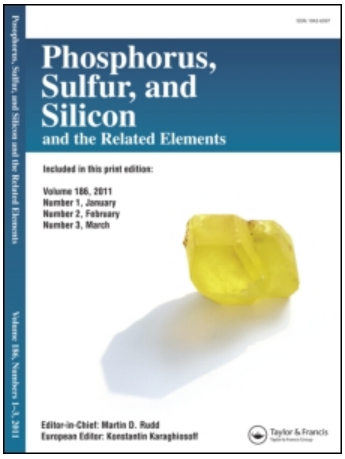


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Pseudo-Geminal [2.2]-Paracyclophane as Spacer for Bisallenyl Sulfoxides and Sulfones

Mihail Lucian Birsa[a]; Henning Hopf[a]
[a] Institute of Organic Chemistry, Technical University Braunschweig, Braunschweig, Germany

To cite this Article Birsa, Mihail Lucian and Hopf, Henning(2005) '*Pseudo-Geminal* [2.2]-Paracyclophane as Spacer for Bisallenyl Sulfoxides and Sulfones', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 5, 1453 — 1454
To link to this Article: DOI: 10.1080/10426500590913041
URL: http://dx.doi.org/10.1080/10426500590913041

Phosphorus, Sulfur, and Silicon, 180:1453–1454, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590913041

Taylor & Francis
Taylor & Francis Group

Pseudo-Geminal [2.2]-Paracyclophane as Spacer for Bisallenyl Sulfoxides and Sulfones

Mihail Lucian Birsa
Henning Hopf
Institute of Organic Chemistry, Technical University Braunschweig, Braunschweig, Germany

INTRODUCTION

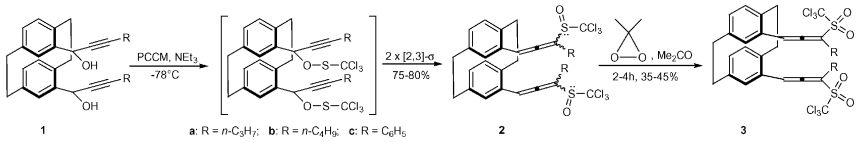
The [2,3]-sigmatropic rearrangements of propargylic sulfenates to allenic sulfoxides have received extensive application in organic synthesis. This reaction takes place spontaneously at low temperature. On the other hand, by using doubly substituted [2.2]-paracyclophanes as spacers for bisallenic moieties, interesting starting materials for intra- or intermolecular reactions can be realized.

RESULTS

We describe here the synthesis of the first *pseudo-geminal* bisallenyl[2.2]-paracyclophanes by the reaction of the corresponding propargylic alcohols (**1**) with trichloromethanesulfenyl chloride. The double [2,3]-sigmatropic rearrangement of *pseudo-geminal* bispropargylic trichloromethylsulfenates takes place spontaneously at low temperature, affording the desired *pseudo-geminal* bisallenyl trichloromethylsulfoxides (**2**) in good yields (75–80%). All three bisallenyl sulfoxides have been obtained as a mixture of four inseparable diastereoisomers. The reaction of bisallenyl sulfoxides with dimethyl dioxirane, a mild oxidizing agent, resulted in the formation of the desired *pseudo-geminal* bisallenyl sulfones (**4**) in moderate yields (35–45%). To our knowledge, these are the first *pseudo-geminal* bisallenyl[2.2]-paracyclophanes known to date.

Allenyl sulfones can easily be prepared by the reaction of propargylic alcohols with sulfonyl chlorides, followed by *in situ* reduction of the sulfonate to propargylic sulfinate. By applying this reaction sequence

Received July 9, 2004; accepted October 5, 2004.
Address correspondence to Mihail Lucian Birsa, Institute of Organic Chemistry, Technical University Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany. E-mail: lbirsa@uaic.ro



to the *pseudo-geminal* bispropargylic alcohols (**1**), the corresponding *pseudo-geminal* bisallenyl sulfones (**3**) should be formed, *via* a double [2,3]-sigmatropic rearrangement. Following the appropriate reaction conditions for our substrate, this reaction leads to the formation of an interesting, completely asymmetrical substituted *pseudo-geminal* [2.2]paracyclophane. The two-dimensional NMR analysis of the reaction product revealed a structure of type **4**, rather than the expected bisallenic sulfone.