

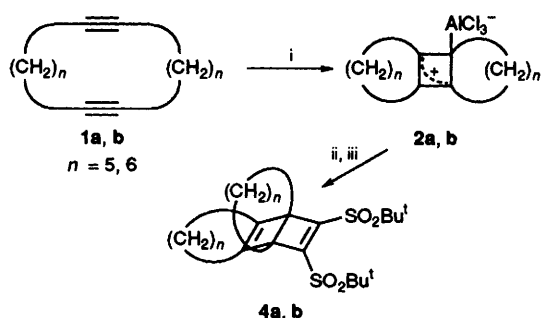
Twofold Bridged Sulfone-substituted Dewar-Benzenes: New Ways to Twofold Bridged Prismanes

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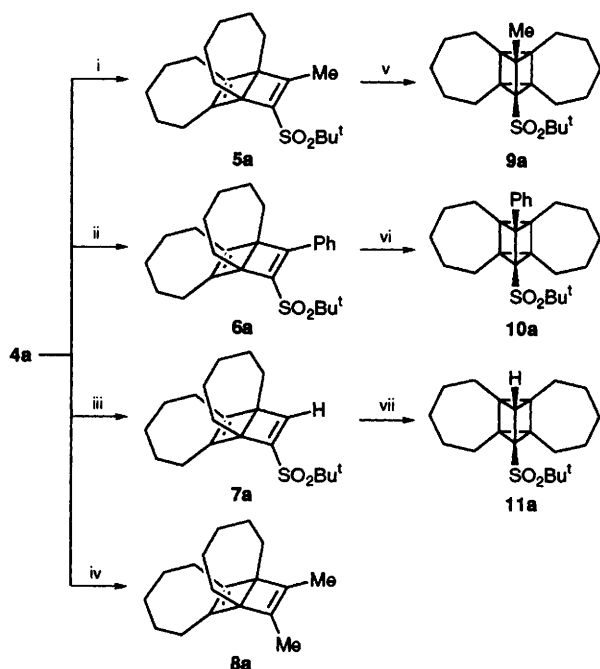
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The di(*tert*-butylsulfonyl) substituents in the 2,3-positions of doubly bridged Dewar benzenes have been replaced by alkyl or aryl substituents; the resulting Dewar benzenes have been transformed to the corresponding prismanes.

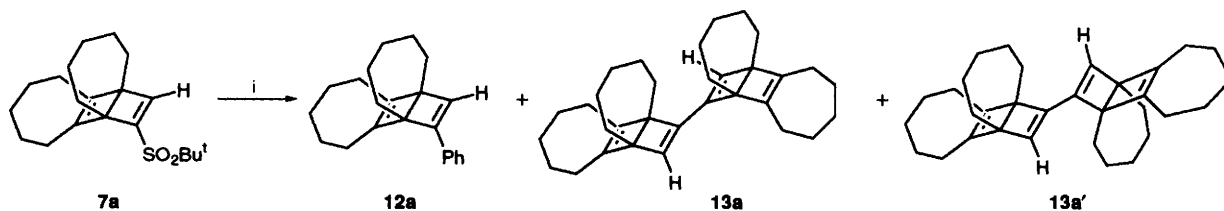
Although tetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane, [3]prismane, promises high reactivity with its strongly bent bonds,¹ its chemistry has hardly been explored. This is due to the fact that prismanes are usually not very stable and are available mostly



Scheme 1 Reagents and conditions: i, AlCl_3 , CH_2Cl_2 , -40°C –room temp.; ii, CH_2Cl_2 , -20°C , $\text{Bu}^t\text{SO}_2\text{-CH=CH-SO}_2\text{Bu}^t$ **3**; iii, $\text{Me}_2\text{SO-CH}_2\text{Cl}_2$, -20°C



Scheme 2 Reagents and conditions: i, MeLi , THF, -78°C , 10 min (50%); ii, PhLi , THF, -78°C , 30 min (95%); iii, SmI_2 , MeOH –THF (1:2), -78°C , 10 min (69%); iv, excess MeMgBr , $\text{Pd}(\text{acac})_2$ (0.1 mol%), THF, reflux, 30 min (80%); v, Et_2O , room temp., $\lambda \geq 280$ nm, 4 h (>95%); vi, Et_2O , room temp., $\lambda \geq 320$ nm, 3 h (>95%); vii, Et_2O , room temp., $\lambda \geq 280$ nm, 4 h (>98%)



Scheme 3 Reagents and conditions: i, excess PhMgBr , $\text{Pd}(\text{acac})_2$ (0.1 mol%), THF, reflux, 30 min

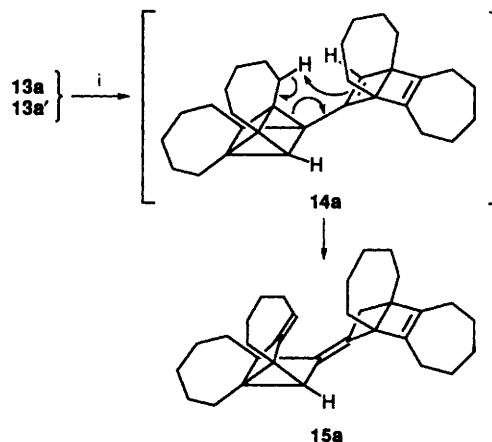
in low yields.^{1,2} Our recent investigations on the properties of cyclic diynes³ have lead to a convenient route to thermally stable doubly bridged [3]prismanes with two ester groups.⁴

To obtain [3]prismanes with other functional groups we have studied the reaction of the complexes **2a** and **b** with di(*tert*-butylsulfonyl)acetylene **3**⁵ (Scheme 1). The reaction of **2a** and **b** with **3** at -20°C in CH_2Cl_2 yields only the 1,4 and 5,6-bridged Dewar-benzene derivatives **4a**[†] and **b**[†] in 50 and 10% yields, respectively. The products have been purified by chromatography on silica gel with pentane–diethyl ether and subsequent recrystallization from hexane. Following the work of Pericas *et al.*^{5,6} we succeeded in exchanging one or both *tert*-butylsulfonyl groups in **4a** with other nucleophiles. One *tert*-butylsulfonyl group has been exchanged for a methyl and phenyl group by treating with MeLi or PhLi , respectively, at -78°C in THF. Reaction of **4a** with SmI_2 – MeOH in THF at -78°C yields **7a**.[†] The replacement of both *tert*-butylsulfonyl groups by two methyl groups can be achieved with MeMgBr and Pd catalysis at 70°C (see Scheme 2).

Irradiation of a highly diluted solution of **5a**, **6a** and **7a**[†] in diethyl ether at room temperature yields the corresponding twofold bridged [3]prismanes **9a**, **10a** and **11a**.[‡] All three species are stable at room temperature (Scheme 2).

By treating **7a** with PhMgBr in THF in the presence of $\text{Pd}(\text{acac})_2$ we obtained (60%) **12a**[†] as the main product (Scheme 3). The side-products **13a**[†] and **a**[†] (20%) proved to be dimers of doubly-bridged Dewar-benzenes. A related dimerization with a β,β -disubstituted vinylsulfone has been observed by Eberle and Julia.⁷

Irradiation of a mixture of **13a** and **a**[†] in diethyl ether at room temperature at $\lambda > 320$ nm gives **15a** (ca. 90% yield) as the only product.[‡] As indicated in Scheme 4 we assume that



Scheme 4 Reagents and conditions: i, Et_2O , room temp., $\lambda \geq 320$ nm, 9 h (>90%)

one Dewar-benzene unit reacts in a [2 + 2] cycloaddition to the prismane **14a**, followed by a thermally allowed 1,5-H-shift to **15a**.§

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Footnotes

† Selected spectroscopic data of Dewar-benzenes: (in CDCl₃ unless stated otherwise). **4a**: ¹³C NMR (75 MHz) δ: 159.8, 148.4, 64.9, 60.4, 32.8, 29.2, 28.2, 25.8, 23.9. **4b**: ¹³C NMR (50 MHz) δ: 160.6, 147.6, 65.1, 61.0, 27.8, 26.5, 25.4, 24.9, 24.5, 24.1. **5a**: ¹³C NMR (75 MHz) δ: 173.5, 149.4, 147.5, 139.9, 63.5, 61.9, 57.8, 33.2, 29.3, 29.1, 28.8, 28.7, 27.2, 26.1, 25.6, 23.4, 23.3. **6a**: ¹³C NMR (75 MHz) δ: 166.9, 149.5, 146.9, 139.3, 63.6, 61.0, 60.5, 33.1, 29.3, 29.2, 29.1, 28.8, 28.2, 26.3, 26.1, 23.6. **7a**: ¹³C NMR (in C₆D₆), 50 MHz) δ: 156.0, 151.7, 148.6, 148.1, 66.1, 61.0, 57.4, 33.5, 29.5, 29.4, 29.1, 29.0, 28.8, 28.6, 26.6, 26.5, 23.4. **8a**: ¹³C NMR (50 MHz) δ: 148.9, 143.5, 60.5, 33.8, 29.7, 29.0, 28.7, 28.1, 26.6, 11.4. **12a**: ¹³C NMR (50 MHz) δ: 155.0, 149.5, 147.6, 136.0, 135.3, 128.4, 125.4, 127.1, 61.5, 59.3, 33.7, 29.7, 29.65, 29.59, 29.0, 28.92, 28.86, 28.80, 26.8, 26.7. **13a** + **13a'**: ¹³C NMR (75 MHz) δ: 150.2, 150.0, 149.1, 149.1, 148.23, 148.15, 136.2, 135.9, 62.6, 62.5, 60.6, 60.6, 33.7, 29.8, 29.6, 29.1, 29.0, 28.94, 28.87, 28.5, 27.0, 26.9, 26.8, 26.6.

‡ The structure of **15a** has been confirmed by X-ray analysis.

§ Selected spectroscopic data of prismanes: (in C₆D₆). **9a**: ¹H NMR (200 MHz) δ: 1.29 (s, 9 H), 1.16 (s, 3 H), 0.92–2.18 (m, 20 H). ¹³C NMR (50 MHz) δ: 57.5, 55.8, 53.4, 44.6, 42.4, 32.6, 31.7, 31.4, 26.3, 24.2, 23.9, 8.8. **10a**: ¹H NMR (200 MHz) δ: 7.55 (m, 2 H), 6.95–7.1 (m, 3 H), 1.14 (s, 9 H), 0.85–2.20 (m, 20 H). ¹³C NMR (50 MHz) δ: 135.3, 129.6, 128.5, 127.0, 58.3, 55.1, 50.2, 48.4, 32.6, 31.4, 31.3, 26.1, 25.8, 24.0. **11a**: ¹H NMR (200 MHz) δ: 2.42 (s, 1 H), 1.30 (s, 9 H), 0.8–2.1 (m, 20 H). ¹³C NMR (50 MHz) δ: 59.2, 56.7, 43.7, 42.1, 37.1, 32.7, 31.8, 31.4, 27.1, 25.9, 23.8. **15a**: ¹H NMR (200 MHz) δ: 4.93 (t, 1 H, ³J 3.6 Hz), 2.41 (s, 2 H), 2.16 (s, 1 H), 1.0–2.36 (m, 38 H). ¹³C NMR (50 MHz) δ: 148.2, 146.14, 146.11, 138.0, 117.4, 102.5, 64.6, 62.5, 55.2, 53.1, 42.7, 37.4, 33.8, 33.5, 33.4, 33.0, 31.5, 31.1, 31.1, 30.0, 30.0, 29.6, 29.43, 29.36, 28.3, 28.1, 27.9, 27.6, 27.5, 27.4, 27.3.

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