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Differential Reactivity Pattern of Hybrid *o*-Quinodimethane Precursors: Strategic Expansion to Annulated Benzocycloalkanes via Rongalite

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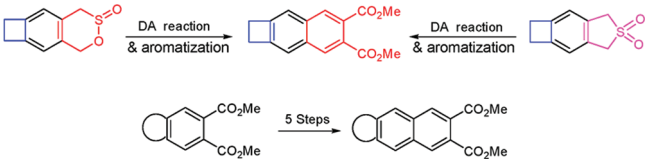
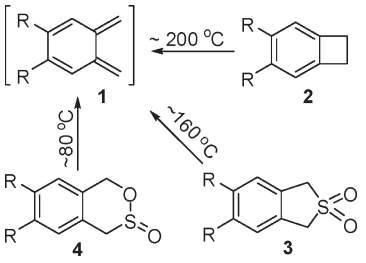


A hybrid benzocyclobutene (BCB) molecular frames embedding sultine or sulfone moiety has been synthesized via utilization of rongalite. The selective Diels−Alder reaction has been realized at sultine or sulfone terminus in the hybrid BCB system to prepare functionalized BCB molecular frames. The methodology has been generalized for assembling various benzocycloalkanes containing a sultine unit and the strategy has been expanded to generate various annulated benzocycloalkanes.

The transient intermediates related to *o*-quinodimethane (*o*-QDM)[1] or *o*-xylylene **1** have a remarkable utility in Diels−Alder (DA) chemistry[2] and they provide a simplified route toward the synthesis of complex polycyclic compounds.[1] Although several methods are available for the generation of *o*-QDM intermediates,[1] benzocyclobutenes[3] **2** and sulfones[4] **3** are employed extensively for this purpose. Surprisingly, sultine **4** and its derivatives[5] which can generate *o*-QDM at relatively lower temperatures are less explored (Scheme 1). However, the nature of substituents present in the aromatic precursor seems to influence the temperature required for the generation of *o*-QDM derivatives.

SCHEME 1. Synthetic Routes to *o*-QDM Intermediate



In connection with our interest related to bezocyclobutene chemistry,[3f] we have identified two hybrid molecules[6] (**5** and **6**, Figure 1) as useful precursors to demonstrate intricate DA chemistry. These unique molecular frames enclose two *o*-QDM precursors of differential reactivity pattern. The interesting aspect of these hybrid molecules is the possibility of generating *o*-QDM intermediates in a stepwise manner. Thus, a selective DA reaction can be envisioned in structural frames **5** and **6** by taking the advantage of the fact that benzosultines and benzosulfones can be opened at different temperatures than the BCBs. Generally, BCB derivatives serve as valuable starting materials for the DA reaction by opening up the cyclobutene unit,[2,3] whereas we have proposed the hybrid BCB molecules, which retains the cyclobutene moiety during the DA reaction. Strategically, preparation of molecular frames such as **5** and **6** might open up new routes to a library of BCB derivatives which can be further manipulated synthetically after the DA reaction to prepare diverse polycycles.

Herein, we report a simple strategy for the synthesis of a novel BCB derivative such as **5** containing sultine moiety in its molecular architecture. In this regard, the ability of rongalite to deliver sultine derivatives has been exploited. Rongalite is the trade name for sodium hydroxymethane sulfinate or sodium formaldehyde sulfoxylate. It is commonly used in the textile industry as a decolorizing agent.

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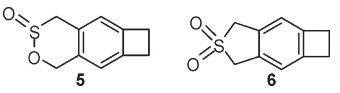
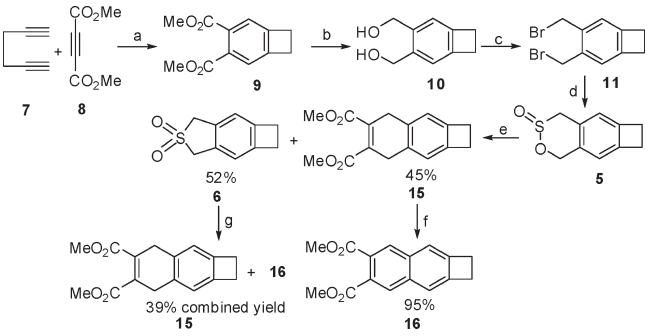


FIGURE 1. Hybrid systems containing two *o*-QDM precursors.

Few reports[7] are available in the literature demonstrating its utility in organic synthesis. In our laboratory, we have asseembled a variety of compounds[8] including sulfones,[8e,8f] unusual amino acid derivatives,[8a−8d,8h] and benzannulated crown ethers[8g] using rongalite.

Transition metal-catalyzed [2 + 2 + 2] cyclotrimerization[9] of three unsaturated substrates leading to annulated benzene derivatives in a chemo- and regioselective manner has been an important topic and has drawn the attention of several research groups. On the basis of our earlier experience with the [2 + 2 + 2] cyclotrimerization reaction,[10] the diyne **7** was subjected to the [2 + 2 + 2] cyclotrimerization reaction with DMAD **8** under high dilution conditions with η^5-cyclopentadienyldicarbonylcobalt, $CpCo(CO)_2$, catalyst.[11] To the refluxing solution of $CpCo(CO)_2$ catalyst in *n*-octane was added the solution of diyne **7** and DMAD **8** in toluene/*n*-octane mixture with the help of a syringe pump to obtain the desired starting material **9** in 35% yield. Next, compound **9** was reduced with lithium aluminum hydride to generate the diol **10** in 67% yield. The treatment of diol **10** with PBr_3/pyridine was found to induce the cleavage of the cyclobutene ring. However, when diol **10** was treated with sodium bromide in the presence of $BF_3 \cdot OEt_2$,[12] the corresponding dibromo derivative **11** was generated in a moderate yield (55%). When the dibromide **11** was reacted with rongalite in the presence of tetrabutylammonium bromide (TBAB) as a phase-transfer catalyst (PTC), to our satisfaction, the BCB derivative **5** was obtained in 75% yield (Scheme 2).

SCHEME 2. Preparation of BCB System Containing Sultine Moiety[a]



[a]Reagents and conditions: (a) $CpCo(CO)_2$, toluene/*n*-octane, high dilution conditions, 125 °C (oil bath), 35%; (b) $LiAlH_4$, THF, 0 °C−rt, 67%; (c) $NaBr\text{-}BF_3 \cdot OEt_2$, acetonitrile, 0 °C−rt, 55%; (d) rongalite, TBAB, DMF, 0 °C−rt, 75%; (e) DMAD, toluene, N_2 bubbling, 100 °C; (f) MnO_2, 1,4-dioxane, 60 °C, 95%; (g) DMAD, DPE, 190−210 °C.

The next task is to realize the DA reaction at the sultine terminal of the hybrid molecule **5** in a selective manner. When the reaction was performed under conventional heating conditions poor yields of the desired product were obtained and in addition the starting sultine was found to convert into the corresponding sulfone (**6**). When the DA reaction was performed under microwave irradiation conditions the yields improved marginally; however, partial aromatization of the DA product was also observed. In this case, the exact reaction time required could not be inferred and therefore eliminating aromatization sequence during the DA reaction seems to be a difficult task. Another nagging problem was that the major portion of the starting material has undergone polymerization. The literature studies suggested that the *o*-QDM is produced from sultine as a result of cheletropic elimination of sulfur dioxide and the formation of sulfone may be the outcome of [4 + 1] cycloaddition of diene with sulfur dioxide generated during the elimination sequence.[13] On the basis of this mechanistic insight, a large amount of the dienophile was employed during the DA reaction. The idea of using the excess amount of dienophile is to increase the probability of diene to react with dienophile instead of reacting with the in situ generated sulfur dioxide. However, performing the reaction with an excess amount of DMAD led to the formation of polymeric material. Next, we anticipated that removing the sulfur dioxide as it is generated from the reaction mixture by continuous bubbling of nitrogen may be a useful alternative. To test this idea, compound **12** was selected as a model compound. Fortunately, under nitrogen bubbling conditions the DA adduct **13** was obtained in good (53%) yield accompanied by the formation of sulfone **14** (47%) (Scheme 3).

Subsequently, a selective DA reaction at the sultine terminus of **5** was performed with DMAD **8** as a dienophile to

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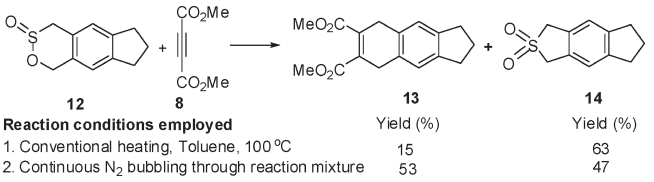
(12) Vankar, Y. D.; Trinadha Rao, C. *Tetrahedron Lett*. **1985**, *26*, 2717.

(13) Rickborn, B. *Org. React*. **1998**, *53*, 223.

SCHEME 3. DA Reaction Performed at Sultine Terminal

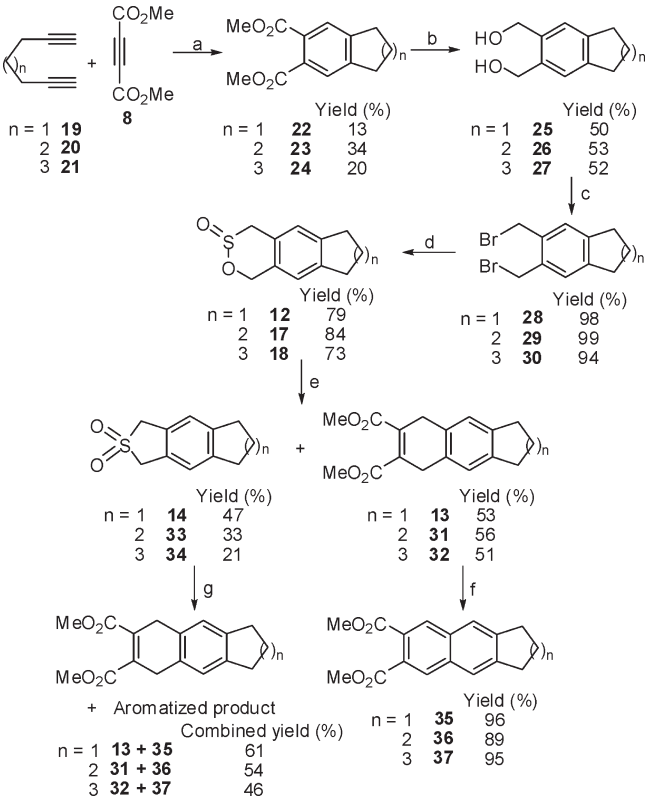


obtain the cycloadduct **15** in 45% yield along with sulfone **6** (52% yields). Oxidation of the cycloadduct **15** with MnO_2 furnished the benzoannulated BCB derivative **16** in 95% yield (Scheme 2). The next task was to carry out the DA reaction selectively at the sulfone part of the hybrid molecule **6**. To this end, when compound **6** was heated with DMAD **8** at 170 °C in *o*-dichlorobenzene (*o*-DCB), the starting material was recovered and no desired product was formed, whereas heating the reaction mixture at 190−210 °C in diphenyl ether (DPE) was found to deliver DA adduct **15** along with some aromatized product **16** in 39% combined yield. The DA reaction was found to occur only at the sulfone terminal, whereas the other *o*-QDM precursor, BCB moiety, remained intact (Scheme 2).

Delighted with the preparation of BCB derivative **5**, a similar methodology has been extended for the preparation of various benzocycloalkanes containing sultine moiety in their molecular framework (**12**, **17**, and **18**). In this regard, $CpCo(CO)_2$-catalyzed cyclotrimerization of α,ω-diynes **19**, **20**, and **21** with DMAD **8** delivered the diesters **22**, **23**, and **24**.[11] The reduction of these diester derivatives with $LiAlH_4$ gave the expected diols **25**, **26**, and **27**, which were converted to the corresponding dibromides **28**, **29**, and **30** with PBr_3. Next, the dibromides **28**, **29**, and **30** were treated with rongalite and TBAB to deliver sultines **12**, **17**, and **18**, respectively (Scheme 4). Later, the DA reaction has been realized at the sultine side of benzocycloalkane derivatives **12**, **17**, and **18** to furnish cycloadducts **13**, **31**, and **32**, respectively. Also, the DA reaction was performed on the sulfone part of all benzocycloalkane derivatives **14**, **33**, and **34** generated during the DA reaction of the corresponding sultines. Aromatization of DA products **13**, **31**, and **32** delivered the annulated benzocycloalkanes **35**, **36**, and **37** which are endowed with diester functionality, useful for further synthetic manipulation (Scheme 4).

In conclusion, we have devised a simple methodology for the synthesis of novel hybrid BCB derivatives containing sultine and sulfone functionalities in their molecular frame. These unique hybrid molecules containing two latent *o*-QDM units of differential reactivity pattern add a new dimension to the DA chemistry. Interestingly, selective DA reaction has been realized at the sultine side of the hybrid system **5** and the sulfone portion of molecule **6**. Generally, the BCB system opens up during the DA reaction, whereas we have prepared functionalized BCBs via DA chemistry and the BCB portion is intact during the DA sequence. To the best of our knowledge, this is the first example demonstrating the synthesis of molecular frames containing two *o*-QDM precursors of different reactivities. In view of some literature reports dealing with the synthetic utility of molecular frames containing two or more same *o*-QDM precursors,[14] these hybrid systems with differential reactivity pattern may find interesting applications in organic synthesis. The methodology has been extended for the synthesis of other benzocycloalkane derivatives containing sultine and sulfone functionalities. The DA reaction performed at the sultine and sulfone terminal furnished cycloadducts which upon aromatization produced benzocycloalkanes equipped with additional functional groups useful for synthetic exploitation.

SCHEME 4. Preparation of Functionalized Benzocycloalkanes[a]



[a] Reagents and conditions: (a) $CpCo(CO)_2$, toluene/*n*-octane, high dilution conditions, 125 °C (oil bath); (b) $LiAlH_4$, THF, 0 °C−rt; (c) PBr_3, benzene, 0 °C−rt; (d) rongalite, TBAB, DMF, 0 °C−rt; (e) DMAD, toluene, N_2 bubbling, 100 °C; (f) MnO_2, 1,4-dioxane, 60 °C; (g) DMAD, DPE, 190−210 °C.

Experimental Section

Preparation of Compound 9.[11] The solution of 1,5-hexadiyne **7** (500 mg, 6.4 mmol) and DMAD **8** (1.15 g, 8.1 mmol) in 1:1.5 *n*-octane−toluene (total volume 25 mL) was added (syringe pump: addition time 6 h) to a refluxing solution of $CpCo(CO)_2$ (200 μL) in *n*-octane (12 mL) maintained under N_2. The reaction mixture was heated at 125 °C (oil bath temperature) for 24 h (including 6 h addition time). Then, the reaction mixture

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was allowed to cool to rt and the solvent was removed under reduced pressure to deliver black, sticky material that was charged on a silica gel (100−200 mesh) column. Elution of the column with 5% EtOAc−petroleum ether gave the desired compound **9** as a colorless solid (500 mg, 35% yield). R_f 0.40 (silica gel, 20% EtOAc−petroleum ether); mp 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (s, 4H), 3.88 (s, 6H), 7.39 (s, 2H).

Preparation of Compound 10. To a stirred solution of compound **9** (100 mg, 0.45 mmol) in dry THF (15 mL) under N_2, at 0 °C, was added an excess amount of $LiAlH_4$ (47 mg, 1.23 mmol) in 4−5 portions with the help of a solid addition funnel. The reaction mixture was stirred at 0 °C for 15 min and then at 15−20 °C for 6 h. At the conclusion of reaction (TLC monitoring), the reaction was quenched by slowly adding ethyl acetate (1 mL) followed by the addition of water (1 mL), maintaining the temperature at 0 °C. The reaction mixture was filtered through a short pad of Celite and the filtrate was concentrated to deliver the crude compound, which was charged on a silica gel (100−200 mesh) column. Elution of the column with 30% EtOAc−petroleum ether gave the desired compound **10** as a colorless crystalline solid (50 mg, 67% yield). R_f 0.27 (silica gel, 50% EtOAc−petroleum ether); mp 123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (s, 6H), 4.67 (s, 4H), 7.04 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.7 (CH_2), 64.8 (CH_2), 124.3 (CH), 138.6(C), 146.5(C); IR (KBr) 3334, 2916, 2385, 1637, 1412, 1136 cm^{-1}; HRMS (Q-Tof) m/z $[M+Na]^+$ calcd for $C_{10}H_{12}O_2Na$ 187.0735, found 187.0734.

Preparation of Compound 11. To a stirred solution of the diol **10** (80 mg, 0.48 mmol) in dry acetonitrile (15 mL) under N_2 were added sodium bromide (350 mg, 3.43 mmol) and $BF_3\cdot OEt_2$ (277 mg, 1.95 mmol), maintaining the temperature at 0 °C. The reaction mixture was stirred at rt for 24 h and then filtered over a short pad of Celite mixed with sodium bicarbonate (500 mg). The filtrate was concentrated to deliver the crude compound, which was charged on a silica gel (100−200 mesh) column. Elution of the column with petroleum ether gave the desired compound **11** as a colorless crystalline solid (78 mg, 55% yield). R_f 0.47 (silica gel, petroleum ether); mp 102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (s, 4H), 4.68 (s, 4H), 7.05 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.7 (CH_2), 31.4 (CH_2), 125.3 (CH), 135.6 (C), 147.6 (C); IR (KBr) 2924, 1628, 1403, 1196, 1107 cm^{-1}; HRMS (Q-Tof) m/z $[M-Br]^+$ calcd for $C_{10}H_{10}Br$ 208.9966, found 208.9966.

Preparation of Compound 5. To a stirred suspension of the dibromide **11** (60 mg, 0.20 mmol) and tetrabutylammonium bromide (35 mg, 0.1 mmol) in DMF (10 mL) was added rongalite (230 mg, 1.5 mmol) at 0 °C and the reaction mixture was stirred at 0 °C for 30 min and then at rt for 6 h. At the conclusion of the reaction (TLC monitoring), the reaction mixture was taken in water (50 mL) and the aqueous phase was extracted with ether (3 × 25 mL). The combined organic layers were washed with water (100 mL) and brine and dried over anhydrous sodium sulfate. The solvent was removed to deliver the crude compound, which was charged on a silica gel (100−200 mesh) column. Elution of the column with 10% EtOAc−petroleum ether gave the desired compound **5** as a colorless solid (30 mg, 75% yield). R_f 0.28 (silica gel, 20% EtOAc−petroleum ether); mp 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.20 (s, 4H), 3.51 (d, J = 14.8 Hz, 1H), 4.45 (d, J = 14.8 Hz, 1H), 5.03 ($^1/_2$ABq, J = 12.8 Hz, 1H), 5.12 ($^1/_2$ABq, J = 12.8 Hz, 1H), 6.95 (s, 1H), 6.99 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.7, 29.7, 59.1, 65.2, 120.7, 123.8, 125.6, 133.8, 146.1, 147.0; IR (KBr) 2925, 1409, 1400, 1305, 1195, 1108 cm^{-1}; HRMS (Q-Tof) m/z $[M+H]^+$ calcd for $C_{10}H_{11}O_2S$ 195.0480, found 195.0483.

Preparation of Compound 15. A solution of sultine **5** (27 mg, 0.13 mmol) and DMAD **8** (40 mg, 0.28 mmol) in toluene (15 mL) was heated at 100 °C (oil bath temperature) for 8 h, maintaining a slow and continuous flow of nitrogen through the reaction mixture. Then the reaction mixture was allowed to cool to rt and the solvent was removed under reduced pressure to deliver the crude material, which was charged on a silica gel (100−200 mesh) column. Elution of the column with 5% EtOAc−petroleum ether gave the desired compound **15** as a colorless crystalline solid (17 mg, 45% yield). R_f 0.54 (silica gel, 20% EtOAc−petroleum ether); mp 128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.15 (s, 4H), 3.69 (s, 4H), 3.82 (s, 6H), 6.85 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.4 (CH_2), 32.2 (CH_2), 52.5 (CH_3), 122.1 (CH), 130.2 (C), 133.7 (C), 144.6 (C), 168.3 (C); IR (KBr) 2932, 1716, 1432, 1276, 1136 cm^{-1}; HRMS (Q-Tof) m/z $[M+H]^+$ calcd for $C_{16}H_{17}O_4$ 273.1127, found 273.1133. Further elution of the column with 10% EtOAc−petroleum ether furnished the sulfone **6** (14 mg) as a colorless solid in 52% yield. R_f 0.28 (silica gel, 20% EtOAc−petroleum ether); mp 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (s, 4H), 4.32 (s, 4H), 6.98 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.6 (CH_2), 57.1 (CH_2), 120.5 (CH), 129.4 (C), 146.7 (C); IR (KBr) 2925, 1737, 1464, 1391, 1205, 1140 cm^{-1}; HRMS (Q-Tof) m/z $[M+H]^+$ calcd for $C_{10}H_{11}O_2S$ 195.0480, found 195.0472.

Preparation of Compound 16. To a stirred solution of compound **15** (19 mg, 0.07 mmol) in dry 1,4-dioxane (15 mL) under N_2 was added MnO_2 (600 mg, large excess). The reaction mixture was heated at 60 °C for 60 h. At the conclusion of reaction (TLC monitoring), the reaction mixture was allowed to cool to rt and filtered over a short pad of Celite. The filtrate was concentrated to deliver the crude compound, which was charged on a silica gel (100−200 mesh) column. Elution of the column with 10% EtOAc−petroleum ether furnished the desired compound **16** as a colorless crystalline solid (18 mg, 95% yield). R_f 0.54 (silica gel, 20% EtOAc−petroleum ether); mp 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37 (s, 4H), 3.94 (s, 6H), 7.51 (s, 2H), 8.18 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.7 (CH_2), 52.7(CH_3), 121.3 (CH), 127.2 (C), 130.3 (CH), 133.9 (C), 148.0 (C), 168.6 (C); IR (KBr) 2947, 1719, 1435, 1273, 1126 cm^{-1}; HRMS (Q-Tof) m/z $[M+H]^+$ calcd for $C_{16}H_{15}O_4$ 271.0970, found 271.0979.

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Supporting Information Available: Experimental procedures for the synthesis of compounds which are not given in the Experimental Section together with their characterization data, and copies of the ^{1}H and ^{13}C NMR spectra for all the new compounds reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.