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5,6-Bis(trimethylsilyl)benzo[*c*]furan: a versatile building block for linear polycyclic aromatic compounds[†]

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Abstract

Benzo[*c*]furans are a class of interesting compounds. Being very reactive, they readily undergo Diels–Alder cycloaddition with dienophiles to restore their aromaticity. For this reason, they can be utilized to construct six-membered ring compounds which are common building blocks of many natural and non-natural molecules. In connection with our use of silylated furans in the preparation of polysubstituted furans, we sought to extend our work to include silylated benzo[*c*]furans as well. Herein, we report the synthesis of the title molecule and its further manipulation for the preparation of several silylated linear polynuclear aromatic compounds. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: isobenzofurans; Diels–Alder reaction; polycyclic aromatic compounds.

Benzo[*c*]furan (isobenzofuran) (**1**) has been postulated[1] and detected[2] as a reactive intermediate that readily undergoes Diels–Alder reactions with alkyne or alkene dienophiles to form the corresponding endoxide adducts. Subsequent deoxygenation[3] or dehydration[4] of these endoxides should lead to benzenoid frameworks. In this way, benzo[*c*]furan could serve as a potential building block for the construction of fused six-membered ring aromatic compounds. As part of our continuing program concerning the use of silylated furans in the regiospecific synthesis of polysubstituted furans,[5,6] we sought to extend the chemistry to include a silylated benzo[*c*]furan, namely 5,6-bis(trimethylsilyl)benzo[*c*]furan (**2**), which is expected to react with various dienophiles to provide Diels–Alder adducts. The synthesis of several benzo[*c*]furans containing trimethylsilyl groups on the furan ring has been reported by Rickborn.[7–10] Because of the β-effect of silicon,[11] aromatic rings substituted with trimethylsilyl groups are very useful precursors in many organic transformations.[5,6] It is therefore believed that the combined use of the silicon-directing effect and the deoxygenation protocol can lead to the realization of silylated linear polycyclic aromatic skeletons.

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[†] Dedicated to Professor Dr Richard Neidlein on the occasion of his 70th birthday.

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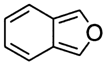
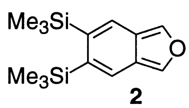
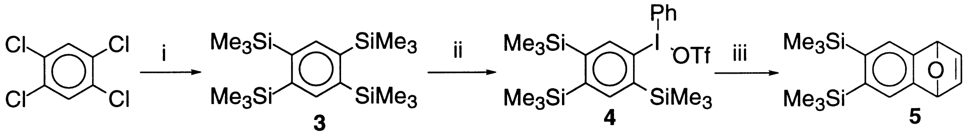


1



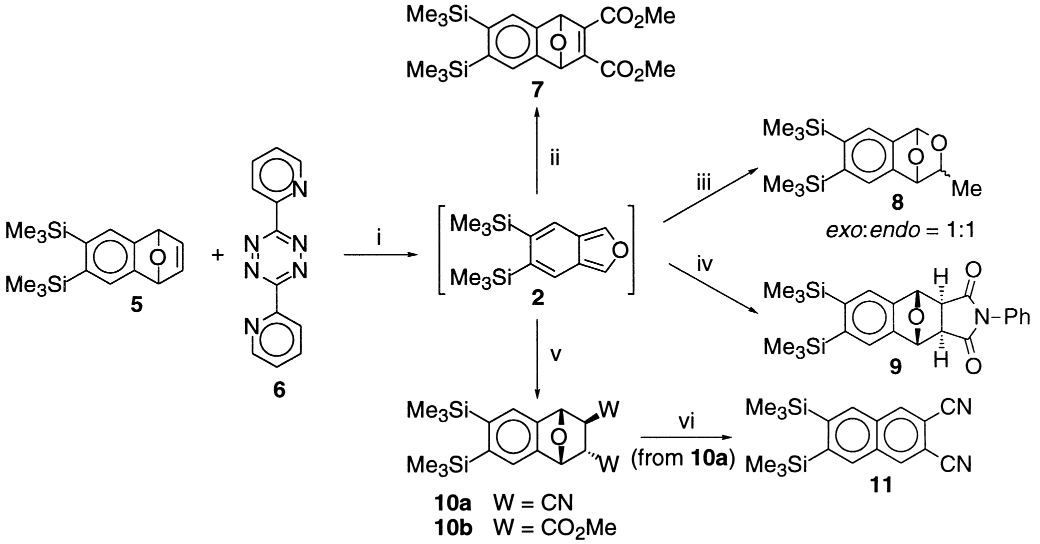
2

The *s*-tetrazine approach[12] established by Warrener was chosen as the key step in our generation of **2**. The starting material, 1,4-endoxy-1,4-dihydro-6,7-bis(trimethylsilyl)naphthalene (**5**), was readily accessible in three steps from commercially available 1,2,4,5-tetrachlorobenzene as illustrated in Scheme 1.[13,14] 1,2,4,5-Tetrakis(trimethysilyl)benzene (**3**) was obtained from tetrachlorobenzene by reaction with magnesium and trimethylsilyl chloride.[14] The silylbenzene **3** was then converted to the iodonium triflate **4**[14] by employing a standard procedure developed by Kitamura.[15,16] Upon treatment of **4** with TBAF, a benzyne was presumably generated, which was trapped by furan to afford **5**.[14,17]



Scheme 1. *Reagents and conditions*: (i) Mg, Me_3SiCl, HMPT, THF, reflux, 48%; (ii) $PhI(OAc)_2$, CF_3SO_3H, *i*-Pr_2NH, CH_2Cl_2, 61%; (iii) furan, *n*-Bu_4NF, THF, 98%

The generation of 5,6-bis(trimethylsilyl)benzo[*c*]furan (**2**) was accomplished by treating **5** with 3,6-di(pyridin-2′-yl)-*s*-tetrazine (**6**) in a chloroform solution. In the presence of various dienophiles, benzo[*c*]furan **2** furnished the expected Diels–Alder adducts **7**, **8**, **9**, **10a** and **10b**, in yields ranging from good to excellent, as depicted in Scheme 2.[17,18] A representative procedure is given here: To a well stirring solution of **5** (1.5 g, 5.2 mmol) and fumaronitrile (0.5 g, 6.25 mmol) in chloroform (20 mL) was added **6** (1.5 g, 6.25 mmol) in portions over 30 min. The reaction



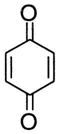
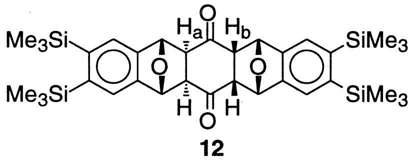
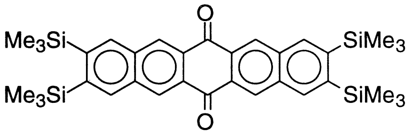
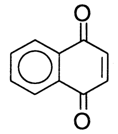
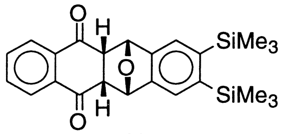
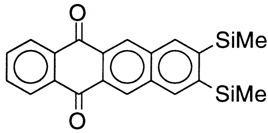
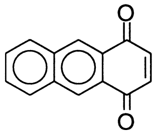
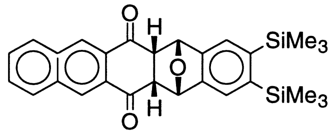
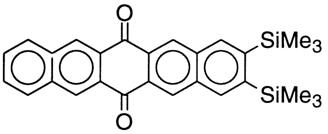
Scheme 2. *Reagents and conditions*: (i) $CHCl_3$; (ii) $MeO_2C{-}C{\equiv}C{-}CO_2Me$, 82%; (iii) MeCHO, 24%; (iv) *N*-phenylmaleimide, 76%; (v) *trans*-W–C=C–W (**10a**, 98%, **10b**, 86%); (vi) LiI, DBU, THF, reflux, 88%

mixture was allowed to stir for a further 2 h. After evaporation of solvent, the residue was chromatographed on silica gel (100 g, hexanes:ethyl acetate, 10:1) to afford **10a** as colorless crystals.

Nitrile **10a** can be dehydrated by treatment with a strong base such as bis(trimethylsilyl)amide, affording fair yields of the corresponding naphthalenenitriles which are commonly employed in the preparation of naphthalocyanines.[19] In our hands, we discovered that dehydration of compound **10a** was smoothly accomplished in a much more acceptable yield by reaction with a mixture of lithium iodide and 1,8-diazabicyclo[5,4,0]undec-1-ene in refluxing THF, giving naphthalenenitrile **11**.[17,18]

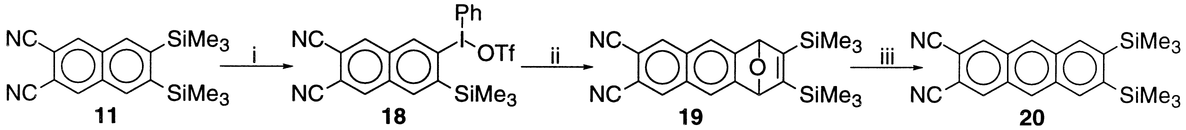
Benzo[*c*]furan **2** also reacted readily with quinones and the results are summarized in Table 1. For naphthoquinone and anthra-1,4-quinone,[20] only the *endo* adducts **13** and **14** were observed.[17,18] This was confirmed by ^{1}H NMR spectroscopy which showed two sets of doublet of doublets for the two groups of aliphatic protons in the ring systems.[17,18] However, benzoquinone gave the bis *exo–endo* adduct **12** exclusively.[17,18] The adducts **12**, **13** and **14** were dehydrated in refluxing 80% acetic acid, leading to the aromatic compounds **15**, **16** and **17** as bright yellow crystals.[17,18]

Table 1
Diels–Alder adducts of **2** and their corresponding dehydration products

Entry	Dienophile	Diels-Alder Adduct	Yield (%)	Dehydration Product	Yield (%)
1		 **12**	54	 **15**	38
2		 **13**	58	 **16**	75
3		 **14**	72	 **17**	75

The most notable feature of our program is the manipulation of trimethylsilyl substituents in the realization of linear polycyclic aromatic skeletons. In order to elongate the benzo framework **11** was allowed to react with iodobenzenediacetate in triflic acid, affording the iodonium triflate **18**. The iodonium salt **18** was then eliminated with TBAF to generate presumably a benzyne intermediate,[15,16] which provided endoxide **19** upon subsequent trapping with 3,4-bis(trimethylsilyl)furan.[5] The final deoxygenation step was accomplished by employing $TiCl_4$-$LiAlH_4$-Et_3N in THF, furnishing anthracene **20** in a good yield (Scheme 3).[17,18,21]

In conclusion, we have successfully synthesized and trapped 5,6-bis(trimethylsilyl)benzo[*c*]furan (**2**) under very mild conditions. In addition, one of the two trimethylsilyl substituents serves as a handle for the synthesis of higher acene members as demonstrated by the conversion of **11** to **20**. The synthesis of higher members in the acene series is in progress.



Scheme 3. *Reagents and conditions*: (i) $PhI(OAc)_2$, CF_3SO_3H, CH_2Cl_2, 50%; (ii) 3,4-bis(trimethylsilyl)furan, *n*-Bu_4NF, CH_2Cl_2, 62%; (iii) $TiCl_4$, $LiAlH_4$, Et_3N, THF, 78%

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17. Selected data for compounds **5**, **7**, **9**, **11**, **12**, **13** and **14**, **15**, **16**, **17** and **20**. Compound **5**: (300 MHz, $CDCl_3$) δ 0.37 (s, 18H), 5.73 (s, 2H), 7.03 (s, 2H), 7.61 (s, 2H). Compound **7**: (300 MHz, $CDCl_3$) δ 0.36 (s, 18H), 3.81 (s, 6H), 5.96 (s, 2H), 7.74 (s, 2H). Compound **9**: (300 MHz, $CDCl_3$) δ 0.39 (s, 18H), 3.15 (s, 2H), 6.00 (s, 2H), 7.33 (d, $J=7.2$ Hz, 2H), 7.42–7.52 (m, 3H), 7.71 (s, 2H). Compound **11**: (300 MHz, $CDCl_3$) δ 0.47 (s, 18H), 8.22 (s, 2H), 8.32 (s, 2H). Compound **12**: (300 MHz, $CDCl_3$) δ 0.20 (s, 18H), 0.31 (s, 18H), 3.76 (dd, $J=3.0$, 2.1 Hz, 2H), 5.61 (s, 2H), 5.68 (dd, $J=3.0$, 2.1 Hz, 2H), 7.51 (s, 2H), 7.55 (s, 2H). The ^1H–^1H COSY spectrum showed no spatial correlation between the two sets of protons H_a and H_b adjacent to the carbonyl group which indicates that they are arranged in a *trans* geometry. Compound **13**: (300 MHz, $CDCl_3$) δ 0.14 (s, 18H), 3.78 (dd, $J=3.6$, 1.8 Hz, 2H), 5.84 (dd, $J=3.6$, 1.8 Hz, 2H), 7.26 (s, 2H), 7.42 (dd, $J=5.7$, 3.3 Hz, 2H), 7.62 (dd, $J=5.7$, 3.3 Hz, 2H). Compound **14**: (300 MHz, $CDCl_3$) δ –0.07 (s, 18H), 3.87 (dd, $J=3.6$, 2.1 Hz, 2H), 5.87 (dd, $J=3.6$, 2.1 Hz, 2H), 7.24 (s, 2H), 7.57 (dd,

$J = 6.3$, 3.3 Hz, 2H), 7.84 (dd, $J = 6.3$, 3.3 Hz, 2H), 8.12 (s, 2H). Compound **15**: (300 MHz, $CDCl_3$) δ 0.49 (s, 36H), 8.40 (s, 4H), 8.90 (s, 4H). Compound **16**: (300 MHz, $CDCl_3$) δ 0.48 (s, 18H), 7.82 (dd, $J = 6.3$, 3.3 Hz, 2H), 8.37, (s, 2H), 8.39 (dd, $J = 6.3$, 3.3 Hz, 2H), 8.80 (s, 2H). Compound **17**: (300 MHz, $CDCl_3$) δ 0.49 (s, 18H), 7.70 (dd, $J = 6.3$, 3.3 Hz, 2H), 8.11 (dd, $J = 6.3$, 3.3 Hz, 2H), 8.39 (s, 2H), 8.88 (s, 2H), 8.93 (s, 2H). Compound **20**: (300 MHz, $CDCl_3$) δ 0.49 (s, 18H), 8.38 (s, 2H), 8.52 (s, 2H), 8.53 (s, 2H).

18. All new compounds were identified by means of ^1H and ^{13}C NMR spectroscopy and mass spectrometry, as well as elemental analyses or high resolution mass spectral data.
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