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Barrelene, a New Convenient Synthesis

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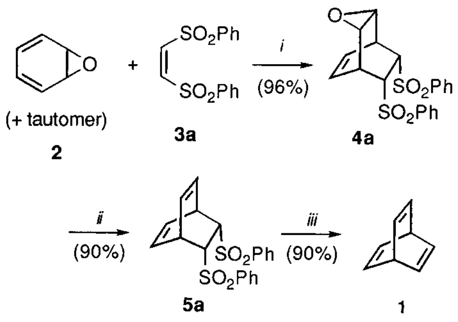
Barrelene (bicyclo[2.2.2]octa-2,5,7-triene, **1**) is the formal Diels−Alder adduct of acetylene to benzene.[1] Since neither acetylene nor benzene is reactive in cycloaddition reactions, the synthesis of **1** requires the definition of both an efficient acetylene equivalent[2] and of a reagent able to temporarily suppress the aromatic character of benzene, in such a way as to allow it to react as a diene.[3] In other words, this equals the definition of a synthon of cyclohexatriene in cycloaddition reactions.[3] In addition to the synthetic challenge, barrelene is interesting by itself, theoretically (it can be considered as a unique Möbius-like molecule),[1] and spectroscopically.[1] Finally, barrelene is the starting material for the preparation of the equally interesting semibullvalene via the photochemical di-π-methane rearrangement.[4]

In addition to the first preparation of **1** reported by Zimmerman and co-workers, which employes a multistep reaction sequence starting from α-pyrone,[1] two other preparations of **1** were later reported by Dauben[5a] and de Meijere,[5b] employing the maleic anhydride adducts to cyclooctatetraene and hydroquinone. All these procedures produce barrelene by photolysis and/or thermolysis so that it becomes contaminated with byproducts that are difficult to eliminate.

Following our interest in the synthesis of unsaturated polycyclic compounds, we report an inexpensive and expeditious preparation of high quality **1**, based on the cycloaddition of 1,2-bis(phenylsulfonyl)alkenes[6] to oxepin (**2**)[7] (Scheme 1).

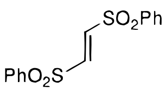
The starting reagents are rapidly available in multigram quantities and close-to-quantitative yields, oxepin (**2**) from 1,4-cyclohexadiene via bromination, epoxidation, and elimination[8] and (*Z*)-1,2-bis(phenylsulfonyl)ethylene (**3a**) from (*Z*)-dichloroethylene and thiophenol followed by oxidation.[6,9] The latter can also be purchased from standard chemical suppliers. The Diels−Alder reaction between **2** and **3** takes 2 days to reach completion. It is wise to add oxepin (**2**) from time to time during this period to avoid unwanted decomposition of the diene and formation of side products. We found it best to add a half equivalent of **2** at the beginning and to add the remaining quantity of the reagent in aliquots each day. A rise in the temperature is detrimental to the yields and purity of the reaction. In addition to polymeric materials, a number of products formed that were not identified. Lewis acids or other methods known to activate the Diels−Alder reaction[10] have been tried, but most of them are not compatible with the nature of the diene, leading to decomposition of oxepin (**2**) and formation of phenol.

Scheme 1[a]

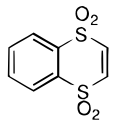


[a] Reaction conditions: (i) benzene, 48 h, 80 °C; (ii) WCl_6/BuLi, THF, 24 h, rt; (iii) Na/Hg, buffered MeOH.

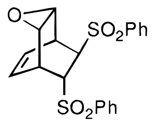
The reaction with other sulfonyl dienophiles has been carried out. With either the (*E*)-isomer **3b** or with the 1,4-benzodithiin 1,1′,4,4′-tetraoxide **3c**[11] an improvement of the reactivity was observed. The reaction of oxepin (**2**) with (*E*)-**3b** takes 20 h in refluxing benzene, while with benzodithiin **3c** 48 h at rt. Both afford adducts **4b** or **4c** quantitatively. Such a trend in reactivity has already been observed in other experiments and is reported in the literature.[6]



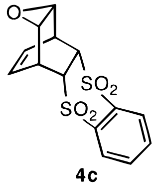
3b



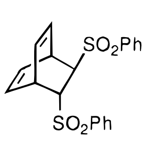
3c



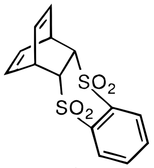
4b



4c



5b



5c

Adducts **4a**−**c** can be deepoxidized readily with WCl_6 and *n*-buthyllithium in very high yields.[12] Other methods of deoxygenation[13] were tested; however, none of these were superior to WCl_6/BuLi. The compatibility of the reducing agent with the sulfonyl group as well as the double bonds is responsible for the observed reactivity. Reductive desulfonylation with sodium amalgam in

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[3] A review article covering this topic is in preparation.

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[6] Cossu, S.; De Lucchi, O.; Fabbri, D.; Licini, G.; Pasquato, L. *Org. Prep. Proc. Int.* **1991**, *23*, 571.

[7] Oxepin appears to have been used only once as a synthetic equivalent of cyclohexatriene: Nakazawa, T.; Kubo, K.; Murata, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 189.

[8] Vogel, E.; Boll, W. A.; Gunther, H. *Tetrahedron Lett.* **1965**, 609. Rastetter, W. H. *J. Am. Chem. Soc.* **1976**, *98*, 6350. Gillard, J. R.; Newlands, M. J.; Bridson, J. N.; Burnell, D. J. *Can. J. Chem.* **1991**, *69*, 1337. The oxidation of 4,5-dibromocyclohexene to the epoxide occurs in 95% yield in refluxing benzene for 1.5 h using a 5% excess of *m*-chloroperbenzoic acid.

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[13] See, for example: Vedejs, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1973**, *95*, 822. Kauffmann, T.; Bisking, M. *Tetrahedron Lett.* **1984**, *25*, 293. Barton, D. H. R.; Fekih, A.; Lusinchi, X. *Tetrahedron Lett.* **1985**, *26*, 6197.

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buffered methanol occurs uneventfully, leading to barrelene in high yields. It is worth mentioning that among the several methods of desulfonylation,[6] the sodium amalgam reduction of bis(phenylsulfonyl) compounds, when leading to hydrocarbons, allows the clean separation of the hydrocarbon from the other products by a simple extraction with pentane. The overall yields of barrelene from **2** and **3a**−**c** is near 75%.

It should be noted that other conceivable procedures for the synthesis of **1**, especially considering *cis*-3,5-cyclohexadiene-1,2-diol and derivatives, have also been tested. These procedures were recently used to prepare benzobarrelenes[14] and when applied to **1** turned out to be less practical and/or more expensive than the one presented here.

Experimental Section

8-*endo*,9-*endo*-Bis(phenylsulfonyl)-3-oxatricyclo[3.2.2.$0^{2,4}$]non-6-ene (4a). A mixture of freshly prepared oxepin (**2**)[8] (0.5 g, 5.3 mmol), (*Z*)-1,2-bis(phenylsulfonyl)ethylene (**3a**) (1.09 g, 3.5 mmol), and benzene (10 mL) was placed in a screw-capped Pyrex test tube purged with argon, sealed, and stirred at 80 °C. After 20 h, an extra amount of **2** (0.5 g, 5.3 mmol) was added. After 48 h, the reaction reached completion (TLC). The solid was separated, washed with cold benzene (20 mL), and dried to afford 1.34 g (96% yield) of colorless crystals: mp 157−8 °C (CH_2Cl_2−Et_2O); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05−7.92 (4 H, m, Ar), 7.71−7.53 (6 H, m, Ar), 6.14−6.03 (2 H, m), 3.86 (2 H, s), 3.60 (2 H, bs), 3.20−3.07 (2 H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.87, 129.06 (2 C), 128.9, 126.49, 66.96, 46.09, 36.90.

8-*endo*,9-*exo*-Bis(phenylsulfonyl)-3-oxatricyclo[3.2.2.$0^{2,4}$]non-6-ene (4b). A mixture of freshly prepared oxepin (**2**)[8] (1.0 g, 10.6 mmol), (*E*)-1,2-bis(phenylsulfonyl)ethylene (**3b**) (1.09 g, 3.5 mmol), and benzene (10 mL) was placed in a screw-capped Pyrex test tube, purged with argon, sealed, and stirred at 80 °C. After 20 h, the reaction reached completion (TLC). The solid was collected by suction, washed with cold benzene (20 mL), and recrystallized from dichloromethane−diethyl ether, affording 1.34 g (96% yield) of colorless crystals: mp 222−4 °C (CH_2Cl_2−Et_2O); ^1H NMR (200 MHz, $CDCl_3$) δ 8.00−7.56 (10 H, series of m, Ar), 5.96−5.83 (2 H, m), 3.98 (1 H, dd, $J = 6.0, 2.6$ Hz), 3.86 (1 H, dd, $J = 6.0, 2.6$ Hz), 3.82 (1 H, t, $J = 3.9$ Hz), 3.69−3.51 (2 H, m), 3.39 (1 H, t, $J = 3.9$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.39 (2 C), 134.14 (2 C), 129.16 (2 C), 128.37 (2 C), 127.36, 125.53, 65.07, 62.60, 45.59, 45.09, 35.66, 35.45.

14-Oxa-3,10-dithiapentacyclo[10.3.2.$0.^{2,11}0.^{4,9}0^{13,15}$]heptadeca-4(9),5,7,16-tetraene 3,3,10,10-Tetraoxide (4c). A dichloromethane (4 mL) solution of **3c** (0.4 g, 1.74 mmol) in a Pyrex test tube, equipped with a rubber septum and magnetic stirring band, was purged with argon and sealed. An ethereal solution (8 mL) of freshly prepared oxepin **(2)**[8] (0.057 g, 0.6 mmol) was added by syringe, and the resulting mixture was stirred at rt. After 12 and 36 h, two additional amounts of **2** (0.057 g, 0.6 mmol each) were added. The solid was collected by suction, washed with cold diethyl ether (2 × 20 mL), and recrystallized from dichloromethane−diethyl ether, affording 0.54 g (96% yield) of colorless crystals: mp 276 °C dec (CH_2Cl_2−Et_2O); ^1H NMR (200 MHz, $CDCl_3$) δ 8.13−8.02, 7.88−7.78 (4 H, series of m, Ar), 5.63−5.52 (2 H, m), 4.12 (2 H, s), 4.02−3.92 (m, 2 H), 3.45−3.88 (2 H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.22, 138.83, 126.28, 125.67, 64.28, 44.77, 36.29.

Reaction of 4a−c with WCl_6/BuLi. Preparation of 5a−c. General Procedure. A solution of *n*-BuLi (0.4 mL of a 2.5 M solution in hexanes) was added to a deep red solution of WCl_6 (0.2 g, 0.5 mmol) and dry THF (10 mL) stirred at −78 °C, under argon, in the dark. After 40 min, the resulting yellow solution was left to reach rt (*ca.* 1 h), treated with **4a** (or **4b** or **4c**) (0.25 mmol), and stirred at rt for an additional 24 h. During this period, the color changed from yellow to green. The crude reaction mixture was concentrated under reduced pressure, diluted with dichloromethane (2 mL), and purified through a short silica gel column, CH_2Cl_2 eluant.

7α,8α-Bis(phenylsulfonyl)bicyclo[2.2.2]octa-2,5-diene (5a): 90% yield; mp 122−4 °C (CH_2Cl_2−Et_2O); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (4 H, d, $J = 8.0$ Hz, Ar), 7.66 (2 H, t, $J = 8.0$ Hz, Ar), 7.57 (4 H, t, $J = 8.0$ Hz, Ar), 6.75−6.71 (2 H, m), 6.38−6.34 (2 H, m), 4.03 (2 H, quint, $J = 4.0$ Hz), 3.74 (2 H, bs); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.89, 136.77, 133.85, 133.58, 128.95, 128.83, 69.08, 39.73.

7α,8*β*-Bis(phenylsulfonyl)bicyclo[2.2.2]octa-2,5-diene (5b): 85% yield; mp 211−3 °C (CH_2Cl_2−Et_2O); ^1H NMR (200 MHz, $CDCl_3$) δ 8.02−7.48 (10 H, m, Ar), 6.62−6.40 (4 H, m), 4.11−3.98 (2 H, t, $J = 5.0$ Hz), 3.82 (2 H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.44, 135.88, 133.86, 133.79, 129.05, 128.38, 66.81, 38.36.

1,4,4a,10a-Tetrahydro-1,4-ethenothianthrene 5,5,10,10-tetraoxide (5c): 90% yield; mp 220 °C dec (CH_2Cl_2−Et_2O); ^1H NMR (400 MHz, $CDCl_3$) δ 8.13−8.03 (2 H, m, Ar), 7.86−7.78 (2 H, m, Ar), 6.65−6.57 (2 H, m), 6.09−6.01 (2 H, m), 4.50−4.40 (2 H, m), 3.91 (2 H, bs); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.74, 136.06, 133.70, 132.85, 126.18, 66.00, 39.27; IR (KBr disk) 3025, 2954, 1329, 1290, 1267, 1150, 1104, 694, 595.

Bicyclo[2.2.2]octa-2,5,7-triene (1). A mixture of **5a** (or **5b** or **5c**) (6 mmol) and KH_2PO_4 (1 g, 8.4 mmol) in dry methanol (20 mL) was purged with argon, and sodium amalgam (*ca.* 6%, an 8/1 equivalent ratio of sodium to substrate) was added in portions with efficient stirring. The reaction mixture was stirred at room temperature and monitored by TLC, eluting with *n*-hexane. After 2 h, the conversion was complete. Water was added, and the reaction mixture was extracted with *n*-pentane (3 × 50 mL). The combined extracts were washed with brine, dried (Na_2SO_4), and carefully concentrated under reduced pressure (water pump, barrelene is highly volatile!) to furnish **1** (0.55 g, 90% yield), which was recognized by comparison of the spectroscopic data with those reported in literature.[1,15]

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Supporting Information Available: Copies of NMR spectra (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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