THE CHEMISTRY OF BENZYNE

NEW BENZYNE PRECURSOR – BENZOTRISOXADISILOLE

By

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(02010305)

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Date: 22th April 2005
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THE CHEMISTRY OF BENZYNE
NEW BENZYNE PRECURSOR – BENZOTRISOXADISILOLE

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Abstract
Benzyne is a well-known reactive intermediate. To produce the extremely reactive intermediate in an effective and mild controlled way, two new benzyne precursors –angular benzobisoxdisilole (15) and benzotrisoxadisilole (29) were proposed. The benzyne 31 generated from precursor 29 was trapped by Diels-Alder cycloaddition with heterocyclic dienes (furan, cyclopentadiene and N-tert-butoxycarbonylpyrrole) to give cycloadducts 32a-c. The photo-physical properties of the compound 34 generated from the reduction of cycloadduct 32a were studied by spectrofluorometer. Isobenzofuran (40) was also generated from the Diels-Alder and retro Diels-Alder reaction of cycloadduct 32a with tetrazine (37). Compound 42 was then produced from the Diels-Alder reaction between isobenzofuran (40) and dimethyl acetylenedicarboxylate (41). All products were fully characterized by $^1$H, $^{13}$C NMR and mass spectrometry.
Some Key Chemical Structures in this Project

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Chapter 1

General Introduction

1.1 History of Benzyne

In the past 100 years, arynes were described as one of the major focuses in organic chemistry. First evidence for the existence of an aryne was reported from the Chemical Institute of the University of Rostock: Stoermer and Kahlert observed the formation of 2-ethoxybenzofuran on treatment of 3-bromobenzofuran with bases in ethanol and postulated the formation of ortho-didehydrobenzofuran (1) as a reactive intermediate.\(^1\)

ortho-Benzyne was first suggested as a reactive intermediate in 1927. Roberts et al. found exciting evidence for the intermediate formation of 2 in the reaction of \(^{14}\text{C}\)-labeled chlorobenzene with sodium amide (Scheme 1) in a classical investigation in 1953.\(^1\)

![Scheme 1](image)

**Scheme 1.** In a classical isotopic labeling experiment Roberts et al. demonstrated the involvement of 2 in nucleophilic aromatic substitution. The product distribution can only be understood by assumption of a symmetrical intermediate.\(^1\)

The first direct IR spectroscopy detection of ortho-benzyne was accomplished by Chapman et al., using matrix isolation spectroscopy at very low temperatures to generate 2 starting from phthaloyl peroxide and benzocyclobutenedione. Besides IR spectra, there were now additional experimental data available to judge the quality of theoretical
predictions. In a remarkable piece of work Warmuth et al. were able to isolate ortho-benzyne in a hemicarcerand as a “molecular container” and to measure its NMR spectrum in solution. And the structure of 2 was concluded to be more closely resembles a cyclic alkyne rather than a cumulene.

1.2 Generation of Benzyne

As mentioned before, benzyne is an important reactive intermediate. Benzyne must be generated in situ because of their extraordinary reactivity. Many methods of generating benzyne from a variety of precursors such as o-halogenophenyl anions (3), benzenediazonium-2-carboxylate (4), and o-trimethylsilylphenyl triflate (5) have been reported. The most widely generation methods used are summarised in Scheme 2.

\[ \text{Scheme 2. General methods for the generation of benzyne} \]

A halide can be treated with a strong base such as an amide to remove the o-aromatic proton and generate benzyne via an anion. Alternatively, treating o-dihalosubstituted benzenes with a metal (lithium or magnesium) can give the desired aryne by elimination. And the use of strong bases which may act as nucleophiles can be avoided.

Aryl triflates have been used to generate arynes via other routes than metal – halogen
exchange. For example, fluoride ion displacement of the trimethylsilyl group provides a convenient route to benzyne under mild conditions (Scheme 3).[6]

![Scheme 3. Generation of benzyne from triflates](image)

Besides, oxidation of aminotriazole usually produces good yields, but has the disadvantage of requiring the presence of an oxidant such as lead tetraacetate in the reaction medium.[6] Deprotonation of 7-methyl-1-aminobenzotriazole derivatives leads to 7-substituted-1-aminobenzotriazoles, precursors of o-substituted benzynes (Scheme 4).

![Scheme 4. Generation of benzyne from aminobenzotriazoles](image)

Anthranilic acids are readily diazotized by alkyl nitrites in aprotic media to give benzenediazonium-2-carboxylates, which undergo fragmentation to benzyne, nitrogen, and carbon dioxide (Scheme 5).[10]
Metal-halogen exchange on $o$-halotriflates occurs at $-78^\circ$C with $n$-BuLi to produce arynes (Scheme 6).[^6]

To have synthetic and mechanistic use, the benzyne precursors should fulfill the following requirements: (i) practical facility in their synthesis; (ii) formation of only one aryne for a given precursor; (iii) relative stability and safe ease of handling and (iv) the absence of a requirement to use a strong base or high temperature in the generation of benzyne.

(Phenyl)[$o$-(trimethylsilyl)phenyl]iodonium triflate was reported by Kitamura in 1995.[^11,12] It was suggested as an efficient precursor of benzyne because of satisfying the four requirements. The precursor was readily prepared from $o$-bis(trimethylsilyl)benzene and PhI(OAc)$_2$. The $o$-bis(trimethylsilyl)benzene was prepared from 1,2-dichloromethane via Grignard type reaction in HMPA (Scheme 7). Mild and neutral conditions provided adducts with typical trapping agents (Scheme 8).
Scheme 7. Generation of benzyne from (phenol)[o-(trimethylsilyl)phenyl]iodonium triflate

Scheme 8. Adducts of benzyne generated from (phenol)[o-(trimethylsilyl)phenyl]iodonium triflate

To avoid the use of HMPA, which is carcinogenic, the same research team discovered (phenol)[2-(hydroxydimethylsilyl)phenyl]iodonium triflate as an alternative of 6 in 2000.\(^{[13]}\)

This iodonium triflate was prepared from 1,3-dihydro-1,1,3,3-tetramethyl-2,1,3-benzoazadisilole, which was synthesised from 1,2-bromobenzene without the use of HMPA (Scheme 9).

Scheme 9. Generation of benzyne from (phenol)[2-(hydroxydimethylsilyl)phenyl]iodonium triflate
1.3 Reaction of benzynes

Even at low temperatures, benzynes are extraordinary reactive. Their reactions can be divided into three groups: the pericyclic reactions; the nucleophilic additions and the transition metal-catalysed reactions.

1.3.1 Pericyclic reactions of benzynes

The pericyclic reactions can be divided into several categories such as the Diels-Alder reactions; the [2+2] cycloadditions; the 1,3-dipolar cycloadditions; the 1,4-dipolar cycloadditions; and the ene reactions.

1.3.1.1 Diels-Alder cycloadditions

The Diels-Alder reaction is one of the most important reactions of arynes and is used both as a means of detecting arynes and as a synthetic tool. Because of the highly electrophilic character of arynes, the reaction is observed with a very wide range of dienes including simple benzene derivatives or other benzenoid aromatic compounds.

Derivatives of pyrrole have been studied in cycloaddition reactions, leading to various 1,4-dihydro-1,4-iminonaphthalenes or the corresponding anthracenes (Scheme 10).[6]

Scheme 10. Synthesis of 1,4-dihydro-1,4-iminophthalenes and the corresponding anthracenes.
Variously-substituted oxazoles reacted with benzyne to give the bis(benzyne) adducts.

This outcome requires each of the following steps: a) formation of benzyne; b) Diels-Alder reaction with the oxazole; c) retro-Diels-Alder expulsion of the nitrile; and d) Diels-Alder reaction of benzyne with the isobenzofuran (Scheme 11).[14]

\[
\begin{array}{c}
\text{N} \quad \text{O} \\
\text{Ph} \\
\text{N} \\
\text{O} \\
\text{Ph} \\
\text{-PhCN}
\end{array}
\]

**Scheme 11.** Synthesis of bis(benzyne) adducts

In 1992, Castedo et al. reported a new approach of antitumor benzophenanthridines based on the Diels-Alder reaction between an \(\alpha\)-pyrone and an aryne arising from anthranilic acid (Scheme 12).[15]

\[
\begin{array}{c}
\text{CO}_2\text{Me} \\
\text{N} \\
\text{O} \\
\text{Ph}
\end{array}
\] + \[
\begin{array}{c}
\text{Ph}
\end{array}
\]

\[
\text{CO}_2\text{Me}
\]

**Scheme 12.** Synthesis of benzophenanthridines

In 1998, Kitamura and co-workers employed 2,3-didehydronaphthalene as a useful intermediate for the construction of polycyclic aromatic hydrocarbons and, in this way, 1,2,3,4-tetraphenylanthracene was prepared by treatment of 2,3-didehydronaphthalene with tetraphenylcyclopentadienone (Scheme 13).[6]
Scheme 13. Synthesis of 1,2,3,4-tetraphenylantracene

1.3.1.2 [2+2] Cycloaddition

Benzyne reacts with a wide range of olefins to give the [2+2] cycloadducts benzocyclobutenes. Because of the electrophilic nature of benzyne, the reactions proceed best with alkenes bearing electron-donating substituents and this reaction offers a simple and direct route to useful synthetic intermediates.

The [2+2] cycloaddition of dimethoxyethylene and bromoaryne provided the corresponding benzocyclobutene in a good yield (Scheme 14). [6]

Scheme 14. Synthesis of benzocyclobutene

1.3.1.3 1,3-Dipolar cycloadditions

A wide variety of stable 1,3-dipolar compounds undergo cycloadditions with arynes. 2,3-Didehydronaphthalene generated from (phenyl)[3-(trimethylsilyl)-2-naphthyl] iodonium triflate, reacted with p-methoxyphenyl azide according to a 1,3-dipolar cycloaddition in good yield, providing 1-arylnaphtho[2,3-e]triazoles (Scheme 15). [6]
1.3.1.4 1,4-Dipolar cycloadditions

1,4-Dipolar aryne cycloadditions were previously used as convergent routes to anthracyclinone intermediates. Based on this approach, an important intermediate in the synthesis of daunomycinone was obtained from cycloaddition of a lithiated 3-cyanophthalide and 2-bromo-5,6-dihydro-1,4-dimethoxy-2-naphthalene in the key step (Scheme 16).[6]

1.3.1.5 Ene reactions

The ene reaction of benzyne with olefins bearing an allylic hydrogen atom has been used essentially to detect benzyne, but it has not been extensively employed for synthesis.

Recently, the reactivity of benzyne with diimines has been studied. Most of the time, [4+2] or [2+2] cycloaddition was observed, but in the case of cyclohexyl(4-cyclohexyliminomethylbenzylidine)amine, an ene reaction led to the major product according to the following mechanism (Scheme 17).[6]
**Scheme 17.** Ene reaction of benzyne with cyclohexyl(4-cyclohexyliminomethylbenzylidene)amine

1.3.2 Nucleophilic additions to arynes

Arynes react with practically all kinds of nucleophiles. From a synthetic point of view, the most interesting are the nitrogen-bearing nucleophiles and carbanions. The addition of nucleophiles to arynes is highly regioselective when the position adjacent to the triple bond bears an electron-withdrawing group (EWG) capable of stabilising the negative charge acquired (Scheme 18).[6]

**Scheme 18.** Addition of nucleophiles to arynes

1.3.3 Transition metal-catalysed reactions of arynes

Recently, some new reactions of arynes were studied by Castedo and by Yamamoto, reported about the efficient palladium(0)-catalysed cyclotrimerisation of arynes and the co-cyclisation of diynes and alkynes, allowing the synthesis of various polycyclic aromatic hydrocarbons.
In 1998, Castedo reported an efficient catalytic procedure for the trimerisation of arynes yielding triphenylenes which are found at the core of many discotic liquid crystals and have therefore been the target of many synthetic studies (Scheme 19).[6]

Scheme 19. Synthesis of triphenylenes via trimerisation of arynes

Yamamoto et al. reported that benzyne was very reactive as a carbopalladation partner of \( \pi \)-allylpalladium chloride. Indeed, the palladium-catalysed reaction of allyl chlorides with benzyne produced phenanthrene derivatives (Scheme 20).

Scheme 20. Palladium -catalysed reaction of allyl chlorides with benzyne

The palladium(0)-catalyzed reaction of benzyne with suitably functionalized benzodiynes to afford benzo[b]fluorenones was reported by Castedo et al. in 2003.[18] The outcome of the result was affected by the steric and electronic properties of the diynes and proved to be regioselective when an unsymmetrically substituted aryne was used. The work represents the first example of a partially intramolecular [2+2+2] cycloaddition involving arynes (Scheme 21).
Scheme 21. Synthesis of benzofluorone from the palladium(0)-catalyzed reaction of benzyne with benzodiyne

1.4 Applications of benzyynes

Because of the extreme reactive properties of benzyynes, their reactions are widely used in synthesising some natural products. Planar antitumor benzophenanthridine is an example, which can be synthesised by intermolecular Diels–Alder reaction of pyrones with benzyne (Scheme 22).[16]

Scheme 22. Retrosynthetic analysis of planar antitumor benzophenanthridine

Diels–Alder reaction of 7 with benzyne (generated by thermal decomposition of benzenediazonium 2-carboxylate), followed by CO2 extrusion afforded the tetrahydrobenzophenanthridine (Scheme 23).[16]

Scheme 23. Preparation of tetrahydrobenzophenanthridine from Diels-Alder reaction of 7 with benzyne

Diels-Alder reaction of 9 (generated from dehydroacetic acid 8) with benzyne affords
adduct with a bicyclic [2.2.2] structure, which undergo a retro-Diels-Alder reaction with loss of CO$_2$ reaction to yield naphthalene 10 (Scheme 24).$^{[17]}$

**Scheme 24.** Synthesis of naphthalene 10 from Diels-Alder reaction of 9 and benzyne
1.5 Significance of the Project

1) The project aims to investigate the chemistry of a new benzyne precursor – benzotrisoxadisilole, including the possible benzyynes generated from benzotrisoxadisilole.

2) Naphthobisoxadisilole 34 (generated from deoxygenation of cycloadduct 32a) is compared for any difference in the photo-physical properties with naphthalene by spectrofluorometer.

3) The preparation of isobenzofuran from cycloadduct 32a is practiced and the isobenzofuran is further applied to the synthesis of polycyclic aromatic hydrocarbons (PAHs).
Chapter 2

Synthesis of Angular Benzobisoxadisilole

2.1 Preparation of 1,2,3,4-tetrabromobenzene (13)

Hexabromobenzene was treated with hydrazine hydrate in boiling ethanol. Instead of hydrazinopentabromobenzene (11) only 1,2,3,4-tetrabromobenzene (13) was obtained. Its structure followed both from its NMR spectrum (it showed a singlet resonance at \( \delta 2.53 \)).

The tetrabromobenzene may have been formed by aerial oxidation of the intermediate pentabromohydrazine (11 to 13). The alternative explanation, namely, that hydrazine causes debromination involving two ortho-bromine atoms probably by a concerted route (12 to 13), is also possible. This type of protodehalogenation seems to be due to a combination of the low nucleophilicity of the aromatic bromine atoms when compared to other halogens, and the correct molecular dimensions of the attacking nucleophile (Scheme 25).[19]

![Scheme 25. Generation of tetrabromobenzene with suggested mechanism](image-url)
2.2 Preparation of angular benzobisoxadisilole (15)

The preparation of angular benzobisoxadisilole, which is 1,3,6,8-tetradihydro-1,1,3,3,6,6,8,8-octamethyl-benzo[1,2-c:3,4-c']bis[1,2,5,] oxadisilole (15), based on modified literature procedures is outlined in Scheme 26.\textsuperscript{[20-22]} 1,2,3,4-tetrakis(dimethylsilyl)benzene (14) was prepared from 1,2,3,4-tetrabromobenzene (13) via Grignard type reactions with chlorodimethylsilane without the use of HMPA. Upon treatment with sodium methoxide and warmed in water, tetra(dimethylsilyl)benzene converted into the corresponding angular benzobisoxadisilole (15) as white powder in 65% yield.

\begin{equation}
\text{Scheme 26. Generation of angular benzobisoxadisilole}
\end{equation}

2.3 Stepwise generation of 1,3-benzdiyne from angular benzobisoxadisilole

1,3-Benzenes (tetradehydrobenzene, 16) is extremely labile owing to the high ring strain that arises from the two triple bonds in a benzene ring. However, there are no reports about the generation of 16 as an intermediate in any solution chemistry. Recently, the angular benzobisoxadisilole 15 was reported to be a synthetic equivalent for the stepwise generation of 1,3-benzenes (16).\textsuperscript{[22]}

Intermediates 17 & 18 were generated from the phenyliodination of the angular
benzobisoxadisilole 15 with excess iodobenzene diacetate \{PhI(OAc)} and trifluoromethanesulfonic acid (TfOH). Without isolating the intermediates, the reaction mixture was treated with \( n\)-Bu4NF and \( i\)-Pr2NH to afford benzyne 19 at -50\(^\circ\)C, which was trapped with furan, cyclopentadiene, and \( N\)-tert-butoxycarbonylpyrrole (\( N-t\)-BOC-pyrrole) to afford the racemic cycloadducts 20a-c. And cycloadducts 21b-c were readily hydrogenated to 21b-c in good yields (Scheme 27). More than that, a trace amount of a less polar by-product 22 was also detected. Compound 22 was found out to have a marocyclic siloxy ring in its structure.

![Scheme 27.](image)

To further demonstrate that 15 could serve as a 1,3-benzdyne (16) equivalent, the cyclopentadiene adduct 21b was reacted with 1.5:3 mixture of PhI(OAc)\(_2\) to form intermediates 23 and 24 mixture. The mixture was treated again to afford benzyne 25,
which was trapped with furan as an inseparable mixture of syn- and anti-adducts 26 and 27 (Scheme 28).\textsuperscript{[22]}

\begin{align*}
(+)-21b & \xrightarrow{\text{PhI(OAc)}_2, \text{TIOH}} \xrightarrow{\text{CH}_2\text{Cl}_2, 0^\circ \text{C to rt}} \begin{cases} 
(+)-23 \\
(+)-24 
\end{cases} \\
\xrightarrow{n-\text{Bu}_4\text{NF/THF}, \text{i-Pr}_2\text{NH}, -50^\circ \text{C}} & \begin{cases} \text{25} \\
\text{26 (syn)} \\
\text{27 (anti)}
\end{cases}
\end{align*}

\textit{Scheme 28.}

Angular benzobisoxadisilole (15) can be viewed as a synthetic equivalent for the stepwise generation of 1,3-benziyne (16).
Chapter 3

Synthesis of Benzotrisoxadisilole

3.1 Preparation of benzotrisoxadisilole (29)

The preparation of benzotrisoxadisilole, which is 1,3,4,6,7,9-hexadihydro-
1,1,3,3,4,4,6,6,7,7,9,9-dodecamethyl-benzo[1,2-c:3,4-c’:5,6-c”]tris[1,2,5,]
oxadisilole (28), based on modified literature procedures is outlined in Scheme 29. hexakis(dimethylsilyl)benzene (28)\(^{[23]}\) was prepared from hexabromobenzene via Grignard type reactions with chlorodimethylsilane without the use of HMPA. Upon treatment with sodium methoxide and warmed in water, hexakis(dimethylsilyl)benzene converted into the corresponding benzotrisoxadisilole (29) as white powder in 32% yield.\(^{[21]}\)

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{SiHMe}_2 & \quad \text{SiHMe}_2
\end{align*}
\]

\[\text{Mg}/\text{Me}_2\text{HSiCl} \quad \text{THF, reflux} \quad \text{Me}_2\text{HSi} \quad \text{Me}_2\text{HSi} \quad \text{SiHMe}_2 \quad \text{SiHMe}_2 \]

\[\text{28 (69%)} \quad \text{SiO} \quad \text{SiO} \quad \text{SiO}
\]

\[\text{29 (32%)} \]

\[\text{Br} \quad \text{Me}_2\text{HSi} \quad \text{Br} \quad \text{Br}
\]

\[\text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Br}
\]

\[\text{Br} \quad \text{Br} \quad \text{Br}
\]

\[\text{NaOMe} / \text{MeOH, rt} \quad \text{H}_2\text{O, 50°C}
\]

\[\text{Scheme 29. Generation of benzotrisoxadisilole with the use of sodium methoxide}
\]

In order to improve the yield of production for benzotrisoxadisilole (29), another method for preparation of benzotrisoxadisilole was investigated from the works by Sekiguchi and Kira.\(^{[24,25]}\) The modified literature procedures are outlined in Scheme 30. Hexakis(dimethylsilyl)benzene (28) prepared by the same way as above, was subjected to
bromination in carbon tetrachloride at 0°C in the presence of pyridine, giving hexakis(bromodimethylsilyl)benzene (30) as an intermediate. With the presence of water, hexakis(bromodimethylsilyl)benzene (30) was further converted into the corresponding benzotrisoxadisilole (29) as white powder in 92% yield.

Scheme 30. Generation of benzotrisoxadisilole from bromination of 28

3.2 Generation of benzyne 32 from benzotrisoxadisilole (29)

The benzyne generation chemistry from benzotrisoxadisilole (29) was explored. Phenyliodination of 29 with excess PhI(OAc)2/TfOH (1.5:3) took place readily at 0°C to rt in CH2Cl2 (Scheme 31). Without isolation of the ring-opened intermediate (31), benzyne 32 could be generated in situ upon treatment with another equivalent of i-Pr₂NH, and be trapped with excess dienes (furan, cyclopentadiene, and N-t-BOC-pyrrole) and ammonium fluoride in THF solution (n-Bu₄NF) at 0°C to rt. The Diels-Alder products 33a-c of benzyne 32 were formed in 42%, 49% and 31% isolated yields respectively. Hydrogenation of 33a-c was also found to take place readily and afford 34a-c in good yields (Scheme 32).
Scheme 31. Generation of benzyne (31) from benzotrisoxadisilole and its corresponding Diels-Alder products 32a-c

3.3 Preparation of naphthobisoxadisilole (34) and its photo-physical properties

Deoxygenation of the Diels-Alder product 32a by titanium (IV) chloride (TiCl₄), LAH and Et₃N in THF was found to afford naphthobisoxadisilole 34 in 84% yields (Scheme 32).

Scheme 32. Generation of naphthobisoxadisilole 34

Intense fluorescence is found in compounds containing aromatic functional groups with low energy $\pi$ to $\pi^*$ transition levels. Naphthobisoxadisilole has a similar structure of naphthalene (35) and contains aromatic functionality. So, the photo-physical property of naphthobisoxadisilole was studied with the use of
spectrofluorometer and compared the result with that of naphthalene. Fluorescence spectra were recorded on Hitachi F-4500 Spectrophotometer.

Figure 1

Figure 1 shows the fluorescence spectra for 4.5 X 10^{-5}M naphthobisoxadisilole 34 in chloroform. The wavelength (λ_{max-ex}) of absorption maximum for excitation spectrum was 293nm; and the wavelength (λ_{max-em}) of fluorescence maximum for emission spectrum was 345nm.
Figure 2 shows the fluorescence spectra for $4.5 \times 10^{-5}$M naphthalene 35 in chloroform. The wavelength ($\lambda_{\text{max-ex}}$) of absorption maximum for excitation spectrum was 320nm; and the wavelength ($\lambda_{\text{max-em}}$) of fluorescence maximum for emission spectrum was 322nm.

Figure 3 shows the overlay of the fluorescence spectra for 34 & 35. It can observe that a significant difference in photo-physical property between 34 & 35.
Based on the structure difference, 34 has two –SiMe₂-O-SiMe₂- rings than 35 in the molecular structure. The $\lambda_{\text{max-ex}}$ of excitation spectrum for 34 showed a blue shift from 320nm to 293nm; also the $\lambda_{\text{max-em}}$ of emission spectrum for 34 showed a red shift from 322nm to 345nm. Extensive kinetic studies reveal $\pi$-bonding between aromatic structures and the d-orbitals of silicon atoms attached directly to the ring. Therefore it may be assumed that any region of considerable electron density (such as a CH₃ group) which is quite close to a silicon atom may overlap sufficiently with the 3d-orbitals of silicon to give rise to appreciable multiple bonding. As a result, R₃Si groups are both $\sigma$-electron donors and $\pi$-electron acceptors, and this affects the ($\pi \rightarrow \pi^*$) transitions of an aromatic compound, which is the photo-physical property.
Chapter 4

Oxadisilole Fused Isobenzofuran

Isobenzofuran (36) has been postulated and detected as a reactive intermediate that readily undergoes Diels-Alder reactions with alkynes or other dienophiles to the corresponding endoxide adducts.\cite{14,27-31} Subsequent deoxygenation or dehydration of these endoxides could lead to benzenoid frameworks.

4.1 Synthesis of bisoxadisilole fused isobenzofuran (40)

The Warrener’s approach was adopted for the synthesis of bisoxadisilole fused isobenzofuran. Isobenzofuran derivatives can be prepared from the cycloadduct of benzyne with furan 32a through Diels-Alder and retro-Diels-Alder (extrusion) reactions with tetrazine. Cycloadduct 32a reacted with 3,6-di(pyridine-2'-yl)-s-tetrazine (37) in chloroform formed adduct 38. Extrude of N₂ followed by retro-Diels-Alder reaction of 39 afforded bisoxadisilole fused isobenzofuran 40 (Scheme 33).

Scheme 33. Generation of bisoxadisilole fused isobenzofuran 40
Bisoxadisilole fused isobenzofuran could be detected as a shiny spot on TLC, but it could not be easily isolated because of its low stability.

This structure was newly synthesized by our group recently. The structure was defined by using $^1$H NMR spectrum. The following showed the assignment of the peaks for the corresponding protons in the Bisoxadisilole fused isobenzofuran.

![1H NMR Assignment](image)

4.2 Reaction of Bisoxadisilole fused isobenzofuran (40)

Once Bisoxadisilole fused isobenzofuran (40) generated, it was subjected to react with dimethyl acetylenedicarboxylate (DMAD, 41) at room temperature to afford cycloadduct 42 in 73% yields. Compound 42 was found to be able for further deoxygenation by TiCl$_4$-LiAlH$_4$-Et$_3$N in THF, and silyl-substituted naphthalene 43 was produced as end product (Scheme 34).
Besides reacting with DMAD, Bisoxadisilole fused isobenzofuran (40) was found to react with another benzyne 45 generated from linear benzobisoxadisilole 44 at room temperature. Cycloadduct 46 was formed as end product. Similarly, cycloadduct 46 could be deoxygenated as 42 by TiCl₄-LiAlH₄-Et₃N in THF to give product 47 (Scheme 35).

Bisoxadisilole fused isobenzofuran (40) also reacted with the solution of 2,3-naphthyne 49 (generated form 48) at room temperature to give cycloadduct 50. Cycloadduct 50 could be deoxygenated as 42 by TiCl₄-LiAlH₄-Et₃N in THF to give product 51 (Scheme 36).
Scheme 36.
Chapter 5

Summary and Possible developments in future

5.3 Summary and conclusion

a) The preparation of the two precursors – angular benzobisoxadisilole (15) and benzotrisoxadisilole (29) were studied and practiced.

b) The generation of benzyne from 29 was trapped as [4+2] cycloaddition adducts 32a-c. Deoxygenated product – naphthobisoxadisilole (34) was also synthesized.

c) The photo-physical property of naphthobisoxadisilole (34) was compared with that of naphthalene (35) by spectrofluorometer.

d) Bisoxadisilole fused isobenzofuran (40) was synthesized from benzotrisoxadisilole (29). It was reacted with alkyne (DMAD) to give cycloadduct 42.
5.4 Possible developments in future

Stepwise Generation of 1,3,5-benztriyne from benzotrisoxadisilole

Further ring opening followed by benzyne generation and trapping reaction as below can be investigated as depicted in scheme 37. The overall transformation will make benzotrisoxadisilole as a synthetic equivalent of 1,3,5-benztriyne 54.

Scheme 37
Synthesis of PAHs in three dimensions

Based on making the synthetic equivalent of 1,3,5-benztriyne 54, it will be possible of polycyclic aromatic hydrocarbons be synthesized in three dimensions from benzotrisoxadisilole via isobenzofuran as depicted in scheme 38.

Scheme 38
Chapter 6

Experimental Details

General information

NMR spectra were recorded on a Varian INOVA-400FT NMR spectrometer (400MHz for $^1$H and 100.6MHz for $^{13}$C) or a JEOL EX270 NMR spectrometer (270MHz for $^1$H and 67.8MHz for $^{13}$C) with CDCl$_3$ as the solvent. Chemical shift were reported as parts per million (ppm) in $\delta$ unit in the scale relative to the resonance of CDCl$_3$ (7.26ppm in the $^1$H, 77.00ppm for the central line of the triplet in the $^{13}$C modes, respectively). Coupling constants ($J$) were reported in Hz. Low resolution mass spectra (LRMS) were obtained on a Finnigan MAT SSQ-710 spectrometer in FAB (positive ion) mode or E.I. mode and reported as $m/z$. High resolution mass spectra (HRMS) were recorded on a Applied Biosystem QSTAR Pulsar/LC/MS/MS, ESI-QTOF instrument. Melting points were uncorrected. Anhydrous magnesium sulphate and anhydrous sodium sulphate were the drying agents throughout, and the silica gel for chromatography was 230-400mesh.

1,2,3,4-Tetrabromobenzene (13)

Hexabromobenzene (5.03g, 9.12mmol), hydrazine hydrate (100ml) and ethanol (100ml) were mixed and heated to reflux for 24h. The cooled reaction mixture was added to water (200ml). Filtered crude product was dissolved in $n$-hexane. The $n$-hexane was washed with
water for three times and dried over anhydrous sodium sulphate. The organic solution was concentrated and purified by column chromatography on silica gel using \( n \)-hexane as eluent. \( 1,2,3,4 \)-tetrabromobenzene (13) (2.01g, 5.11mmol) was obtained in 56% yield as white powder.

Mp. 62-63°C (lit. mp 62-63°C); \(^1\)H NMR (400 MHz) \( \delta \) 7.45 (s, 2H); \(^{13}\)C NMR (101 MHz) \( \delta \) 124.8, 129.1, 132.7.

\[\text{1,2,3,4–Tetrakis(dimethylsilyl)benzene} \ (14)\]

\( 1,2,3,4 \)-Tetrakis(dimethylsilyl)benzene (14)

Chlorodimethylsilane (2.5ml, 22.82mmol) was added to \( 1,2,3,4 \)-tetrabromobenzene (13) (1.12g, 2.84mmol) and magnesium (0.55g, 22.69mmol) in 20ml of THF. The mixture was heated to reflux at 85-90°C for 8h. The presence of the tetrabromobenzene (13) was monitored by TLC. Once the tetrabromobenzene (13) disappeared, the reaction was stopped and cooled to rt. The solvent was then evaporated. The solid mixture left was extracted with Soxhlet extractor by 100ml \( n \)-hexane at 95-110°C. The extract was concentrated and purified by column chromatography on silica gel using \( n \)-hexane as eluent. Compound 15 (0.49g, 1.58mmol) was obtained in 56% yield as colourless oil.

\(^1\)H NMR (400 MHz) \( \delta \) 0.37 (d, \( J = 3.6\)Hz, 12H), 0.48 (d, \( J = 4.0\)Hz, 12H), 4.68-4.71 (m, 2H), 4.81-4.83 (m, 2H), 7.58 (s, 2H); \(^{13}\)C NMR (101 MHz) \( \delta \) -1.9, -0.6, 134.2, 146.3, 152.1.
1,3,6,8-Tetradihydro-1,1,3,3,6,6,8,8-octamethyl-benzo[1,2-c:3,4-c']bis[1,2,5,]

oxadisilole (15)

A solution of sodium methoxide in methanol (0.29g of sodium, 12.66mmol; 15ml of methanol) was added to 1,2,3,4-tetrakis(dimethylsilyl)benzene 14 (0.49g, 1.58mmol). The mixture was stirred under N₂ for 1h at rt. The reaction mixture was then warmed at 45-50 °C for 3h. 1ml of water was added to the mixture. The mixture was warmed for 2-3h. After compound 14 disappeared (checked by TLC), the crude product was filtered and re-dissolved in EtOAc. After being washed with water and dried over anhydrous sodium sulphate, the organic solution was concentrated. The crude product was purified by column chromatography on silica gel using 2% EtOAc in PE (60-80°C) as eluent. Re-crystallization from CH₂Cl₂/n-hexane mixture afforded compound 15 (0.35g, 1.02mmol) in 65% yield.

Mp. 90-92°C (lit. mp 89-91°C); ¹H NMR (400 MHz) δ 0.38 (s, 12H), 0.43 (s, 12H), 7.62 (s, 2H); ¹³C NMR (101 MHz) δ 1.0, 2.2, 131.1, 149.3, 151.9; MS m/z 338 (M⁺); HRMS for C₁₄H₂₆O₂Si₄: [M+H]^⁺ calcd 339.1088, found 339.1104.

Hexakis(dimethylsilyl)benzene (28)

Chlorodimethylsilane (8.4ml, 75.46mmol) was added to hexabromobenzene (4.43g, 8.04mmol) and magnesium (1.79g, 73.43mmol) in 30ml of THF. The mixture was heated to
reflux at 85-90°C for 8h. The presence of the hexabromobenzene was monitored by TLC. Once the hexabromobenzene disappeared, the reaction was stopped and cooled to rt. The solvent was then evaporated. The solid mixture left was extracted with Soxhlet extractor by 100ml n-hexane at 95-110°C. The extract was concentrated and purified by column chromatography on silica gel using n-hexane as eluent. Compound 28 (2.37g, 5.56mmol) was obtained in 69% yield as white powder.

$^1$H NMR (400 MHz) δ 0.47 (d, $J=3.6$Hz, 36H), 4.82(t, $J=3.6$Hz, 6H); $^{13}$C NMR (101 MHz) δ 0.1, 154.1.

1,3,4,6,7,9–Hexadihydro-1,1,3,3,4,4,6,6,7,7,9,9–dodecamethyl–benzo[1,2-c:3,4-c':5,6-c"]tris[1,2,5,] oxadisilole (29)

Scheme (29)

A solution of sodium methoxide in methanol (1.02g of sodium, 44.32mmol; 15ml of methanol) was added to hexakis(dimethylsilyl)benzene 28 (1.89g, 4.43mmol). The mixture was stirred under N$_2$ for 1h at rt. The reaction mixture was then warmed at 45-50 °C for 3h. 1ml of water was added to the mixture. The mixture was warmed for 2-3h. After compound 28 disappeared (checked by TLC), the crude product was filtered and re-dissolved in EtOAc. After being washed with water and dried over anhydrous sodium
sulphate, the organic solution was concentrated. The crude product purified by column chromatography on silica gel using 2% EtOAc in PE (60-80°C) as eluent. Re-crystallization from CH₂Cl₂/n-hexane mixture afforded compound 29 (0.57g, 1.21mmol) in 32% yield.

Scheme (30)

A solution of bromine in tetrachloromethane (0.18ml of bromine, 3.5mmol; 5ml of tetrachloromethane) was added to a solution of hexakis(dimethylsilyl)benzene 28 in pyridine (0.21g, 0.5mmol; 5ml of pyridine) with stirring under N₂ at 0°C. The mixture was stirred for 5h at 0°C. The reaction mixture was added to water and extracted by EtOAc (30ml) for three times. The organic solution was dried over anhydrous sodium sulphate. The solution was concentrated and purified by column chromatography on silica gel using 2% EtOAc in PE (60-80°C) as eluent. Re-crystallization from CH₂Cl₂/n-hexane mixture afforded compound 29 (0.22g, 0.46mmol) in 92% yield.

Mp. 253-254°C (lit. mp 255-256°C); ¹H NMR (400 MHz) δ 0.44 (s, 36H); ¹³C NMR (101 MHz) δ 2.6, 152.3; MS m/z 468 (M⁺).

Adducts 32a-b from benzyne generated from benzotrisoxadisilole (29)

Trifluoromethanesulfonic acid (0.27 mL, 3.0 mmol) was added with a syringe to a stirred solution of phenyliodium diacetate (0.49g, 1.5 mmol in 10 ml of dichloromethane) at 0 °C. The mixture was stirred under N₂ for 1 h at 0 °C and for 2 h at room temperature. The clear
yellow solution was cooled again to 0 °C followed by dropwise addition of a cold (0 °C) solution of the benzobisoxadisilole 29 (0.47g, 1.0 mmol in 5 mL of dichloromethane). The mixture was stirred for 0.5 h at 0 °C and warmed to rt. After the benzobisoxadisilole 29 disappeared (monitored by TLC), diisopropylamine (0.35 mL, 2.5 mmol) and the diene (furan, cyclopentadiene, N-tert-butoxycarbonylpyrrole, 10 mmol) were added followed by a solution of tetrabutylammonium fluoride (2.5 mL, 2.5 mmol, 1.0 M solution in THF). The mixture was concentrated and purified by column chromatography on silica gel with a gradient of 2-5% EtOAc in petroleum ether (60-80 °C) as eluent.

1,3,4,6,7,10-Hexahydro-1,1,3,3,4,4,6,6-octamethyl-7,10-epoxynaphth[1,2-c:3,4-c']bis[1,2,5]oxadisilole (32a)

42% Yield. mp 148-150°C; ¹H NMR (400MHz) δ 0.34 (s, 6H), 0.38 (s, 6H), 0.40 (s, 6H), 0.48 (s, 6H), 5.69 (s, 2H), 7.01 (s, 2H); ¹³C NMR (101 MHz) δ 1.2, 1.7, 2.4, 82.2, 140.0, 143.0, 148.5, 152.3; MS m/z 404 (M⁺); Anal. Calcd for C₁₈H₂₈O₃Si₄: C, 53.40; H, 6.99. Found: C, 53.42; H, 6.87.

1,3,4,6,7,10-Hexahydro-1,1,3,3,4,4,6,6-octamethyl-7,10-methanonaphth[1,2-c:3,4-c']bis[1,2,5]oxadisilole (32b)

49% Yield. mp 141-143°C; ¹H NMR (400MHz) δ 0.38 (s, 12H), 0.41 (s, 6H), 0.46 (s, 6H),
2.33 (m, 1H), 2.41 (m, 1H), 3.89 (s, 2H), 6.80 (s, 2H); $^{13}$C NMR (101 MHz) $\delta$ 1.4, 1.5, 50.3, 70.0, 141.3, 143.0, 147.5, 155.3; MS $m/z$ 402 (M$^+$); Anal. Calcd for C$_{19}$H$_{30}$O$_2$Si$_4$: C, 56.64; H, 7.52. Found: C, 56.59; H, 7.58.

**N-tert-Butoxycarbonyl-1,3,4,6,7,10-hexahydro-1,1,3,3,4,4,6,6-octamethyl-7,10-iminenaphth[1,2-c:3,4-c']bis[1,2,5]oxadisilole (32c)**

31% Yield. mp 121-123$^\circ$C; $^1$H NMR (400MHz) $\delta$ 0.37-0.39 (m, 18H), 0.50 (s, 6H), 1.39 (s, 9H), 5.41-5.49 (m, 2H), 6.93-6.99 (m, 2H); $^{13}$C NMR (101 MHz) $\delta$ 1.6, 28.1, 65.8, 66.6, 80.8, 142.4, 143.5, 148.4, 151.7, 154.7; HRMS for C$_{23}$H$_{37}$NO$_4$Si$_2$: [M+Na]$^+$ calcd 526.1697, found 526.1689.

**1,3,4,6-Tetrahydro-1,1,3,3,4,4,6,6-octamethyl-naphth[1,2-c:3,4-c']bis[1,2,5]oxadisilole (34)**

Titanium (IV) chloride (TiCl$_4$) (3.1ml, 28mmol) was carefully added to a suspension of LAH (0.38g, 10mmol) in 10ml of anhydrous THF, followed by Et$_3$N (5.0ml, 36mmol) at 0$^\circ$C under N$_2$. The mixture was stirred for 30 mins and then was allowed to warm up to rt. A solution of 32a (0.32g, 0.8mmol) in 10ml of anhydrous THF was added. The mixture was refluxed for 5h and then was poured into crushed ice (20g) containing 20ml of 1N CH$_2$Cl$_2$. 
The organic extract was dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 2-5% EtOAc in petroleum ether (60-80°C) as the eluent to afford product 34 in 84% yield.

Mp. 116-118°C; $^1$H NMR (400 MHz) $\delta$ 0.48 (s, 12H), 0.54 (s, 12H), 7.36-7.39 (m, 2H), 7.89-7.91 (m, 2H); $^{13}$C NMR (101 MHz) $\delta$ 2.1, 2.8, 127.2, 130.8, 135.9, 151.0, 151.5; MS $m/z$ 388.1 (M$^+$).

**Cycloadduct 42 via the formation of bisoxadisilole fused isobenzofuran (40)**

3,6-di(pyridine-2'-yl)-s-tetrazine (0.50g, 0.21mmol) was added to a suspension of furan adduct 32a (0.68g, 1.68mmol) in 5ml chloroform. The mixture was stirred under N$_2$ at rt for 10 mins. TLC checking was done for any disappearance of cycloadduct 32a and the formation of shiny spot by isobenzofuran 40. Without isolating the intermediate 40, dimethyl acetylenedicarboxylate (DMAD, 0.2ml, 2.08mmol) was added to the mixture and stirred for 15 mins. TLC checking was done for any disappearance of isobenzofuran 40. The mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 5-10% EtOAc in petroleum ether.
(60-80°C) as the eluent to afford product 42 in 73% yield.

**Bisoxadisilole fused isobenzofuran (40)**

$^1$H NMR (400 MHz) $\delta$ 0.36 (s, 12H), 0.44 (s, 12H), 7.76 (s, 2H).

**Cycloadduct 42**

$^1$H NMR (400 MHz) $\delta$ 0.38 (s, 6H), 0.40 (s, 12H), 0.47 (s, 6H), 3.82 (s, 6H), 5.94 (s, 2H);

$^{13}$C NMR (101 MHz) $\delta$ 1.3, 2.3, 52.4, 84.7, 141.6, 149.3, 150.3, 151.1, 162.7; HRMS for C$_{22}$H$_{32}$O$_7$Si$_4$: [M+Na]$^+$ calcd 543.1122, found 543.1144.

Proton, carbon and mass spectra for reaction products labeled 13, 14, 15, 28, 29, 32a-c, 34, 40, 42. These materials are available in the section of Supporting Information.
References


20. Fink, W.; Helvetica Chimica Acta; 1974, 57, 1010-1015


# THE CHEMISTRY OF BENZYNE

**NEW BENZYNE PRECURSOR – BENZOTRISOXADISILOLE**

Sam, Chun-kit, Hau  
(02010305)

## Supporting Information

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$^{13}$C NMR spectrum of compound 28
$^1$H NMR spectrum of compound 29

S 152
Pulse Sequence: eisp1
Solvent: CDCl3
Ambient temperature
INDEP-400 "Inova400"

Pulse 59.0 degrees
Acq. time 3.756 sec
With 608.5 Hz
IF 1000 Hz
Opt. gain 4000 MHz, 1.5500 MHz
Data processing
FT size 8192
Total time 1 min, 0 sec
$^{13}$C NMR spectrum of compound 29

Pulse Sequence: s2pl
Solvent: CDCl$_3$
Ambient temperature
File: 88-729-10-C

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.185 sec
Width 25141.0 Hz

Observ: C13, 100.578208 MHz
Decoupled: H1, 99.9368576 MHz
Power 41 dB
continuously on

Data processing: 1.0 Hz
1 Hz
Total time 10 hr, 24 min, 6 sec
Mass spectrum of compound 29
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$^{13}$C NMR spectrum of compound 32a
Mass spectrum of compound 32a
$^1$H NMR spectrum of compound 32b
$^{13}$C NMR spectrum of compound 32b
Mass spectrum of compound 32b
$^1$H NMR spectrum of compound **32c**
$^{13}$C NMR spectrum of compound 32c

32c

$X = \text{N-BOC}$
Mass spectrum of compound 32c
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$^{13}$C NMR spectrum of compound 34
Mass spectrum of compound 34
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$^1$H NMR spectrum of compound 42
$^{13}$C NMR spectrum of compound 42
Mass spectrum of compound 42

Sample Name: D151 - 3
Batch Name: N/A
Acq. Date: Tuesday, October 19, 2004
Acq. File: D151.wiff
Project: N/A
Results Path: N/A
Results Name: N/A

Collision Energy: N/A
Scan Method: Start: 80.0, Stop: 870.0, Step: 0.0
Start: 270.0, Stop: 270.0, Step: 0.0
Polarity/Scan Type: Positive
Sample ID: TuneSampleID

Max. 792.0 counts.

543.1144
521.1369