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Aromatization

Hexasilylated Total Carbomer of Benzene**

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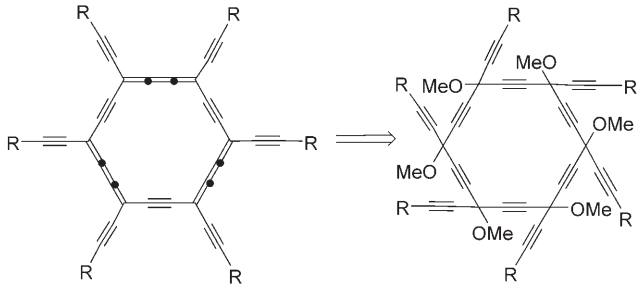
The total carbomer of benzene, **1b** ($C_{18}(C_2H)_6$), was first evoked in 1995 as an illustration of the general definition of carbomers (Scheme 1).[1] At the same time, two reports dealt



Scheme 1. The target total carbobenzene **1b**, its silyl-protected analogue **1a**, and their envisioned precursors **2a**,**b**.

with the synthesis of (partial) ring carbomer of benzene,[2] later named simply "carbobenzene" derivatives.[3] Whereas carbobenzene itself ($C_{18}H_6$) remains unknown,[2b] Ueda and co-workers described the first examples of tri- and hexaaryl derivatives ($C_{18}R_3Ar_3$).[2a,4] Since then, all reported carbobenzene derivatives bore aromatic substituents to enhance their stability by radial electron delocalization; however, the possibility of combining aromatic and non-aromatic substituents was also demonstrated, as well as the possibility of the presence of adjacent nonsubstituted vertices.[5] Encouraged by the preparation of a dialkynyl derivative,[5b] we envisioned the preparation of the hexaalkynyl carbobenzene **1a**, which is a protected version of the total carbomer **1b** and was studied recently at the level of density functional theory (DFT; Scheme 1).[6] The target **1a** is also a skeletal carbomer of hexa(trialkylsilyl)benzenes, such as **1a′**[7] and **1a″**.[8] Our experience in the synthesis of *n*-oxy[*n*]pericyclynes ($n = 5$, 6)[9] led us to tackle the proposed challenge through the "classical" strategy based on the reductive aromatization of the corresponding hexaoxy[6]pericyclynes **2a**,**b** (Scheme 1).

The selected method relies on an [8+10] ring formation that proved to be efficient for the preparation of other [6]pericyclynes.[5a] For the synthesis of the "C_8" key precursor **10a** (Scheme 2), the trispropargylic alcohol **3** was first prepared by a four-step procedure inspired by a method developed by Diederich and co-workers for the synthesis of an expanded cubane.[10]

After selective O methylation of **3**, the magnesium salt of the resulting ether **4** was added to aldehyde **5** to give the tetraynol intermediate **6**. This alcohol was treated directly with MnO_2 to give tetraynone **7** as a mixture with residual triyne **4** (ca. 20%). The mixture was treated with ethynylmagnesium bromide to provide pentayne **8** (compound **4** could be removed easily at this stage). After O methylation of **8**, the selective deprotection of the trimethylsilyl-substituted triple bond in the resulting ether **9** was first attempted by treatment with aqueous 1N NaOH.[10] The procedure was not successful in this case (only the fully deprotected product **10b** was obtained), but treatment with K_2CO_3 (0.1 equiv) in methanol for 10 minutes afforded the monodeprotected bisterminal pentayne **10a** in 88% yield. The "C_8" precursor **10a** was thus obtained in 10 steps and 34% overall yield as a mixture of *threo*/*erythro* diastereomers in an undetermined ratio. As the stereochemical information would be deleted in the final aromatization step, the preparative or analytical resolution of **10a** and its derivatives was not attempted.

The "C_{10}" precursor **13** was prepared in a convergent manner from the "C_8" intermediate **10a**. First, the addition of the dimagnesium salt of **10a** to two equivalents of aldehyde **5** gave heptaynediol **11** as a mixture with the monoadduct **12.** The treatment of this mixture with activated MnO_2 afforded diketone **13** in 70% yield over two steps (Scheme 3). Monoketone **14** was also isolated in 15% yield.

The "C_{18}" ring was formed by the addition of the dimagnesium salt of pentayne **10a** to diketone **13** under dilute conditions (Scheme 4). The hexaalkynyl hexaoxy[6]-pericyclyne **15** was expected to form as a mixture of the 20 theoretically possible stereoisomers corresponding to six chiral and eight achiral diastereomers. Separation by chromatography on two columns afforded four samples of the pericyclyne **15** in 34% yield. Its topographical structure was

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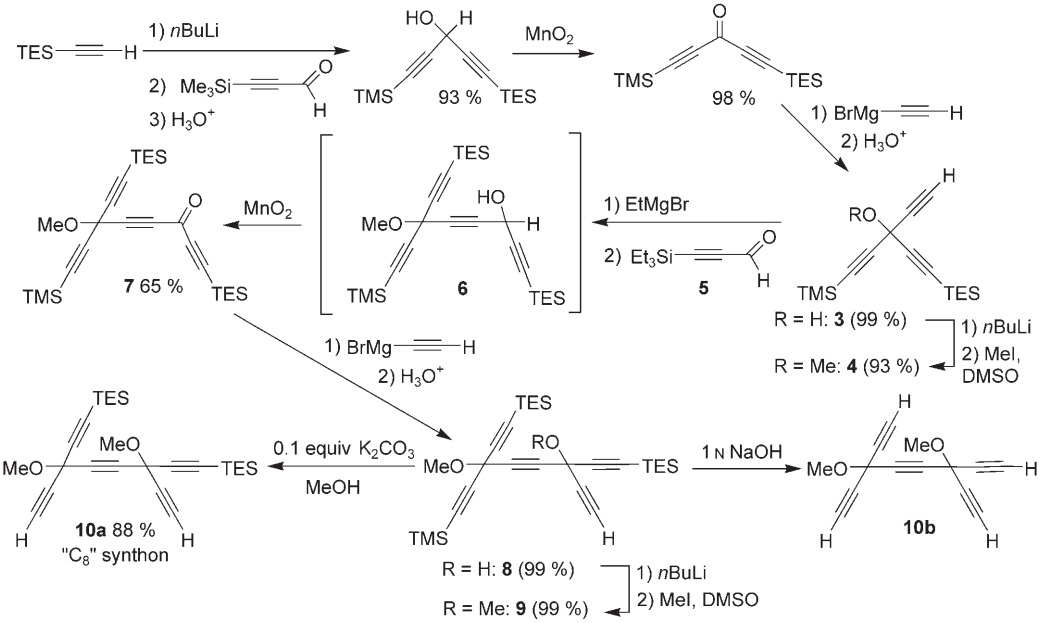
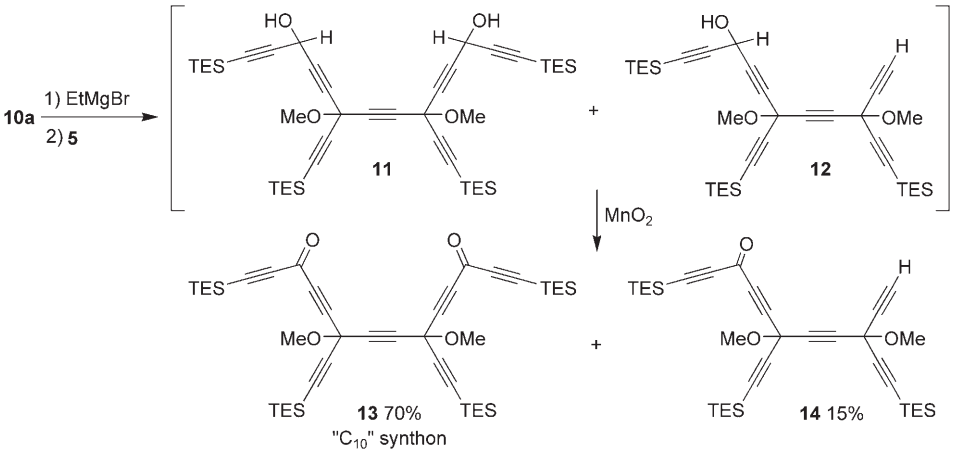
Supporting information for this article, including synthetic procedures and the characterization of all new compounds, as well as details of the crystal-structure determination of **2b**$_1$, is available on the WWW under http://www.angewandte.org or from the author.



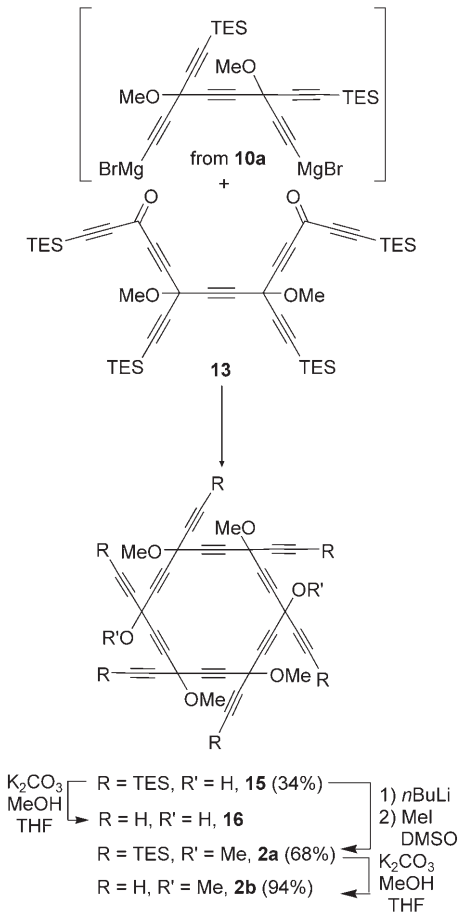
Scheme 2. Synthesis of the "C_8" precursor **10a** (DMSO = dimethyl sulfoxide, TES = $SiEt_3$, TMS = $SiMe_3$).



Scheme 3. Preparation of the "C_{10}" precursor **13**.

confirmed by ^{13}C NMR spectroscopic analysis and HRMS analysis. ^1H NMR spectroscopic analysis of each fraction indicated the presence of several signals close to one another for both the OCH_3 and the OH groups and thus revealed the variation in the environments of these functional groups in the different stereoisomers. Although, the stereoisomeric purity of the samples could not be ascertained, the hexaalkynyl hexaoxy[6]pericyclyne **15** was obtained in 13 steps and 8% overall yield.

The desilylation of **15** (Scheme 4) gave the hexaethynyl[6]pericyclyne **16**, as confirmed by ^1H NMR and IR spectroscopic analysis and MS analysis. However, the [6]pericyclynediol **16** decomposes in the solid state even at low temperature and therefore has to be stored in solution. The totally O-methylated dodecayne **2a** could also be prepared from **15**. This more symmetrical pericyclyne has only nine stereoisomers, two of which are enantiomers. The increase in molecular symmetry results in a simplification of the ^1H and ^{13}C NMR spectra relative to the spectra of **15**. The desilylation of **2a** afforded **2b** as a stable white powder, the structure of which was confirmed by NMR and IR spectroscopic analysis and MS analysis. One of the stereoisomers of **2b**, the all-*trans* compound $\mathbf{2b_1}$, cocrystallized with a dichloromethane molecule, and its structure was confirmed by XRD analysis (Figure 1).[11] For reference, X-ray crystal structures of permethylated [*n*]pericyclynes, including for the case $n = 6$, were obtained by Scott and co-workers,[12a,b] while the X-ray crystal structure of an expanded [6]pericyclyne was obtained by Bunz and co-workers.[12c] Previous conformational analyses at the molecular-mechanics (MM)[12a] and DFT levels[3,13] concluded that [6]pericyclyne can adopt not only the conformations of the parent cyclohexane (chair, boat), but also "twisted-boat" conformations. In the solid state, $\mathbf{2b_1}$ was found to adopt a chair (D_{3d}) conformation. As expected, the ethynyl substituents and the bulkier methoxy substituents lie in axial and equatorial orientations, respectively. The bond angles in the endocyclic C–C≡C and ≡C–C–C≡ units correspond to nonconstrained C(sp) (178.4° on average) and C(sp^3) centers (109.9°), respectively. No tendency to bond-length equalization is evidenced: the endocyclic C(sp)–C(sp) and C(sp)–C(sp^3) distances (1.19 and 1.48 Å, respectively) are "classical". Thus, the possible, but unlikely, homoaromatic character of **2b** has no influence at the structural level.[13,14]



Scheme 4. Preparation by an [8+10] cyclization and reactivity of the hexaalkynyl hexaoxy[6]pericyclyne **15**.

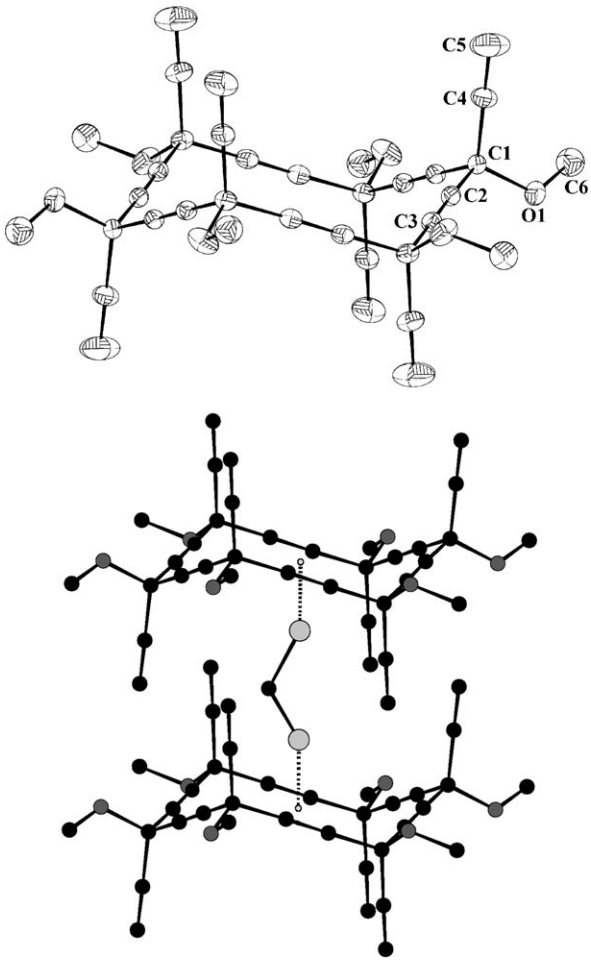
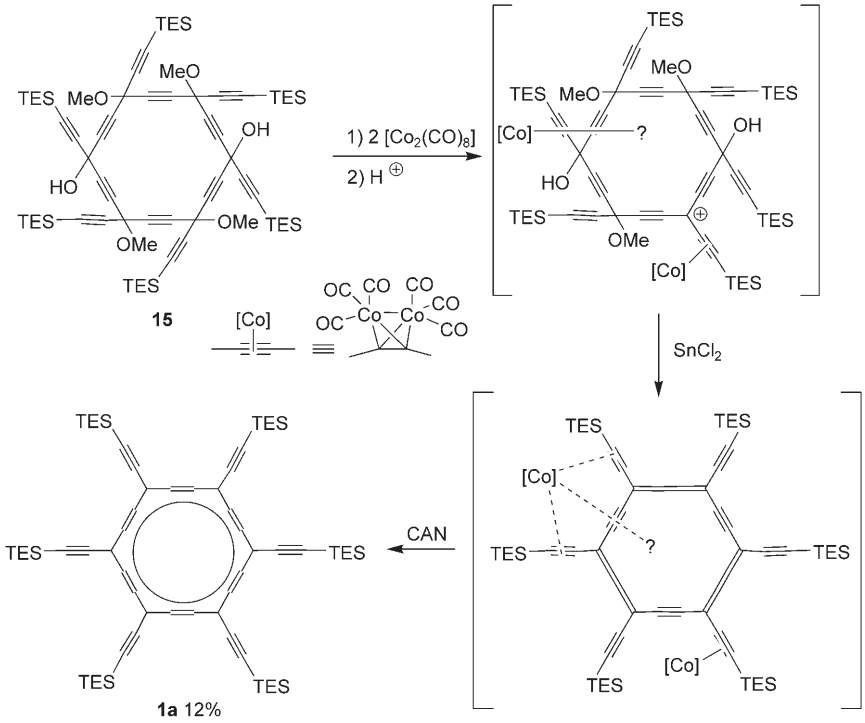


Figure 1. ORTEP view of the all-*trans* stereoisomer $\mathbf{2b_1}$ (top) and its crystallographic packing (below; C black, O dark gray, Cl light gray). Distances [Å]: C1–C2 1.478(5), C1–C3′ 1.479(5), C1–C4 1.471(5), C1–O1 1.425(4), C2–C3 1.188(5), C4–C5 1.162(6), C6–O1 1.386(7), C7–O1 1.366(8), Cl1–C8 1.73(3), Cl1–C8′ 1.60(4); angles [°]: C2-C1-C3′ 109.9(3), C2-C1-C4 109.4(3), C3′-C1-C4 110.4(3), C2-C1-O1 107.2(3), C3′-C1-O1 107.8(3), C4-C1-O1 112.0(3), C1-C2-C3 178.3(4), C1′-C3-C2 178.6(3), C1-C4-C5 179.0(6), C1-O1-C6 114.1(4), C1-O1-C7 130.0(6), Cl1-C8-Cl1′ 121.0(14).

In the crystal, molecules of $\mathbf{2b_1}$ stack as channels of regular, not tilted, hexagonal section. The chlorine atoms of two successive CH_2Cl_2 molecules in the channel are in van der Waals contact at the centroid of the intercalated C_{18} ring ($Cl\cdots Cl \approx 3.66$ Å, $r_{vdW}(Cl) = 1.84$ Å),[15] as previously noted for $CDCl_3$ molecules on both sides of a carbobenzene ring.[5b] The C≡C−H termini of one molecule point towards the C(sp^3) centers of the next rings. Intermolecular dehydromethoxylation along a channel would afford the original expanded nanotubes (carbo-CNTs; CNT = carbon nanotube); however, more reasonably, the oxidative dehydrocoupling of $\mathbf{2b_1}$ in solution could afford axially doubly expanded CNTs. In such putative CNTs, a homogeneous axial and sectional electronic delocalization has been predicted at the DFT level.[6,16]

The reductive aromatization of hexaalkynyl hexaoxy[6]-pericyclynes **15**, **16**, and **2b** was attempted with ethereal $SnCl_2$/HCl, but no reaction occurred even at reflux in diethyl ether. These observations suggest the resistance of the trialkynyl carbinol vertices to the formation of the corresponding trialkynyl carbocations. The successful aromatization of aryl-substituted hexaoxy[6]pericyclynes could indeed be attributed to the benzylic character of the corresponding vertices.[5b,c] In the absence of aryl substituents, complexation of the more accessible external triple bonds by $Co_2(CO)_6$ units could restore the possibility of the formation of carbocationic vertices. Indeed, the propargylic carbocations described by Nicholas are known to exhibit controlled reactivity,[17] and Melikyan et al. showed that trialkynyl carbocations are stabilized by complexation to $Co_2(CO)_6$ units.[18] After several attempts to assist the aromatization of **15** with stoichiometric and substoichiometric amounts of a cobalt complex (competing complexation of the endocyclic triple bonds could not be ruled out), it was found that the use of only two equivalents of $Co_2(CO)_8$, followed by treatment with $SnCl_2$/HCl and direct oxidative decomplexation with ceric ammonium nitrate (CAN), afforded the hexaalkynyl carbobenzene **1a** in 12% yield over three steps (Scheme 5).

The ^{1}H NMR spectrum of **1a** showed that the triethylsilyl groups are particularly deshielded as a result of a remote ring-current effect ($\delta = 1.02$ and 1.35 ppm versus 0.62 and 0.99 ppm for the [6]pericyclyne precursor **15**). Four ^{13}C NMR signals between $\delta = 86$ and 118 ppm were attributed to the six equivalent C(sp^2) carbon atoms and the three



Scheme 5. Cobalt-assisted aromatization of **15** to give **1a**, a protected version of **1b**, the total carbomer of benzene.

distinct C(sp) carbon atoms of **1a**. The UV/Vis spectrum also provided evidence of extended delocalization over the carbobenzene ring with characteristic absorptions at 458, 500, and 517 nm. The structure was confirmed finally by MALDI-TOF mass spectrometry. The attempted desilylation of **1a** with tetrabutylammonium fluoride afforded only insoluble black material. Although the planar $C_{30}H_6$ total carbomer of benzene **1b** is likely to be graphitelike and insoluble, no C≡C-*H* signal was detected in the ^{1}H NMR spectra of soluble extracts ($CDCl_3$, [D_6]DMSO). The corresponding chemical shift was expected to occur near $\delta =$ 4.5 ppm, as calculated at the B3PW91/6-31 + G** level[6] and previously observed for a bis(trimethylsilylethynyl)-carbobenzene.[5b] Attempts to obtain **1b** by cobalt-assisted aromatization of the unprotected [6]pericyclyne **2b** were unsuccessful.

In summary, the first hexaalkynyl [6]pericyclyne and carbobenzene have been synthesized. The stereochemical resolution of the hexaethynyl[6]pericyclyne **2b** and its crystal packing open new horizons for the synthesis of novel expanded CNTs. A TES-protected analogue **1a** of the total carbomer of benzene has been prepared by the metal-assisted reductive aromatization of **15**. Although the TES termini ensured high solubility and allowed full spectroscopic characterization of **1a**, other more crystallogenic derivatives, such as a triisopropylsilyl-protected derivative, are the next reasonable targets. Finally, the controlled desilylation of **1a** could lead to the genuine total carbomer of benzene, **1b**, or to novel carbon allotropes derived from **1b**.

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[11] Crystal data and structure refinement for **2b$_1$**: $C_{36}H_{24}O_6 \cdot CH_2Cl_2$, $M_r = 637.51$ g mol^{-1}, crystal dimensions: $0.25 \times 0.30 \times 0.50$ mm^3, $T = 180$ K, trigonal, space group $R\bar{3}$, $a = 21.479(5)$, $b = 21.479(5)$, $c = 6.560(5)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 180°$, $V = 2621(2)$ Å^3, $Z = 3$, $\rho = 1.21$ g cm^3, $\mu = 0.228$ mm^{-1}, 27634 reflections measured, 1952 unique (R(int) = 0.0200), $\theta_{max} = 32.20°$, index ranges: $-31 \le h \le 31$, $-31 \le k \le 31$, $-9 \le l \le 9$, $\sigma(I)$ limit = 2.00, 70 refined parameters, 747 reflections used ($I > 2\sigma(I)$), $R_1 = 0.0720$, w$R_2 = 0.0834$, $\Delta\rho_{min} = -0.42$ e Å^{-3}, $\Delta\rho_{max} = 0.48$ e Å^{-3}, GOF = 1.127. CCDC-632362 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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