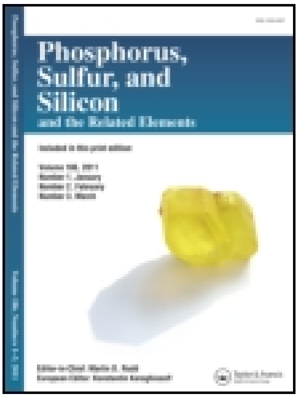
This article was downloaded by: [Lulea University of Technology]
On: 11 September 2013, At: 05:05
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Application of “Click” Cycloaddition for Synthesis of New Sulfur-Containing Oligomeric System

Jarosław Romański [a] & Monika Stefaniak [a]

[a] Department of Organic and Applied Chemistry , University of Łódź , 91-403 Łódź, Tamka , 12 , Poland

Accepted author version posted online: 24 Oct 2012.

To cite this article: Jarosław Romański & Monika Stefaniak (2013) Application of “Click” Cycloaddition for Synthesis of New Sulfur-Containing Oligomeric System, Phosphorus, Sulfur, and Silicon and the Related Elements, 188:4, 496-498, DOI: 10.1080/10426507.2012.736106

To link to this article: http://dx.doi.org/10.1080/10426507.2012.736106

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.

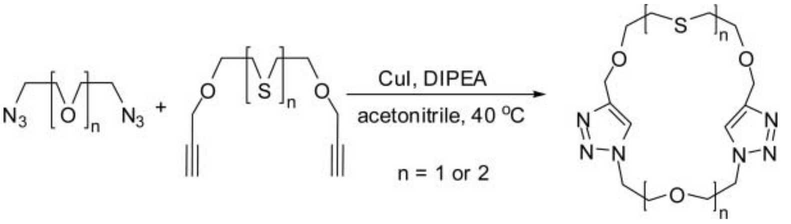
This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at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

Phosphorus, Sulfur, and Silicon, 188:496–498, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2012.736106

APPLICATION OF "CLICK" CYCLOADDITION FOR SYNTHESIS OF NEW SULFUR-CONTAINING OLIGOMERIC SYSTEM

Jarosław Romański and Monika Stefaniak
Department of Organic and Applied Chemistry, University of Łódź, 91-403 Łódź, Tamka 12, Poland

GRAPHICAL ABSTRACT



Abstract *The efficient synthesis of new sulfur-containing macrocycles via "click"-type alkyne–azide cycloaddition was described. Preliminarily, under aqueous conditions (water–methanol) using $CuSO_4$/sodium ascorbate as a source of Cu(I), the yields of the products were very poor. Using the Cu(I) in nonaqueous solution (MeCN), the yields of the products grow significantly (approx. 50%).*

Keywords Macrocyclic systems; click chemistry; 1,3-dipolar cycloaddition; sulfur oligomers

INTRODUCTION

Recently, among many synthetic methods the "click"-type reactions are frequently utilized in the last decade. Alkyne–azide Huisgen 1,3-dipolar cycloaddition[1] is one of the most popular reactions, due to the regioselective Cu(I)-catalyzed version introduced by Meldal[2] and Sharpless[3] in the contrast of non-regioselective Huisgen thermal process.

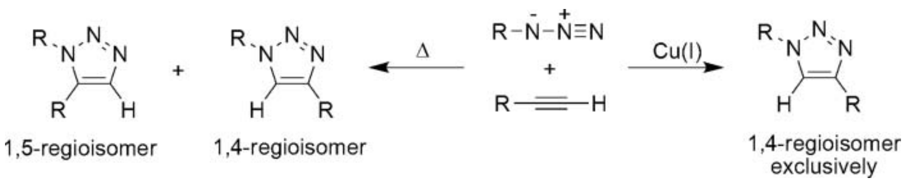
The syntheses of starting materials were performed according to known protocols,[4] however, the sulfur-containing propargyl derivatives **2a**-**b** have been obtained at first time.

The azides of di-triethylene glycols **3a**-**b** were obtained according to known procedure via their tosyl derivatives (Schemes 1–4).[5,6]

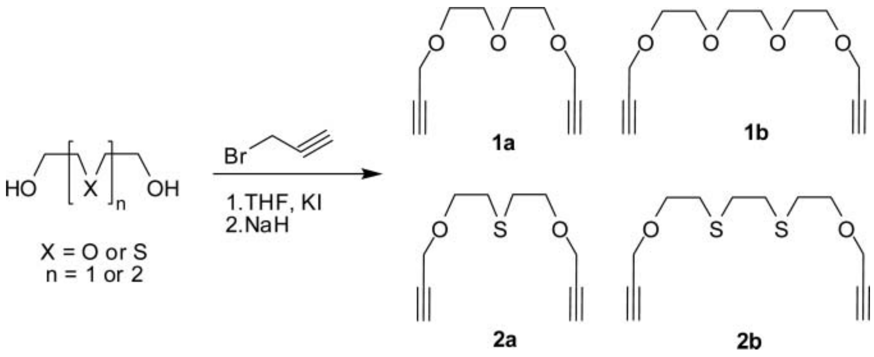
Received 25 September 2012; accepted 25 September 2012.

Authors acknowledge financial support from National Science Center (NCN, Grant No. 2011/01/B/ST5/06613).

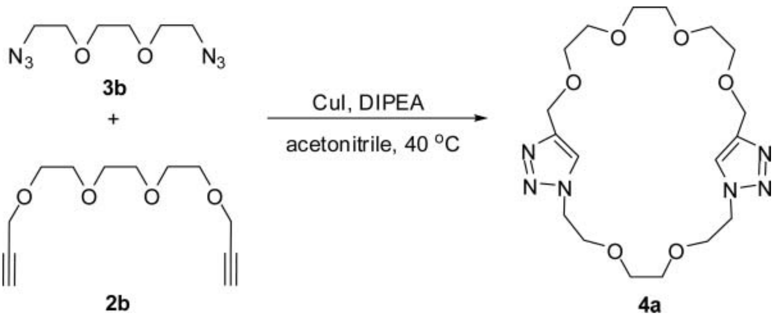
Address correspondence to Jarosław Romański, Department of Organic and Applied Chemistry, University of Łódź, 91-403 Łódź, Tamka 12, Poland. E-mail: romanski@uni.lodz.pl



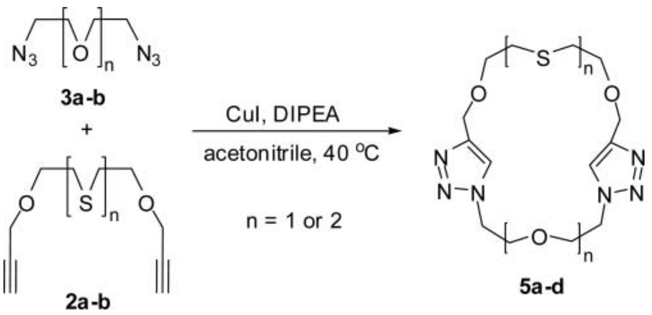
Scheme 1 Huisgen 1,3-dipolar cycloaddition thermal versus Cu(I)-catalyzed “click” cycloaddition.



Scheme 2 Synthesis of propargyl derivatives.



Scheme 3 Preparation of oxygen-containing oligomer.



Scheme 4 Preparation of sulfur-containing oligomers.

RESULTS

Initially cyclization reaction was carried out in the presence of $CuSO_4$ and sodium ascorbate in water–methanol mixture at 60°C, but in this case only one oligomer was obtained with very low yield. The 24-membered oligomeric compound **4a** was obtained with significantly better yield (37%) in the presence of Cu(I) as a catalyst. The reaction was carried out in the acetonitrile with addition of diisopropylethylamine (DIPEA) at 40°C.

The best conditions for the "click" cycloaddition toward new sulfur-containing oligomers **5a-d** were developed using Cu(I) in the presence of DIPEA in high-diluted version, obtaining **5a-d** with average yields 50%. Similar structures using intramolecular "click"-type cycloaddition were obtained from linear substrates.[6]

In conclusion, we have developed the straightforward access to the new sulfur-containing macrocyclic compound with built-in 1,2,3-triazole ring. In all cases, the "click" methodology of cycloaddition reaction was utilized. The study of complexing properties of obtained oligomeric compounds is under investigation.

REFERENCES

1. Huisgen, R.; Szeimies, G.; Moebius, L. *Chem. Ber.* **1967,** 100, 2494-2507.
2. Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002,** 67, 3057-3064.
3. Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, B. K. *Angew. Chem. Int. Ed.* **2002,** 41, 2596-2599.
4. Yao, Z. J.; Wu, H. P.; Wu, Y. L. *J. Med. Chem.* **2000,** 43, 2484-2487.
5. Gao, Y.; Chen, L.; Zhang, Z.; Gu, W.; Li, Y. *Biomacromolecules* **2010,** 11, 3102-3111.
6. Bonger, K. M.; Heitman, L. H.; Oosterom, J.; Timmers, C. M.; Overkleeft, H. S.; van der Marel, G. A. *Bioorg. Med. Chem.* **2007,** 15, 4841-4856.
7. Binauld, S.; Hawker, C. J.; Fleury, E.; Drockenmuller, E. *Angew. Chem. Int. Ed.* **2009,** 48, 6654-6658.