Double Elimination Protocol for Synthesis of 5,6,11,12-Tetradehydrodibenzo[*a*,*e*]cyclooctene

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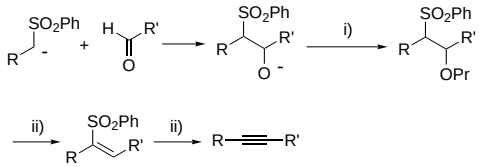
Abstract: A new method for constructing 5,6,11,12-tetradehydrodibenzo[*a*,*e*]-cyclooctene is described on the basis of one-pot double elimination protocol. The target molecule, which is the smallest cyclophane with alternate arylene–ethynylene linkage, is synthesized in 61% yield through oxidative dimerization of *ortho*-(phenylsulfonylmethyl)-benzaldehyde. The initial carbon–carbon bond formation between sp^3 carbons followed by stepwise conversion to sp^2 and finally sp carbons bypasses the difficulty encountered in direct coupling of the sp carbon in the terminal acetylene. The mechanism of this process is discussed. The Wittig–Horner-type coupling is a key reaction employed for the carbon–carbon bond formation. Generation of (*E*)-vinylsulfone moiety in the first coupling between α-sulfonyl anion and aldehyde functions is crucial for the effective second coupling to complete the cyclization. The *syn*-elimination of the (*E*)-vinylsulfone moieties in the cyclized intermediate furnishes the acetylenic bonds.

Keywords: alkynes · C–C coupling · cyclization · elimination · sulfones

Introduction

5,6,11,12-Tetradehydrodibenzo[*a*,*e*]cyclooctene (**1**) is the smallest cyclophane with alternate arylene–ethynylene linkage. As expected, this compound was found to possess highly bent acetylenic bonds (155.7°) on the basis of X-ray analysis.[1] Quite naturally, such acetylenic bonds are highly reactive. They work as a dienophile in Diels–Alder reaction[2] and also undergo cyclopropenation upon treatment with diazoalkanes.[3] In addition, reactions with Pt^0 complex and *ortho*-bis(dimethylsilyl)benzene afforded platinacyclopropenes and benzodisilahexene rings, respectively.[4] The synthesis of **1** was first achieved by Sondheimer et al.[5] Bromination of *sym*-dibenzocyclooctatetraene under irradiation (≈75% yield) followed by dehydrobromination of the resulting tetrabromide with *t*BuOK (48% yield) furnished **1**. Besides a relatively low overall yield (36%) of this process, two procedures for preparing *sym*-dibenzocyclooctatetraene with recourse to Wittig[6] and Knoevenagel[7] condensations were reported to result in less than 20% yield starting from *ortho*-phthalaldehyde. As such, the Sondheimer process is not efficient.[8] More recently, Youngs et al. invoked Sonogashira coupling to dimerize an *ortho*-ethynyl iodobenzene derivative with bulky substituents at *ortho*-positions, yet only a 10% yield of the desired cyclophane was obtained.[9] The low yield was ascribed to the highly reactive acetylenic bonds of the product under the reaction conditions. It is apparent, therefore, that the direct C–C bond formation at terminal acetylenes is not easy to generate cyclic acetylenes on account of the propensity of the sp carbon to adopt the linear disposition. Such drawback is particularly conspicuous with small rings such as **1**.[10]

In earlier works we presented the double elimination methodology for creating an acetylenic bond (Scheme 1).[11, 12] Aldolates resulting from treatment of α-sulfonyl carbanions with aldehyde are transformed to β-substituted sulfones



Scheme 1. i) MOMCl or Ac_2O or TMSCl; ii) base.

which, then, undergo double elimination to give acetylenes.[11] Notably, a sequence of these reactions can be integrated into one pot, thus establishing an extremely convenient process.[12] In this pathway, the initial carbon–carbon bond is formed between sp^3 carbons and the successive eliminations follow giving rise to sp^2 and finally sp carbons in a stepwise manner. Accordingly, it is reasonable to assume that involvement of

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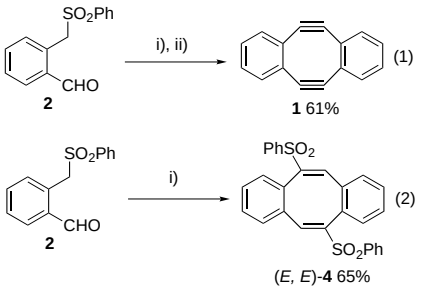
bent sp^3 or sp^2 carbons allows this protocol to construct arylene–ethynylene cyclophane skeletons more easily than the terminal acetylene coupling modes. We report herein that this is indeed the case through efficient synthesis of **1**.

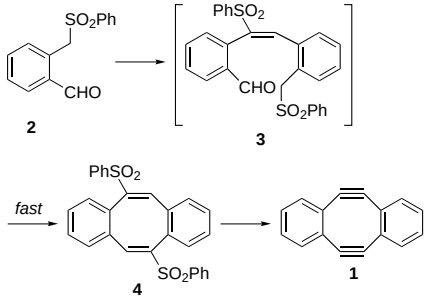
Results and Discussion

Our procedure is quite simple [Scheme 2, Eq. (1)]. A mixture of *ortho*-(phenylsulfonylmethyl)benzaldehyde (**2**) and $(EtO)_2P(O)Cl$ was treated with $LiN(TMS)_2$ (LiHMDS) at $-78\,^\circ C \rightarrow$ r.t. Subsequently LDA was added to the reaction mixture at $-78\,^\circ C$ to afford **1** in 61 % yield.[13] Notably, all operations were performed in one pot. Also, the selection of the above combination of bases turned out to be rather crucial. The starting material **2** could be readily obtained from commercially available tolunitrile (see Experimental Section).



Scheme 2. i) $ClP(O)(OEt)_2$, LiHMDS, THF, $-78\,^\circ C \rightarrow$ RT, 2 h; ii) LDA, $-78\,^\circ C$, 2 h.

A plausible reaction pathway is shown in Scheme 3. Initially, **2** undergoes phosphonation and subsequent intermolecular Wittig–Horner reaction to afford mono(vinylsulfone) intermediate **3** that probably consists of (*E*)- and (*Z*)-isomers.[14] Only the (*E*)-isomer can undergo the second



Scheme 3. Possible reaction pathway.

intramolecular Wittig–Horner reaction to arrive at bis(vinylsulfone) **4** while the (*Z*)-counterpart presumably oligomerizes as a result of intermolecular condensations. In fact, when the reaction was quenched before addition of LDA, **4** was isolated in 65 % yield after column chromatography [Scheme 2, Eq. (2)]. TLC monitoring of the reaction exhibited highly polar material presumably due to the oligomers derived from (*Z*)-**3**. X-ray diffraction study confirmed the (*E*,*E*)-structure for **4** (Figure 1). Apparently, the *E*-geometry of **3** is crucial for

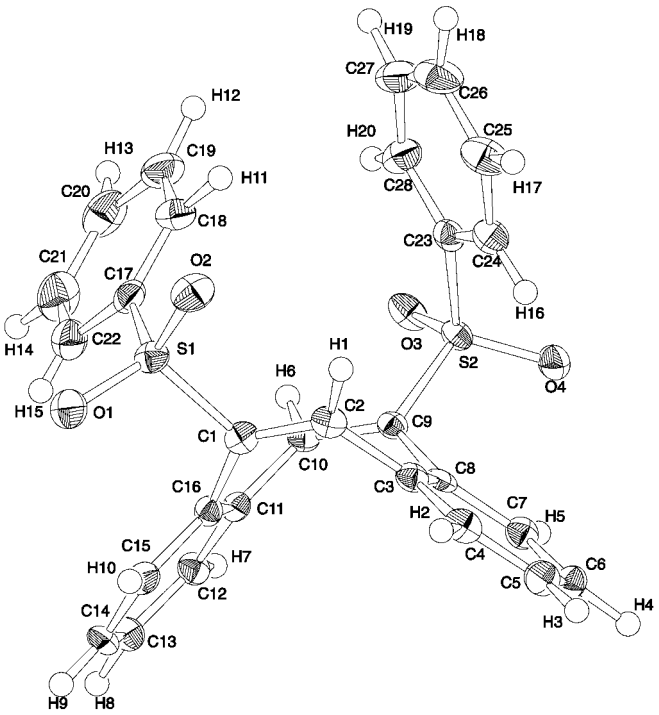
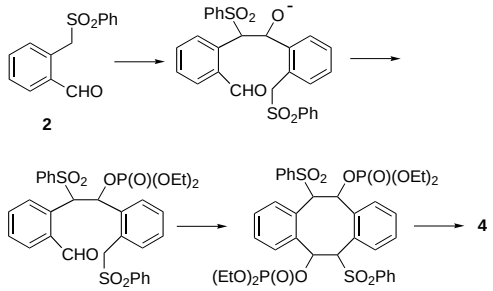


Figure 1. ORTEP drawing of (*E*,*E*)-**4**.

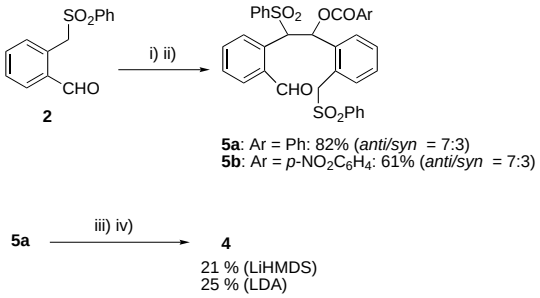
arriving at **4** so that the second formyl and sulfonylmethyl groups could get close to each other whereas no effective interaction between these two groups are feasible with *Z*-geometry. The failure of all attempts to isolate **3** suggests that this intermediate was consumed as soon as it had been generated. Obviously, the rigid *E*-geometry is responsible for the acceleration of the second Wittig–Horner reaction.

Another possibility for the carbon–carbon bond formation is the aldol-type pathway where initially the addition of α-sulfonylcarbanion to aldehyde takes place and, then, the resulting enolate is trapped by the phosphoryl chloride (Scheme 4).



Scheme 4. Possible aldol-reaction-type pathway.

Actually, when benzoyl chloride derivatives were employed in place of $(EtO)_2P(O)Cl$, monoaldolates **5** were obtained in reasonable yields (Scheme 5). However, treatment of **5a** with LiHMDS (3 equiv) or LDA (3 equiv) in the presence of $(EtO)_2P(O)Cl$ furnished **4** only in 21 or 25 % yield. Apparently, the flexible conformation resulting from the sp^3–sp^3 carbon bond in **5** disfavors the intramolecular aldol-type reaction. Thus, the double bond formation by Wittig–Horner

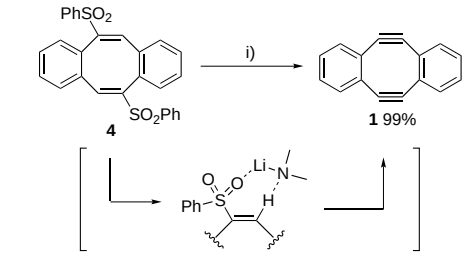


Scheme 5. i) ArCOCl; ii) LiHMDS; iii) $(EtO)_2P(O)Cl$; iv) LiHMDS or LDA.

condensation prior to the second carbon–carbon bond formation is crucial for the effective cyclization.

The generation of (*E*,*E*)-**4** can be accounted for on the basis of the equilibration as shown in Scheme 6. The intermediate **3** is converted to **6** through consecutive lithiation, phosphonation, and a second lithiation. The anion **6** undergoes intramolecular carbon–carbon bond formation to give **7**. The diastereomer **7a** is readily transformed to (*E*,*E*)-**4** through *syn*-elimination via a four-membered intermediate while the analogous elimination is not allowed for **7b** due to the conformational rigidity arising from the pre-existing (*E*)-sulfonyl alkene linkage. Since **7a** and **7b** are involved in an equilibrium via **6** due to the well-recognized fluttering of α-sulfonylbenzyl anion[15] as well as rotation of the aryl–formyl bond, the equilibrium is biased in favor of **7a**.

The elimination of **4**, upon treatment with LDA (4 equiv), proceeded completely to give **1** even at $-78\,^{\circ}C$ (Scheme 7). Such facile reaction has never been encountered since the elimination of vinyl sulfones usually demands higher reaction temperatures (rt $\rightarrow 60\,^{\circ}C$) and the yield is not as high as in the present case.[11] Furthermore, the progress of the reaction itself is counter-intuitive in terms of the increase in the ring strain as the elimination advances. The uphill variation is apparent from the heats of formation calculated by PM3[16] for relevant species (Figure 2).[17] Hence, the high reactivity should be accounted for on the kinetic ground. Probably, the facile *syn*-elimination[18] as depicted in Scheme 7 is responsible. It should be noted that the difference of the heat of formation ($\Delta\Delta H_f$) is larger in the first elimination than in the second one (Figure 2).[19] This is in accord with experimental results that no mono(vinylsulfone) species was detected even by use of lesser amounts of LDA indicating much faster second elimination than the first one.



Scheme 7. i) LDA (4 equiv), THF, $-78\,^{\circ}C$, 2 h.

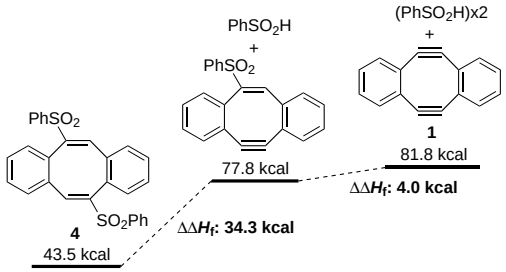
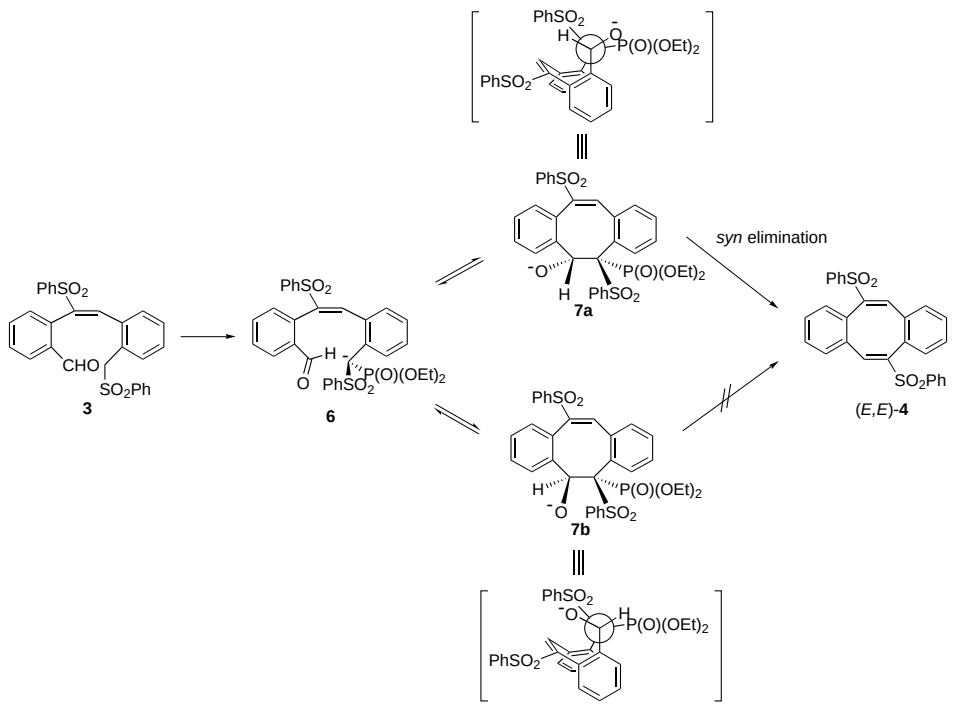


Figure 2. PM3-calculated heat of formation.

In conclusion, the concise, high-yielding process for **1** has been established according to the reaction pathway given in Scheme 3. It is reasonable to assume that the initial Wittig–Horner reaction provides mono(vinylsulfone) intermediate **3** that is composed of (*E*)- and (*Z*)-isomers in about 60:40 to 70:30 ratio.[14] Of these two isomers, only the (*E*)-isomer is capable of undergoing cyclization to furnish **4**. Provided that the second Wittig–Horner reactions proceeded quantitatively, then the isolated yield of **4** (65 %) in Equation (2) is understandable. As it has been dis-



Scheme 6. Equilibrium which leads to (*E*,*E*)-**4**.

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closed that the final elimination took place completely (Scheme 7), the yield in the one-pot process [61% in Scheme 1, Eq. (1)] is recognized as being reminiscent of the yields of the respective steps.

Now, we are in a position to obtain enough amount of **1** and thus synthetic utilization of this compound is undertaken in our laboratories.

Experimental Section

General: All reactions were carried out under an atmosphere of nitrogen with freshly distilled solvents, unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. A THF solution of LiHMDS was purchased from Aldrich and used without titration. A hexane solution of BuLi was purchased from Aldrich and titrated before use by Gilman method.[20] A THF/hexane solution of LDA was prepared from diisopropylamine and a hexane solution of BuLi. Silica gel (Daiso gel IR-60) was used for column chromatography. NMR spectra were recorded at 25 °C on Varian Gemini-300, JEOL Lambda 300 and JEOL Lambda 500 instruments and calibrated with tetramethylsilane (TMS) as an internal reference. Mass spectra were recorded on JEOL MStation JMS-700 Shimadzu/Kratos MALDI 4 and Platform II single quadrupole (Micromass, Altrinchan, UK) mass spectrometers. Elemental analyses were performed by the Perkin–Elmer PE 2400.

X-ray structure determination: X-ray diffraction measurements were made on crystals of the appropriate size, which were mounted onto a glass fiber and transferred to a Rigaku-RAXIS-IV automatic diffractometer using graphite monochromated $Mo_{K\alpha}$ radiation for unit cell determination and data collection. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SAPI91)[21] and subsequently refined by difference Fourier techniques (DIRDIF94).[22] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found by successive Fourier difference maps and refined. All calculations were performed using the teXsan crystallographic software package.[23]

CCDC-173591 (**4**) and -173592 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Preparation of 2

i) α-Bromotolunitrile: A 100 mL flask was charged with *ortho*-tolunitrile (2.37 mL, 20.0 mmol), *N*-bromosuccinimide (3.74 g, 21.0 mmol), AIBN (328 mg, 2.0 mmol), and CCl_4 (30 mL). After the mixture had been stirred at 80 °C for 5 min and at 90 °C for 2 h, the reaction mixture was cooled to room temperature and filtered. The filtrate was washed with aqueous $NaHCO_3$, dried over $MgSO_4$ and filtered. The solvent was evaporated in vacuo, and the residue was purified by chromatography (AcOEt/hexane 1:9) to give α-bromotolunitrile (3.14 g, 80%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.64$ (s, 2H), 7.43 (dt, $J = 1.6$, 7.5 Hz, 1H), 7.55–7.63 (m, 2H), 7.68 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.30$, 112.36, 116.70, 128.90, 130.41, 133.13, 133.22, 141.05.

ii) *ortho*-(Phenylsulfonylmethyl)benzonitrile: A 100 mL flask was charged with α-bromotolunitrile (3.92 g, 20.0 mmol), benzenesulfinic acid sodium salt dihydrate (4.80 g, 24.0 mmol), and DMF (30 mL). After the mixture had been stirred at 80 °C for 2 h, the reaction mixture was cooled to room temperature. After usual work-up with water and ethyl acetate, the solvent was evaporated in vacuo, and the residue was subjected to recrystallization from AcOEt/hexane to give *ortho*-(phenylsulfonylmethyl)benzonitrile (4.58 g, 89%) as colorless needles. M.p. 157–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.57$ (s, 2H), 7.27–7.57 (m, 4H), 7.62–7.73 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 60.46$, 114.33, 116.51, 128.67 (2C), 129.25 (2C), 129.36, 131.60, 132.18, 132.77, 132.93, 134.28, 137.48.

iii) *ortho*-(Phenylsulfonylmethyl)benzaldehyde (2): A 100 mL flask was charged with *ortho*-(phenylsulfonylmethyl)benzonitrile (1.29 g, 5.0 mmol) and CH_2Cl_2 (15 mL), and DIBAL-H (1.0 M in hexane, 11.5 mL, 11.5 mmol) was added at −78 °C. After the mixture had been stirred at this temperature for 2 h, aqueous NH_4Cl was poured into the mixture. After usual work-up with 1N HCl and CH_2Cl_2, the solvent was evaporated in vacuo, and the residue was subjected to filtration through a thin pad (silica gel; CH_2Cl_2) and recrystallization from CH_2Cl_2/hexane gave **2** (1.01 g, 78%) as colorless needles. M.p. 143–145 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.03$ (s, 2H,), 7.43–7.48 (m, 3H), 7.55–7.63 (m, 3H), 7.69–7.75 (m, 3H), 9.83 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 57.67$, 128.68 (2C), 128.82, 128.85 (2C), 129.49, 133.57, 133.83, 133.88, 134.49, 134.61, 138.20, 192.04; MS (EI): calcd for 260.0507, found: 260.0510 $[M]^+$.

Synthesis of 1 from 2: A 100 mL flask was charged with **2** (260 mg, 1.0 mmol), $ClP(O)(OEt)_2$ (0.17 mL, 1.2 mmol) and THF (30 mL), and LiHMDS (1.0 M in THF, 2.0 mL, 2.0 mmol) was added at −78 °C. After the mixture had been stirred at −78 °C for 30 min and, then, at room temperature for 1.5 h, LDA (1.0 M in THF/hexane, 5.0 mL, 5.0 mmol) was added dropwise at −78 °C. The reaction mixture was stirred at this temperature for 2 h, and aqueous NH_4Cl was poured into the mixture. After usual work-up with water and AcOEt, the solvent was evaporated in vacuo, and the residue was purified by chromatography (CH_2Cl_2/hexane 2:3) to give **1** (61 mg, 61%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.71–6.77$ (m, 4H), 6.90–6.96 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 109.28, 126.68, 129.01, 132.83.

Synthesis of 4: A 100 mL flask was charged with **2** (260 mg, 1.0 mmol), $ClP(O)(OEt)_2$ (0.17 mL, 1.2 mmol) and THF (30 mL), and LiHMDS (1.0 M in THF, 2.0 mL, 2.0 mmol) was added at −78 °C. After the mixture had been stirred at −78 °C for 30 min and, then, at room temperature for 1.5 h, the reaction mixture was poured into aqueous NH_4Cl. After usual work-up with water and AcOEt, the solvent was evaporated in vacuo, and the residue was purified by chromatography (AcOEt/hexane 3:7) to give **4** (157 mg, 65%) as a pale yellow foam. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 6.97–6.99 (m, 2H), 7.22–7.30 (m, 4H), 7.36–7.50 (m, 12H), 7.61–7.66 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 126.89$, 128.03, 128.28, 128.81, 128.92, 129.30, 130.70, 133.83, 135.55, 138.79, 138.81, 144.64; elemental analysis calcd (%) for $C_{28}H_{20}O_4S_2$: C 69.40, H 4.16; found: C 69.22, H 4.14. Recrystallization from AcOEt/EtOH/hexane (2:2:1) gave single crystals suitable for X-ray analysis: m.p. 195–199 °C.

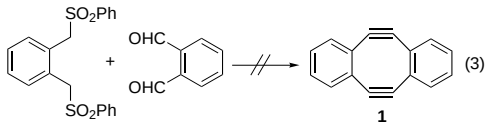
Synthesis of 1 from 4: A 100 mL flask was charged with **4** (485 mg, 1.0 mmol) and THF (30 mL), and LDA (1.0 M in THF/hexane, 4.0 mL, 4.0 mmol) was added dropwise at −78 °C. The reaction mixture was stirred at this temperature for 2 h, and aqueous NH_4Cl was poured into the mixture. After usual work-up with water and AcOEt, the solvent was evaporated in vacuo, and the residue was purified by chromatography (CH_2Cl_2/hexane 2:3) to give **1** (199 mg, 99%) as a yellow solid.

Synthesis of 5a: A 100 mL flask was charged with **2** (260 mg, 1.0 mmol), PhCOCl (0.14 mL, 1.2 mmol) and THF (30 mL), and LiHMDS (1.0 M in THF, 1.0 mL, 1.0 mmol) was added at −78 °C. After the mixture had been stirred at −78 °C for 30 min and, then, at room temperature for 1.5 h, aqueous NH_4Cl was added. After usual work-up with water and AcOEt, the solvent was evaporated in vacuo, and the residue was purified by chromatography (AcOEt/hexane 3:7) to give **5a** (256 mg, 82%, 7:3 *anti*/*syn* mixture) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.59$, 4.88 (major)/5.95, 5.97 (minor) (each AB, $J_{AB} = 14.5$ (major), 15.8 Hz (minor), 2H), 5.04 (major)/6.41 (minor) (d, $J = 3.5$ Hz (major); s (minor), 1H), 6.24 (major)/6.74 (minor) (d, $J = 3.5$ Hz (major); s (minor), 1H), 6.51 (major) (s, 1H), 6.95–7.95 (major)/7.05–8.24 (minor) (m, 23H (major); m, 24H (minor)); ^{13}C NMR (75 MHz, $CDCl_3$) (major): $\delta = 59.06$, 66.93, 70.54, 89.43, 125.71, 126.39, 127.92, 128.27, 128.30, 128.38, 128.56, 128.81, 128.95, 129.14, 129.28, 129.38, 129.88, 130.21, 131.08, 133.51, 133.61, 133.68, 133.82, 137.08, 137.21, 138.67, 165.11; (minor): $\delta = 66.96$, 69.31, 71.63, 90.31, 124.64, 126.30, 127.79, 128.25, 128.46, 128.55, 128.66, 128.74, 129.00, 129.20, 129.36, 129.50, 129.73, 129.88, 130.35, 131.20, 132.42, 133.03, 133.51, 133.62, 133.14, 134.33, 134.50, 136.30, 137.17, 137.39, 139.18, 165.13, 190.38; elemental analysis calcd (%) for $C_{35}H_{28}O_7S_2$: C 67.29, H 4.52; found: C 67.53, H 4.49.

p-Nitrobenzote **5b** was prepared according to the same procedure, and single crystals were obtained by recrystallization from EtOH/AcOEt/CH_3CN (2:1:1). X-ray analysis of this single crystal suggested that the major product of benzoate was the *anti* stereoisomer.

Attempted synthesis of 4 from 5a: A 100 mL flask was charged with **5** (625 mg, 1.0 mmol), $ClP(O)(OEt)_2$ (0.17 mL, 1.2 mmol) and THF (30 mL), and LDA (1.0 M in THF/hexane, 3.0 mL, 3.0 mmol) was added dropwise at −78 °C. The reaction mixture was stirred at room temperature for 1.5 h and

aqueous NH_4Cl was added. After usual work-up with water and AcOEt, the solvent was evaporated in vacuo, and the residue was purified by chromatography (AcOEt/hexane 3:7) to give an inseparable mixture of **4** (25%) and **5a** (69%).



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