Pergamon

Tetrahedron Letters 43 (2002) 2259–2262

TETRAHEDRON
LETTERS

Cycloaddition reactions of benzynes generated from benzobisoxadisilole, benzotrisoxadisilole and naphthoxadisilole[†]

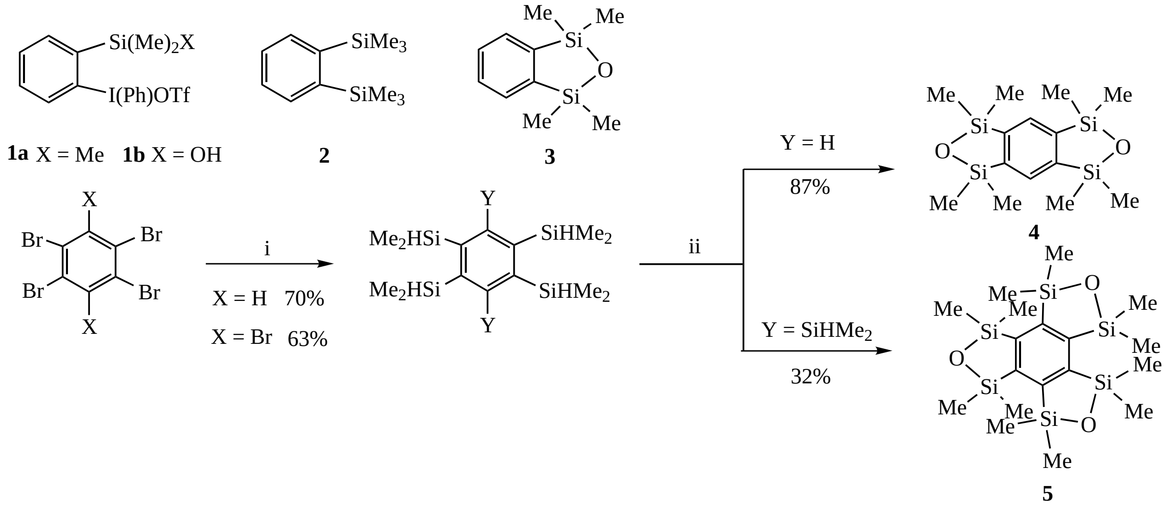
Ya-Li Chen, Hong-Kui Zhang, Wai-Yeung Wong and Albert W. M. Lee*

Department of Chemistry and Central Laboratory of the Institute of Molecular Technology for Drug Discovery and Synthesis,[‡]
Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

Received 5 December 2001; revised 25 January 2002; accepted 31 January 2002

Abstract—Benzynes (**7**, **16**) generated from benzobisoxadisilole and benzotrisoxadisilole were trapped as the furan cycloaddition adducts. Naphthoxadisilole and naphthobisoxadisilole were also synthesized. © 2002 Elsevier Science Ltd. All rights reserved.

Benzynes are important reactive intermediates. They have been the subject of theoretical interest and mechanistic studies.[1] Benzynes have also been widely used in organic syntheses of functional materials, natural products and theoretically interesting molecules.[2] There are many known precursors for the generation of benzynes. A recent addition, (phenyl)[*o*-(trimethylsilyl)phenyl]-iodonium triflate **1a**, was reported by Kitamura and co-workers.[3] The precursor of **1a** is 1,2-bis(trimethylsilyl)benzene **2** which can be prepared from 1,2-dichlorobenzene with the use of HMPA. Since its publication, this hypervalent iodine approach to benzyne generation has caught the attention of many research groups. Various applications, particularly in the syntheses of theoretically interesting molecules and functional materials have been reported.[4] Later on, the same team reported another new benzyne precursor, [2-(hydroxydimethylsilyl)phenyl](phenyl)iodonium triflate **1b**, which was prepared from 1,3-dihydro-1,1,3,3-tetramethyl-2,1,3-benzoxadisilole **3**,[5] which could be readily synthesized from 1,2-bromobenzene without the use of HMPA.



Scheme 1. *Reagents and conditions*: (i) Me_2HSiCl, Mg, THF, reflux; (ii) (a) CH_3OH/CH_3ONa, rt, (b) H_2O, 50°C.

Keywords: cycloaddition; Diels–Alder reaction; benzyne; benzobisoxadisilole; benzotrisoxadisilole; naphthoxadisilole.

* Corresponding author. Tel.: 852-2339 7064; fax: 852-2339 7348; e-mail: alee@hkbu.edu.hk

[†] This paper is dedicated to Professor Barry Sharpless on the occasion of his 60th birthday.

[‡] An Area of Excellence of the University Grants Committee (Hong Kong).

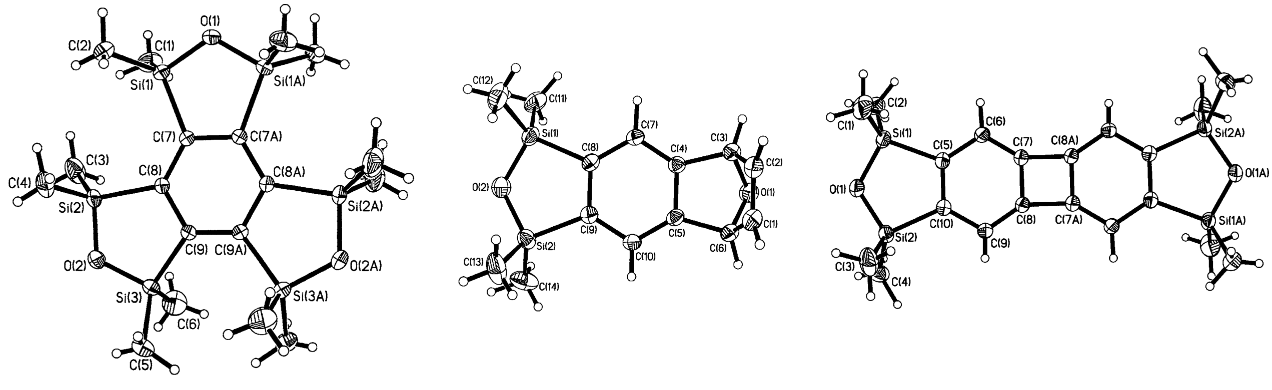
PII: S0040-4039(02)00239-3

In view of the relatively mild conditions for the generation of benzyne from the benzoxadisilole precursor **3** (via **1b**), we began a study of the generation of benzynes from benzobisoxadisilole **4** and benzotrisoxadisilole **5**. In particular, we wanted to discover whether bis-benzynes or any other related intermediates could be detected.

The syntheses of **4** and **5** according to the literature procedures[6] are outlined in Scheme 1. The X-ray structure of **4** had been reported.[7] Herein, we report the first X-ray structure of the benzotrisoxadisilole **5** (Fig. 1). Benzotrisoxadisilole **5** was almost planar including the benzene ring and the silicon and oxygen atoms.

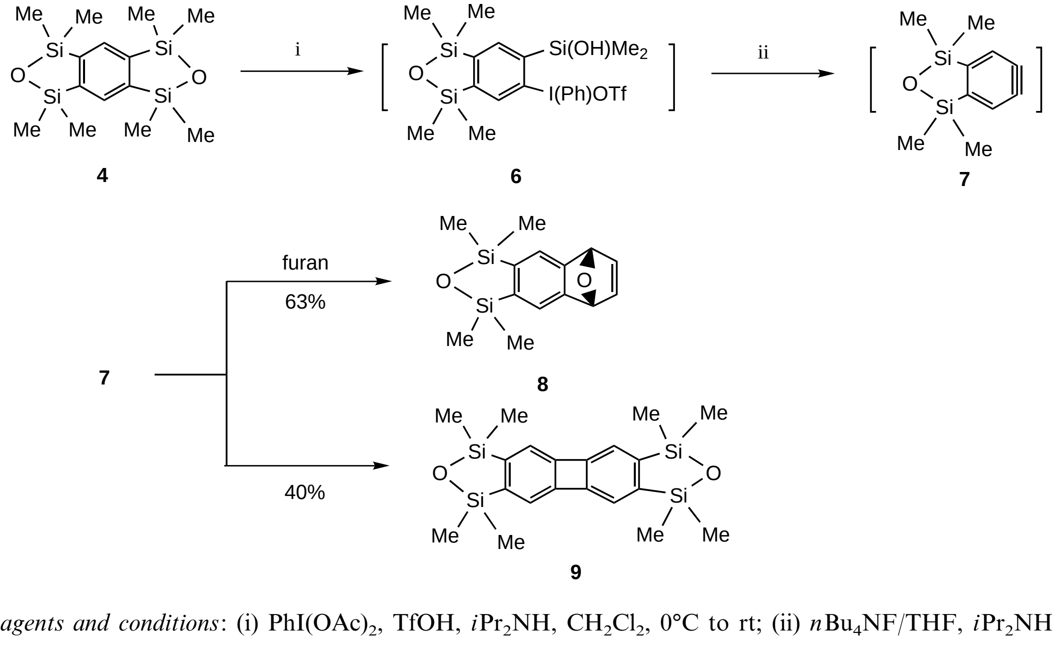
For the generation of benzyne from 1,2-bis(trimethylsilyl)benzene (via **1a**), it had been reported that the addition of diisopropyl amine during the preparation of **1a** and subsequent trapping reaction with diene was advantageous.[4e] Benzobisoxadisilole **4** was treated with excess $PhI(OAc)_2$/TfOH/iPr$_2$NH (3:6:4) in CH_2Cl_2 (Scheme 2). Without isolation of any intermediate, the homogeneous reaction mixture was reacted with another equivalent of iPr$_2$NH, nBu$_4$NF and excess furan. The Diels–Alder product **8** was formed in 63% isolated yield. Repeating the same reaction sequence in the absence of furan, dimer **9** of benzyne **7** was isolated in 40% yield. In addition to standard spectroscopic characterization, the structures of the cycloaddition products **8** and **9** were further confirmed by X-ray analyses (Fig. 1).

It seems that only one of the oxadisilole rings of **4** could be open up to the benzyne precursor **6** under these conditions. Slightly more forcing conditions were then tried. The first step of the reaction sequence was carried out in CH_2Cl_2 at 40°C followed by the furan trapping reaction at room temperature. A good yield of **8** was again obtained but with no indication of the formation of any bis-benzyne cycloadduct. It is also worth noting that both **8** and **9** were completely inert under the phenyliodination conditions (room temperature or 40°C in CH_2Cl_2). No benzyne intermediate would be generated from these two compounds.



5 **8** **9**

Figure 1. X-Ray structures of **5**, **8** and **9**.

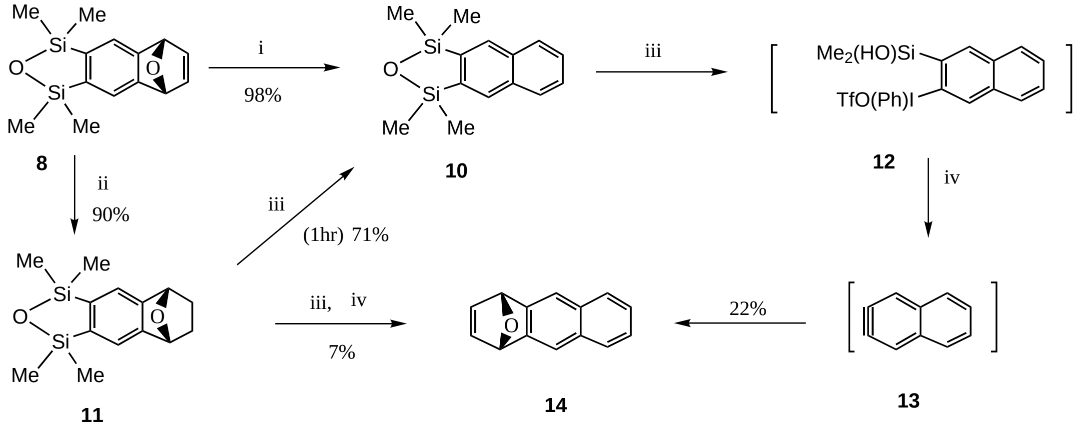


Scheme 2. *Reagents and conditions*: (i) $PhI(OAc)_2$, TfOH, iPr$_2$NH, CH_2Cl_2, 0°C to rt; (ii) nBu$_4$NF/THF, iPr$_2$NH, rt.

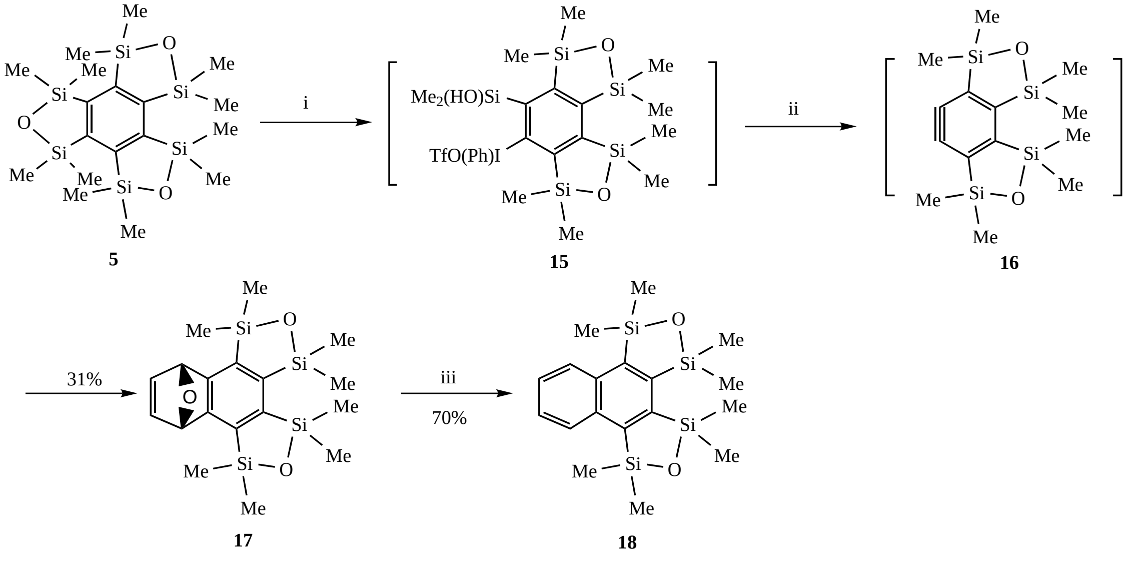
Furan adduct **8** could be deoxygenated in good yield by $TiCl_4$–$LiAlH_4$–Et_3N in THF[8] to 2,3-naphthoxadisilole **10** (Scheme 3). Hydrogenation of **8** also took place readily to afford **11** in good yield. 2,3-Naphthoxadisilole **10** was completely inert to the phenyliodination conditions in the presence of *i*Pr_2NH. However, without the amine, phenyliodination followed by benzyne formation (*n*Bu_4NF) and furan trapping, the Diels–Alder adduct **14** of 2,3-naphthyne **13** was obtained. This represents a synthesis of 2,3-naphthoxadisilole **10** and the use of it as a naphthyne precursor. When compound **11** was treated under the same phenyliodination conditions without *i*Pr_2NH followed by benzyne formation and furan trapping, a trace amount (7%) of **14** was detected. We speculate that **11** was transformed to **10** under these conditions. Indeed, when the phenyliodination of **11** was worked up after 1 h, a good yield (71%) of **10** was isolated.

Benzotrisoxadisilole **5** was again completely inert to the phenyliodination conditions in the presence of *i*Pr_2NH. Nonetheless, without the amine, **5** disappeared slowly (TLC monitoring). Without isolation of any intermediate, the homogeneous reaction mixture was treated with *n*Bu_4NF and excess furan (Scheme 4). The furan Diels–Alder adduct **17** of benzyne **16** was isolated in 31% yield. Once again, only one of the three oxadisilole rings of **5** could be opened up to the benzyne precursor **15** under these conditions. Finally, deoxygenation with $TiCl_4$–$LiAlH_4$–Et_3N in THF completed the synthesis of 1,2,3,4-naphthobisoxadisilole **18**.

In summary, we have demonstrated that benzynes **7** and **16** could be generated from benzobisoxadisilole **4** and benzotrisoxadisilole **5**, respectively. They were trapped as the Diels–Alder adducts of furan or the cycloaddition dimer in case of **7**. The synthesis of naphthoxadisilole **10**, which could serve as a precursor of 2,3-naphthyne, and the preparation of naphthobisoxadisilole **18** are also reported.



Scheme 3. *Reagents and conditions*: (i) $TiCl_4$, $LiAlH_4$, Et_3N–THF, reflux; (ii) H_2, Pd/C, rt; (iii) $PhI(OAc)_2$, TfOH, CH_2Cl_2, 0°C to rt; (iv) *n*Bu_4NF/THF, *i*Pr_2NH, furan, rt.



Scheme 4. *Reagents and conditions*: (i) $PhI(OAc)_2$, TfOH, CH_2Cl_2, 0°C to rt; (ii) *n*Bu_4NF/THF, *i*Pr_2NH, furan, rt; (iii) $TiCl_4$, $LiAlH_4$, Et_3N–THF, reflux.

Acknowledgements

We are grateful to the financial support from the Research Grant Council of the Hong Kong SAR Government (HKBU 2048/97P).

References

1. (a) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967; (b) Gilchrist, T. L. In *The Chemistry of Functional Groups*, *Supplement C*; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1983; Chapter 11.
2. (a) Hart, H. In *The Chemistry of Triple-Bonded Functional Groups*, *Supplement C2*; Patai, S., Ed.; Wiley: Chichester, 1994; Chapter 18; (b) Caster, K. C.; Keck, C. G.; Walls, R. D. *J. Org. Chem.* **2001**, *66*, 2932–2936.
3. (a) Kitamura, T.; Yamane, M. *J. Chem. Soc.*, *Chem. Commun.* **1995**, 983–984; (b) Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674–11679; (c) Kitamura, T.; Todaka, M.; Fujiwara, Y. In *Organic Syntheses*; Roush, W. R., Ed.; Wiley, 2000; Vol. 78, pp. 104–112.
4. (a) Ye, X.-S.; Li, W.-K.; Wong, H. N. C. *J. Am. Chem. Soc.* **1996**, *118*, 2511–2512; (b) Ye, X.-S.; Wong, H. N. C. *J. Org. Chem.* **1997**, *62*, 1940–1954; (c) Kitamura, T.; Todaka, M.; Shin-machi, I.; Fujiwara, Y. *Heterocycl. Commun.* **1998**, *4*, 205–208; (d) Okuma, K.; Shiki, K.; Shioji, K. *Chem. Lett.* **1998**, 79–80; (e) Winling, A.; Russell, R. A. *J. Chem. Soc.*, *Perkin Trans. 1* **1998**, 3921–3923; (f) Kitamura, T.; Fukatsu, N.; Fujiwara, Y. *J. Org. Chem.* **1998**, *63*, 8579–8581; (g) Liu, J.-H.; Chan, H.-W.; Xue, F.; Wang, G.-G.; Mak, T. C. W.; Wong, H. N. C. *J. Org. Chem.* **1999**, *64*, 1630–1634; (h) Yick, C.-Y.; Chan, S.-H.; Woy, H. N. C. *Tetrahedron Lett.* **2000**, *4*, 5957–5961.
5. Kitamura, T.; Meng, Z.; Fujiwara, Y. *Tetrahedron Lett.* **2000**, *41*, 6611–6614.
6. Fink, W. *Helv. Chim. Acta* **1964**, *57*, 1010–1015.
7. Daly, J. J.; Sanz, F. *J. Chem. Soc.*, *Dalton Trans.* **1973**, 2474–2475.
8. Xing, Y. D.; Huang, N. E. *J. Org. Chem.* **1982**, *47*, 140.