

F. Aslan[a]; M. Arslan[b]
[a] Department of Chemistry, Harran University, Sanliurfa, Turkey [b] Department of Chemistry, Firat University, Elazig, Turkey

**To cite this Article** Aslan, F. and Arslan, M.(2008) 'The Synthesis of Hexaphenylcyclotriphosphazene in Improved Yield', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 11, 2875 — 2881
**To link to this Article: DOI:** 10.1080/10426500802023915
**URL:** http://dx.doi.org/10.1080/10426500802023915

*Phosphorus, Sulfur, and Silicon*, 183:2875–2881, 2008

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802023915

Taylor & Francis
Taylor & Francis Group

# The Synthesis of Hexaphenylcyclotriphosphazene in Improved Yield

**F. Aslan[1] and M. Arslan[2]**
[1]Department of Chemistry, Harran University, Sanliurfa, Turkey
[2]Department of Chemistry, Firat University, Elazig, Turkey

*The reaction between phenylmagnesium bromide and hexachlorocyclotriphophazene ($N_3P_3Cl_6$) (**1**) was reinvestigated for the synthesis of hexaphenylcyclotriphosphazene ($N_3P_3Ph_6$) (**2**) in high yield. The reaction is complete within two weeks at room temperature using toluene as solvent. When the reactants (PhMgBr and $N_3P_3Cl_6$) were employed in a 6:1, 36:1 and 72:1 molar ratio, compound **2** was obtained in 2.6%, 14%, and 33.4% yield, respectively. The formation of $N_3P_3Cl_6$ (**2**) during the reaction was followed by thin-layer chromatography. Compound **2** was characterized by elemental analysis, IR, UV-VIS, $^1H$, $^{13}C$, and $^{31}P$ NMR spectroscopy as well as by mass spectrometry.*

**Keywords** Arylcyclotriphosphazene; cyclotriphosphazenes; hexachlorocyclotriphosphazene; hexaphenylcyclotriphosphazene; phosphazenes



## INTRODUCTION

The reaction between halophosphazenes and Grignard reagents is one of the general routes for the synthesis of alkyl or aryl substituted phosphazenes.[1,2] Although the synthesis of linear or cyclic alkyl or aryl substituted phosphazenes had attracted considerable attention between 1970 and 1985, the synthesis of alkyl or aryl substituted phosphazenes was performed with only limited success.[3–7] Such reactions were reported to involve in addition to substitution reactions, also skeletal cleavage, metal-halogen exchange, ether cleavage, and ring-contraction processes.[8] It is known that these reactions belong to the most complex and difficult reactions in phosphazene chemistry.

Cyclic alkyl or aryl phosphazenes that contain side groups attached to the phosphazene skeleton through direct P–C bonds are useful

Received 12 January 2008; accepted 28 February 2008.
We thank the Harran University Research Fund (Project No:293) and Scientific and Technical Council of Turkey (TBAG-153) for support.
Address correspondence to F. Aslan, Department of Chemistry, Harran University, TR-63100 Sanliurfa, Turkey. E-mail: faslan33@yahoo.com

models for preliminary macromolecular reactivity studies or may be used as "monomers" for polymerization reactions.[2] The resulting polymers should possess high photolytic, oxidative and thermal stability, and should also be of considerable interest as biomedical materials.[9] One of the prominent problems in this area is the isolation of cyclic and high polymeric phosphazenes that contain alkyl or aryl groups bonded to the P,N skeleton through P—C bonds.

It was reported previously that partially alkyl or aryl substituted phosphazenes and ring-linked bis(cyclophosphazenes) rather than fully substituted phosphazenes were formed in the reaction of cyclotriphosphazenes with Grignard reagents.[7] The reaction between $N_3P_3Cl_6$ and phenylmagnesium bromide under different conditions (temperature, reaction time, media and mole ratio of reactants) was reported by a number of investigators.[10—12] The phenyl derivate **2** was isolated in very low yield (5%) by Shaw et al.[3,10]



In our previous studies on monophosphazenes, we have reported the synthesis of aryl or alkyl substituted monophosphazenes by reaction of aryl or alkyl Grignard reagents (RMgX) with *N*-dichlorophosphoryl-*P*-trichlorophosphazene.[13,14]

Here we report on the reaction of phenylmagnesium bromide with **1** in toluene at room temperature, which resulted in the formation of hexaphenylcyclotriphosphazene in unexpected high yield (33.4%). We improved the yield of **2** from 5% to 33%.

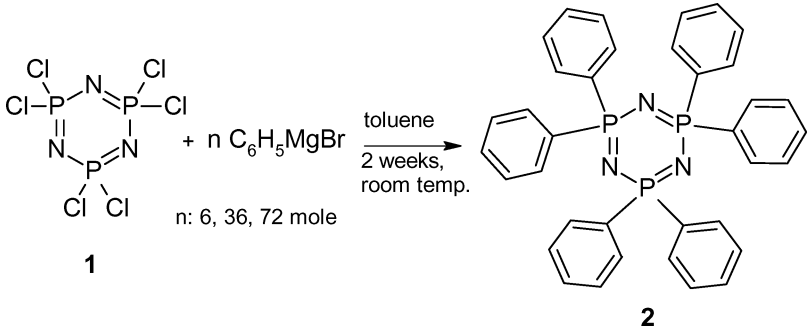
## RESULTS AND DISCUSSION

The reaction of hexachlorocyclotriphosphazene **1** with phenylmagnesium bromide was carried out in various molar ratios of the reactants ($PhMgBr/N_3P_3Cl_6$) at room temperature in toluene as solvent. As show in Table I, compound **2** was obtained in 33.4% yield when the reactants were used in a 72:1 molar ratio. The reactions were repeated two times and the same results were found (Scheme 1).

The formation of $N_3P_3Cl_6$ was monitored by thin layer chromatography during the reaction. It is interesting to note that the increase of

**TABLE I Yields and Molar Ratio of the Reactants**

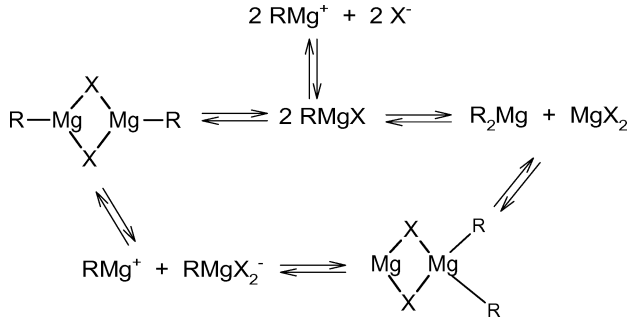
| $N_3P_3Cl_6$ | $C_6H_5MgBr$ | Molar Ratio ($PhMgBr/N_3P_3Cl_6$) | $N_3P_3(C_6H_5)_6$ (amount, yield) |
|---|---|---|---|
| 1.44 mmol, 0.50 g | 8.63 mmol, 2.9 mL | 6 | 0.022 g, 2.6% |
| 1.44 mmol, 0.50 g | 51.78 mmol, 17.3 mL | 36 | 0.120 g, 14.0% |
| 1.44 mmol, 0.50 g | 103.56 mmol, 34.6 mL | 72 | 0.287 g, 33.4% |




**SCHEME 1**

the amount of the cyclotriphosphazene **2** and the observation of only one spot from the TLC indicates for the reaction mechanism to involve an initial cleavage of the phosphazene ring, replacement of the chlorine atoms in the resulting linear intermediate by phenyl groups and finally a recyclization reaction.[7]

It was observed, that the yield of **2** depends upon the molar ratio of the reactants. The results are given in Table I. The yield of **2** increased when an excess of PhMgBr was used. Tesi and Slota reported that when an excess of Grignard reagent was used, the alkyl substituted cyclotriphosphazene was obtained in high yield.[6] The same study was repeated by Allcock et al. and the same results were found. They observed that an increase of the yield of the product is favored by using a threefold excess of Grignard reagent for each P-Cl bond.[6] As shown in Scheme 2, the presence of an equilibrium between various species in the solution has to be considered. The relative position of the equilibrium and the concentrations of the species depend upon the nature of the groups R, the solvent, the halide X, and the temperature. It is known,




**SCHEME 2** Equilibria in a solution of RMgX.

that Grignard reagents (RMgX) in solution are in equilibrium with corresponding dialkylmagnesium compounds ($R_2Mg$) and magnesium dihalides ($MgX_2$) (Schlenk equilibrium).[15,16] Thus, the real concentration of RMgX is different from the calculated concentration. Therefore an excess of RMgX should be used to increase the concentration of RMgX in this kind of reactions.

The solvent used in this reaction is also very important. For example, it was observed that Grignard reagents do not react with halophosphazenes when THF or diethyl ether is used as a solvent,[6] presumably because RMgX forms monomeric four coordinate magnesium complexes in diethyl ether and larger clusters in THF.[14] This prevents the reaction of RMgX with $N_3P_3Cl_6$. Therefore toluene or benzene should be used as solvent.

The identity and structure of the hexaphenylcyclotriphosphazene obtained results from the elemental analysis and the IR, UV-VIS, $^1H$, $^{13}C$, $^{31}P$ NMR, and mass spectra. The analytical data of **2** are given in the experimental section.

One of the most characteristic peaks in the IR spectra of phosphazenes is the P═N strech, which is observed at 1213 and 1190 $cm^{-1}$ for **1**. Compared to **1** this peak is shifted to longer wavelength for **2** (at 1189 and 1167 $cm^{-1}$). The peaks characteristic for C—H, P—C, C═C and P-N-P appear at 3054, 1436, 1589, and 849 $cm^{-1}$, respectively (Figure 1).[1]

As expected, only one peak is observed in the $^{31}P$ NMR spectra of both **1** and **2** at 21.2 and 16.4 ppm, respectively. The $^{31}P$ NMR signal

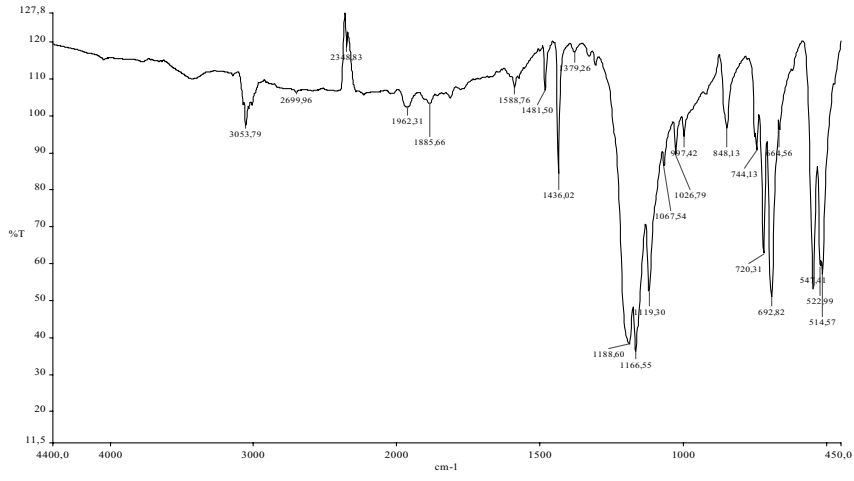



**FIGURE 1** IR spectrum of **2**.

of **2** is shifted to higher field. For arylsubstituted phosphazenes it was observed, that the presence of electron withdrawing phenyl groups at phosphorus favors the delocalization of the skeletal nitrogen lone-pair of electrons to phosphorus and thus generates a high field shift of the $^{31}P$ resonance.[1] In previous investigations $^{31}P$ NMR signals at –19.8 and –14.3 (negative values representing downfield shift) were reported for **1** and **2**, respectively.[1]

The phenyl groups bonded to the phosphazene ring in compound **2** were characterized by $^{1}H$ and $^{13}C$ NMR spectroscopy. In the $^{1}H$ NMR spectrum of **2** three distinct signals are observed between 7.80 and 7.38 ppm for the aromatic protons and the P,H coupling constants could be determined. In the $^{13}C$ NMR spectrum of **2**, four distinct signals for the aromatic carbon atoms are observed between 138.9 and 128.3 ppm. The carbon atoms attached directly to the phosphorus atom display a signal at lowest field and with the largest $J_{PC}$ value ($J_{PC} = 123.0$ Hz).[17]

The electron impact mass spectrum of **2** showed the well-defined molecular ion peak at *m/z* 598 (1%) as M+1. The peak at *m/z* 77 (dominant ion, $C_6H_5^+$, 100%) corresponds to the loss of $C_6H_5$ groups. Other important peaks at *m/z* 199, 230, and 397 show the loss of $(C_6H_5)_2PN$, $(C_6H_5)_2PNP$ and $(C_6H_5)_4P_2N_2$ groups, respectively. The elemental analysis data of **2** are consistent with the formula of $N_3P_3(C_6H_5)_6$.

The bands at 184, 204, and 256 nm in the electronic spectrum of benzene can be attributed to $\pi \rightarrow \pi^*$ transitions of the benzene ring.[18] Hexachlorocyclotriphosphazene shows an absorption maximum at 175 nm[1]. The bands of hexaphenylcyclotriphosphazene are observed at 238 and 272 nm, indicating that the $\pi \rightarrow \pi^*$ transitions of phenyl ring in **2** are shifted to lower energy (Figure 2).

## EXPERIMENTAL

All reagents and solvents were purchased from Merck except hexachlorocyclotriphosphazene and phenylmagnesium bromide (as 3M ether solution), which were purchased from Aldrich. Toluene was distilled over sodium benzophenone under argon prior to use. The reaction was carried out under argon atmosphere using standard Schlenk techniques.

Infrared spectra were recorded with a Perkin-Elmer System 2000 FT-IR spectrophotometer. The UV-VIS absorption spectra were recorded with a MINI 1240 UV-VIS spectrophotometer. All NMR spectra were recorded using a Bruker DPX-400 FT-NMR spectrometer. All data were recorded in $CDCl_3$solutions. The $^{1}H$ and $^{13}C$ chemical shifts are given with respect to $SiMe_4$ as internal standard; the $^{31}P$ chemical shifts

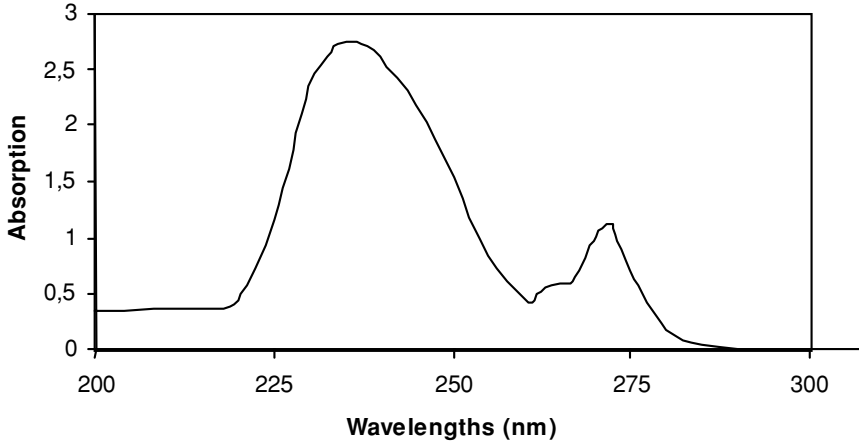



**FIGURE 2** The electronic spectrum of **2**.



are referenced to 85% $H_3PO_4$ as external standard. Chemical shifts downfield from the standard are assigned positive $\delta$ values. Electron impact mass spectra were obtained with a Micromass UK Platform-II spectrometer. Microanalysis was carried out with a LECO932 CHNS-O apparatus.

## Synthesis of Hexaphenylcyclotriphosphazene $N_3P_3Ph_6$ (2)

A phenyl magnesium bromide solution (103.56 mmol, 34.6 mL) was added to **1** (1.44 mmol, 0.50 g) in 100 mL of dry toluene under argon atmosphere. The diethyl ether, which comes from phenyl magnesium bromide solution, was removed from the reaction mixture by distillation under argon atmosphere. After the reaction was continued for 2 weeks at room temperature, the precipitated salt ($MgCl_2$) was filtered off, and the solvent was removed under vacuum. The crude product was purified by column chromatography using aluminum oxide-90 active neutral column and 2/1 (v/v) $CH_2Cl_2$/*n*-hexane as eluent. After the solvent was removed, a white solid (**2**) was obtained; yield: 0.287 g (33.4%); m.p. 232°C. Anal. calcd. for $N_3P_3C_{36}H_{30}$: C, 70.31; H, 5.06; N, 7.03%; Found: C, 71.30; H, 4.53; N, 6.82. $^1$H NMR ($CDCl_3$): $\delta$ = 7.8, A part of AA′ BB′ CX (dd, $^3J_{PH}$ = 9 Hz, *o*-H), 7.43, C part of AA' BB' CX (t, $^5J_{PH}$ = 2 Hz, *p*-H), 7.38, B part of AA′ BB′ CX (t, $^4J_{PH}$ = 3 Hz, *m*-H)[27]. $^{13}$C NMR ($CDCl_3$): 138.9 (d, $^1J_{PC}$ = 133.1 Hz, C-*i*), 131.1 (d, $^2J_{PC}$ =11 Hz, C-*o*), 130.8 (d, $^4J_{PC}$ = 2.2 Hz, C-*p*), 128.3 (d, $^3J_{PC}$ = 13 Hz, C-*m*).

## REFERENCES

[1] H. R. Allcock, *Phosphorus–Nitrogen Compounds* (Academic Press, New York and London, 1972), Chap. 9, pp. 219–220.
[2] H. R. Allcock, P. J. Harris, and M. S. Connolly, *Inorg. Chem.*, **20,** 11 (1981).
[3] M. Biddlestone and R. A. Shaw, *J. Chem. Soc. A*, 1750 (1970).
[4] H. R. Allcock, P. J. Harris, and M. S. Connolly, *Inorg. Chem.*, **20,** 11 (1981).
[5] P. J. Harris, K. B. Williams, and B. L. Fisher, *J. Org. Chem.*, **49,** 406 (1984).
[6] H. R. Allcock, J. L. Desorcie, and L. J. Wagner, *Inorg. Chem.*, **24,** 333 (1985).
[7] H. R. Allcock, P. J. Harris, and R. A. Nissan, *J. Am. Chem. Soc.*, **103,** 2256 (1981).
[8] H. R. Allcock, J. L. Desorcie, and G. H. Riding, *Polyhedron*, **6,** 119 (1987).
[9] H. R. Allcock, J. L. Desorcie, and P. J. Harris, *J. Am. Chem. Soc.*, **105,** 2814 (1983).
[10] M. Biddlestone and R. A. Shaw, *J. Chem. Soc.*, *A*, 178 (1969).
[11] P. J. Harris, J. L. Desorcie, and H. R. Allcock, *J. Chem. Soc., Chem. Commun.*, 852 (1981).
[12] M. Biddlestone and R. A. Shaw, *Inorg. Phys. Theor. A*, 2715 (1971).
[13] M. Arslan, F. Aslan, and A. I. Ozturk, *Heteroatom Chem.*, **14,** 138 (2003).
[14] F. Aslan, A. I. Ozturk, and M. Arslan, *Heteroatom Chem.,* **14,** 413 (2003).
[15] D. F. Shriver, P. W. Atkins, and C. H. Langford, *Inorganic Chemistr*y (Oxford University Press, Oxford, 1994), Chap. 10.
[16] G. L. Miessler and D. A. Tarr, *Inorganic Chemistry*, (Prentice-Hall, Inc., New Jersey, 1999) Chap. 8.
[17] J. Emsley and D. Hall, *The Chemistry of Phosphorus*, (Harper and Row Publishers, London, 1971) Chapter 3.
[18] E. Erdik, *Spectroscopic Methods in Organic Chemistry* (Gazi Bookshop, Ankara, 1998) Chap. 1.