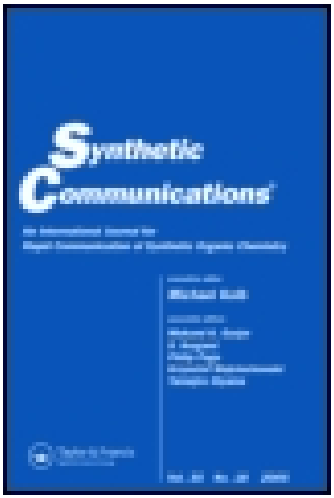
This article was downloaded by: [University of Edinburgh]
On: 19 October 2014, At: 12:59
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Facile Synthesis of Hexakis(4-Formylphenoxy)-Cyclotriphosphazene and Hexakis(4-Acetophenoxy)-Cyclotriphosphazene

Kristine N. Ludwig [a] & Robert B. Moore [a]
[a] School of Polymers and High Performance Materials, University of Southern Mississippi , Box 10076, Hattiesburg, MS, 39406-0076
Published online: 04 Dec 2007.

To cite this article: Kristine N. Ludwig & Robert B. Moore (2000) Facile Synthesis of Hexakis(4-Formylphenoxy)-Cyclotriphosphazene and Hexakis(4-Acetophenoxy)-Cyclotriphosphazene, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:7, 1227-1232, DOI: 10.1080/00397910008087143

To link to this article: http://dx.doi.org/10.1080/00397910008087143

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views

expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [University of Edinburgh] at 12:59 19 October 2014

SYNTHETIC COMMUNICATIONS, 30(7), 1227–1232 (2000)

FACILE SYNTHESIS OF HEXAKIS(4-FORMYLPHENOXY)-CYCLOTRIPHOSPHAZENE AND HEXAKIS(4-ACETOPHENOXY)-CYCLOTRIPHOSPHAZENE

Kristine N. Ludwig and Robert B. Moore*

School of Polymers and High Performance Materials,
University of Southern Mississippi, Box 10076, Hattiesburg, MS 39406-0076

Downloaded by [University of Edinburgh] at 12:59 19 October 2014

Abstract: Synthesis of hexakis(4-formylphenoxy)cyclotriphosphazene and similar compounds may be achieved utilizing a phase-transfer reaction. This one-pot procedure eliminates the need for rigorous drying of solvents, purification of reagents, and reflux conditions during the reaction.

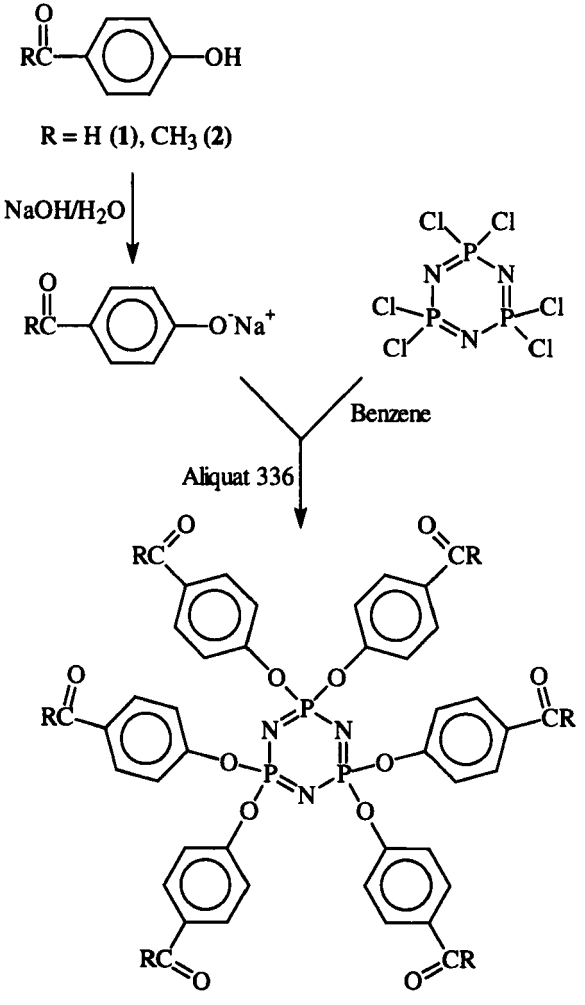
Hexakis(4-formylphenoxy)cyclotriphosphazene (HFP-PNT) has been utilized in the formation of Schiff base networks. These networks have been shown to be effective at reversibly binding bioactive molecules onto the hydrolyzable Schiff base linkage,[1] as well as possessing superior heat, corrosion, and moisture-resistant characteristics when compared to other phosphonitrilic-based resins.[2] Additionally, HFP-PNT has been used as precursor core for synthesis of polystyrene star polymers.[3]

* To whom correspondence should be addressed

Copyright © 2000 by Marcel Dekker, Inc. www.dekker.com

In order to synthesize HFP-PNT, methylphenoxyphosphazene may be photooxidized to yield formylphenoxyphosphazene.[4] For larger scale production, HFP-PNT and related compounds may be synthesized using a sodium hydride-derived sodium salt of 4-hydroxybenzaldehyde (HBA)[1, 5, 6] or by reacting the phosphonitrilic trimer (PNT) with HBA in the presence of triethylamine and *N,N*-dimethylaminopyridine.[3]

Scheme



Downloaded by [University of Edinburgh] at 12:59 19 October 2014

Downloaded by [University of Edinburgh] at 12:59 19 October 2014

The previous techniques for the synthesis of HFP-PNT have typically involved a battery of rigorous procedures including: recrystallization or multiple fractional vacuum sublimations of the PNT, thorough drying of all solvents, performing the reaction in an inert atmosphere under reflux conditions for 48+ hours, filtration via Schlenk techniques, solvent removal via vacuum distillation, and recrystallization of the final product.[1, 3, 5-8] We describe herein a simple, one-pot, phase-transfer procedure that obviates the need for tedious purification of reagents and solvents and rigorous reaction conditions. Sodium salts of 4-hydroxybenzaldehyde and 4-hydroxyacetophenone are prepared utilizing an aqueous NaOH solution (see Scheme). When benzene was used as the PNT solvent in HFP-PNT synthesis, the hexa-substituted product precipitated out of the benzene layer. Hexakis(4-formylphenoxy)cyclotriphosphazene formation appeared to be facilitated by precipitation from the reaction mixture. When the solvent for the PNT phase was chloroform, the substituted product remained in solution, but penta-substitution was the maximum extent of reaction.

EXPERIMENTAL

All reagents were laboratory grade and were used without further purification. The melting points were determined using a Mel-Temp capillary melting point apparatus. ^{1}H-NMR spectra were obtained on a Bruker 300MHz NMR spectrometer, using $CDCl_3$ as the solvent. Proton NMR values are given in δ relative to tetramethylsilane (TMS).

Downloaded by [University of Edinburgh] at 12:59 19 October 2014

Hexakis(4-formylphenoxy)cyclotriphosphazene (HFP-PNT) (1)

Sodium hydroxide (2.00 g, 5.00×10^{-2} mol) was dissolved in 30 mL of deionized water. To this solution was added 5.10 g (4.1×10^{-2} mol) of HBA (98%). The mixture was stirred to achieve complete dissolution. Separately, 2.37 g (6.82×10^{-3} mol) of PNT was dissolved in 30 mL of benzene. The HBA and PNT solutions were combined, and three drops of Aliquat 336 were added. The mixture was stirred at 25°C. Progress of the reaction was monitored by thin layer chromatography (TLC) (mobile phase: 90% benzene, 10% ethyl acetate (EtOAc)). The gradual substitution on the PNT ring generally proceeded with reaction time as follows: mono-substituted: five minutes, di-substituted: 10 minutes, tri-substituted: 15 minutes, tetra-substituted: 30 minutes, penta-substituted: 45 minutes, and hexa-substituted: 90 minutes. After 90 minutes, hexakis(4-formylphenoxy)cyclotriphosphazene precipitated from the benzene layer of the reaction. The reaction was allowed to continue stirring for six hours in order to enhance the yield of the hexa-substituted product. The product was collected via filtration, dried, and recrystallized from EtOAc. Yield: 92%. ^{1}H NMR (300MHz, $CDCl_3$): 7.21 ppm (2H, d), 7.70 ppm (2H, d), 9.94 ppm (1H, s). These shifts are in agreement with those reported in the literature.[3, 7, 8] Melting point: 155-157°C (experimental), 154-158°C (literature[1, 3]).

This reaction was also performed using similar stoichiometry, but utilizing chloroform instead of benzene as the PNT solvent in order to keep the product in solution. After reacting for 24 hours at room temperature, the product consisted

of primarily penta-substituted PNT, as determined by TLC. The reaction was heated at reflux for an additional 24 hours. No further reaction was observed. The aqueous and organic layers were separated, and the chloroform was removed from the organic layer to yield a light yellow oil. In comparison to the reaction performed in benzene, it appears that the formation of the hexa-substituted product (in high yield) is facilitated by the occurrence of product precipitation.

Downloaded by [University of Edinburgh] at 12:59 19 October 2014

Hexakis(acetophenoxy)cyclotriphosphazene (2)

Hexakis(acetophenoxy)cyclotriphosphazene was synthesized in a similar fashion to hexakis(4-formylphenoxy)cyclotriphosphazene, using 4-hydroxyacetophenone as the organic reactant and benzene as the PNT solvent. After reacting at 25°C for six hours, the hexa-substituted product remained dissolved in the benzene layer. The solution was added to 20 mL of deionized water, which resulted in precipitation of the product. The white powder was filtered, dried, and subsequently recrystallized from EtOAc. Yield: 90%. ^{1}H NMR (300MHz, $CDCl_3$): 2.50 ppm (3H, s), 6.95 ppm (2H, d), 7.70 ppm (2H, d). These shifts are in agreement with those reported in the literature.[7, 8] Melting point: 167-169°C.

ACKNOWLEDGMENTS

The authors wish to acknowledge the Mississippi Chemical Corporation and the Patricia Roberts Harris Fellowship program for their financial support.

REFERENCES

1. Allcock, H.R. and P.E. Austin *Macromolecules* **1981**, *14*, 1616.

2. Maruyama, I., H. Fujiwara, Y. Ito, and H. Shigematsu *U.S. Pat. No: 4988791* **1991**, Maruzen Petrochemical Co., Ltd.

3. Inoue, K., S. Negayama, T. Itaya, and M. Sugiyama *Macromol. Rapid Commun.* **1997**, *18*, 225.

4. Minto, F., V. Borzatta, R. Bertani, and M. Gleria *J. Appl. Polym. Sci.* **1997**, *65*, 217.

5. Allcock, H.R., M.S. Connolly, J.T. Sisko, and S. Al-Shali *Macromolecules* **1988**, *21*, 323.

6. Chang, J.Y., H.J. Ji, M.J. Han, S.B. Rhee, S. Cheong, and M. Yoon *Macromolecules* **1994**, *27*, 1376.

7. Carriedo, G.A., L. Fernandez-Catuxo, F.J. Alonso, P.G. Elipe, P.A. Gonzalez, and G. Sanchez *J. Appl. Polym. Sci.* **1996**, *59*, 1879.

8. Carriedo, G.A., F.J. Alonso, and P.A. Gonzalez *Macromol. Rapid Commun.* **1997**, *18*, 371.

(Received in the USA 09 August 1999)

Downloaded by [University of Edinburgh] at 12:59 19 October 2014