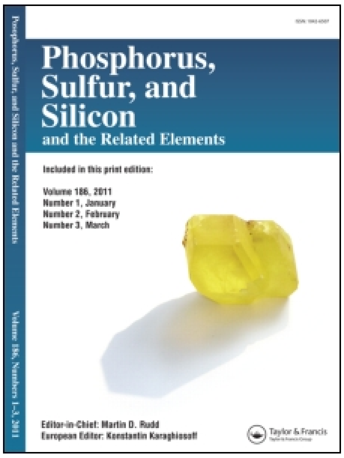


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REDUCTION OF BIS(BROMO(MESITYL)-{2,4,6-TRIS[BIS(TRIMETHYLSILYL)METHYL]- PHENYL}SILYL)BUTADIYNE WITH POTASSIUM GRAPHITE: UNEXPECTED FORMATION OF 2-ALLENYL-1-BENZOSILOLE

Yoshiyuki Mizuhata[a]; Nobuhiro Takeda[a]; Norihiro Tokitoh[a]
[a] Kyoto University, Kyoto, Japan

To cite this Article Mizuhata, Yoshiyuki , Takeda, Nobuhiro and Tokitoh, Norihiro(2004) 'REDUCTION OF BIS(BROMO(MESITYL)-{2,4,6-TRIS[BIS(TRIMETHYLSILYL)METHYL]- PHENYL}SILYL)BUTADIYNE WITH POTASSIUM GRAPHITE: UNEXPECTED FORMATION OF 2-ALLENYL-1-BENZOSILOLE', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 947 — 948

To link to this Article: DOI: 10.1080/10426500490428979

URL: http://dx.doi.org/10.1080/10426500490428979

Phosphorus, Sulfur, and Silicon, 179:947–948, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490428979

REDUCTION OF BIS(BROMO(MESITYL)-{2,4,6-TRIS[BIS(TRIMETHYLSILYL)METHYL]-PHENYL}SILYL)BUTADIYNE WITH POTASSIUM GRAPHITE: UNEXPECTED FORMATION OF 2-ALLENYL-1-BENZOSILOLE

Yoshiyuki Mizuhata, Nobuhiro Takeda, and Norihiro Tokitoh
Kyoto University, Kyoto, Japan

(Received August 18, 2003; accepted October 3, 2003)

*The reductive debromination of an very crowded bis(bromodiarylsilyl)butadiyne **2** was performed with potassium graphite to give the corresponding 2-allenyl-1-benzosilole **3** was isolated as a main product.*

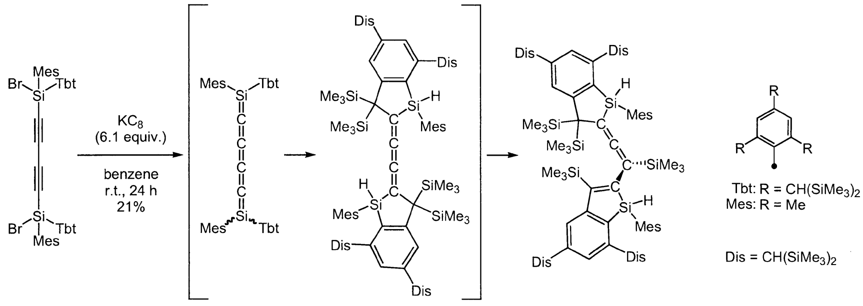
Keywords: 1,6-Disilahexapentaene; benzosilole; bulky substituent; double cyclization

Silacumulenes are highly reactive and no stable example has been reported so far for those having more than two cumulative double bonds. In this article, we present our attempted synthesis of kinetically stabilized 1,6-disilahexapentaene **1**. To the best of our knowledge, 1,6-disilahexapentaene is completely unprecedented, elusive silacumulenes even as a transient species.

The reaction of suitable precursor **2** bearing 2,4,6-tris[bis (trimethylsilyl)methyl]phenyl (Tbt) and Mes substituents with potassium graphite resulted in the formation of the corresponding 2-allenyl-1-benzosilole **3** as a main product. Finally, the molecular structure of **3** was unambiguously determined by x-ray crystallographic analysis.

The formation of such silole ring systems in the reduction of **2** is reasonably interpreted in terms of the double cyclization of the highly reactive Si=C units of the initially formed 1,6-disilahexapentaene **1** toward the *o*-benzyl positions of Tbt groups giving an intermediary 1,2,3-butatriene **4**, followed by the migration of one of the trimethylsilyl groups of **4** probably due to the intramolecular steric repulsion in **4**. It

Address correspondence to Norihiro Tokitoh, Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan. E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp



2 **1** **4** **3**

is interesting that only one of the trimethylsilyl groups of **4** migrated to give the final product **3** having a 2-allenyl-1-benzosilole skeleton. With the hope of isolating **1** as a stable compound, further investigation on the reductive debromination of **2** under various conditions are currently in progress.