Unexpected Formation of Dienes in the Diels−Alder Reaction of Exocyclic 1-Bromobutadienes of Polycyclic Hydrocarbons

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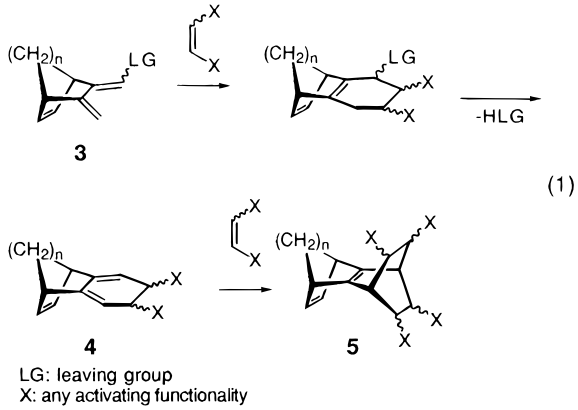
Received August 3, 1995⊗

Polycyclic dienes having an exocyclic 1-bromobutadiene moiety react with dienophiles and fullerene-C_{60} to afford exclusively dienes *via* a cycloaddition−elimination mechanism. Neither the primary adducts nor the double addition products derived from a second cycloaddition of the dienophile to the diene could be detected. In one case only, *i.e.* with 4-phenyl-1,2,4-triazoline-3,5-dione, was the double addition product formed. Contrary to expectations, X-ray diffractometric analysis shows that this adduct is formed following a contrasteric approach.

In recent times we have been interested in the synthesis of olefins contained in polycyclic systems, as exemplified by *anti*-sesquinorbornene **1**.[1,2] Beside their peculiar chemical behavior, these endocyclic olefins possess a geometry that allows only very limited trajectories of approach, thus providing a tool for understanding the mechanism of olefin addition reactions.[3] We are also interested in the synthesis of the hitherto unknown compound **2** as the smallest hydrocarbon $C_{14}H_{12}$ possessing five nonconjugated double bonds.

1 **2**

These aims prompted us to study the reaction illustrated in eq 1 in the hope to develop a short and simple synthetic method that could give access to a large number of variably functionalized polycycles possessing the requisite internal unsaturation.

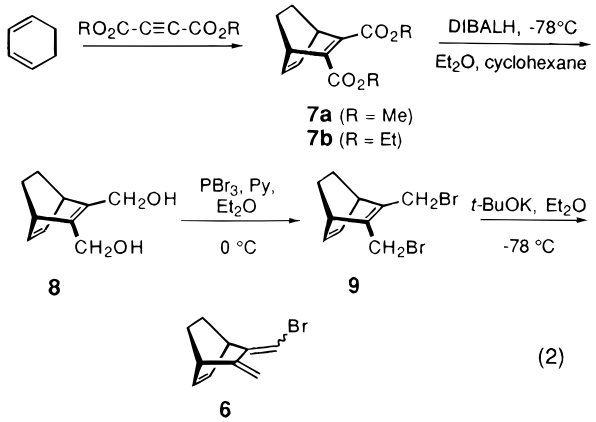


(1)

The reaction sequence considers an exocyclic diene possessing a leaving group (LG) capable, after a first cycloaddition with a proper dienophile, to generate a second diene **4** by eliminating, possibly spontaneously, the leaving group. A second mole of dienophile should complete the reaction sequence in a tandem-type process affording the final polycycle **5**. With proper modifications and with the right choice of reagents, the same sequence should allow the synthesis of **2** and of a large variety of other polycyclic molecules. Although there are a few examples in the literature of such tandem reactions,[4,5] as it will be shown in the discussion, the reaction of polycyclic dienes of type **3** with a number of dienophiles stops at the stage of the diene **4** and only in a single case, *i.e.* with the use of the very reactive dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) it could be possible from **4** to obtain a double adduct of type **5**.

Results and Discussion

The molecule that was considered for carrying out this study was bromo diene **6**, that is rapidly available by the sequence of reactions shown in eq 2.



(2)

The Diels−Alder reaction of dimethyl or diethyl acetylenedicarboxylate occurs in high yields[6] with the precau-

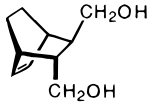
† Author to whom inquiries concerning the X-ray structure analysis should be directed.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) De Lucchi, O.; Licini, G.; Pasquato, L. *J. Chem. Soc., Chem. Commun.* **1985**, 418. Paquette, L. A.; Künzer, H.; Green, K. E.; De Lucchi, O.; Licini, G.; Pasquato, L.; Valle, G. *J. Am. Chem. Soc.* **1986**, *108*, 3453.3.

0022-3263/96/1961-0153$12.00/0

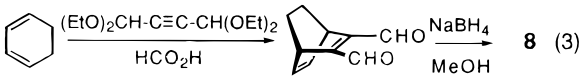
tion of not heating the reaction mixture over 80 °C to avoid retro-Diels−Alder splitting of ethylene from **7a,b** to dimethyl- or diethylphthalate. The subsequent reduction of the carboxylic functions without reduction of the double bonds represents the crucial step of the synthesis. Indeed, while there are a number of cases in which such a transformation has been accomplished with apparent ease, these methods are applied to structurally different molecules. For example, the method with $LiAlH_4$ which has been described successfully with a thiophene derivative[7] or $LiAlH_4/AlCl_3$ that has been used with a cyclooctatetraene derivative[8] proved not sufficiently selective affording at best a 5:1 mixture of **8** and its overreduced product **10**. Also other procedures involving both **7a** and **7b** and $TiCl_4$,[9] $NaBH_4/Me_3SiCl$,[10] or $LiAlH_4$/ EtOH,[11] or pyrazole complexes of nickel[12] proved unsatisfactory, giving variable ratios of **8** and overreduced product **10**. The latter was characterized as its ditosylate.



10

The method that gives the more consistent results for the transformation of **7** into **8** utilizes diisobutylaluminum hydride (DIBALH, 1.0 M in cyclohexane) and the methyl derivative **7a**, and it is carried out at −78 °C in anhydrous ethyl ether.[13] Under such reaction conditions, diol **8** was obtained reasonably pure in several runs with no detectable amount of **10** and thus directly used for the following transformation.

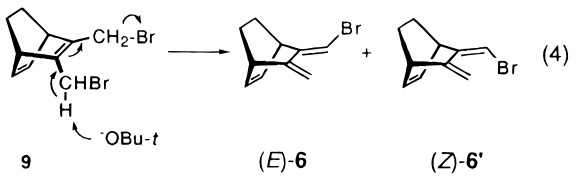
It should be noted that diol **8** can also be obtained via the alternative route of eq 3 that engages the use of acetylenedicarbaldehyde generated *in situ* from its diacetal.[14]



11

In this case, the higher reactivity toward reduction of the dialdehyde **11** with respect to the dicarboxylic functions of **7a,b** allows for the use of milder reducing agents such as $NaBH_4$ and leads to high yields of the desired **8**. Despite the high cost of the reagents of eq 3 as compared with the previous route of eq 2, the large number of adducts available from acetylenedicarbaldehyde makes this method an alternative entry to the compounds under consideration.

The following step of eq 2 engages the transformation of the allylic alcohol into the dibromide **9**. The reaction is carried out with phosphorus tribromide in diethyl ether at 0 °C in 70% yield. The product **9** is sufficiently pure for the vinylogous dehydroalogenation shown in eq 4.

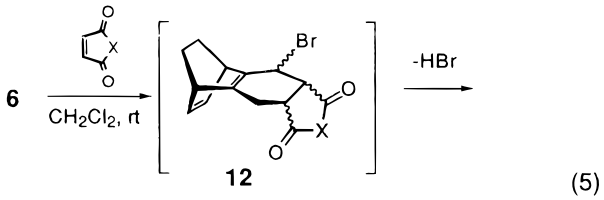


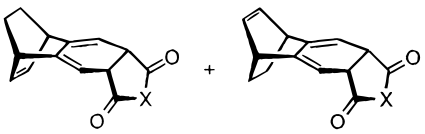
9 (*E*)-**6** (*Z*)-**6'**

The reaction carried out in diethyl ether with potassium *tert*-butoxide gives almost exclusively the unsaturated bromide (*E*)-**6** while the cis isomer (*Z*)-**6′** forms in traces. The assignment of the stereochemistry of **6** *vs* **6′** is based, in addition to steric considerations, on NOE experiments. Especially diagnostic is a quite large NOE effect between the vinylic proton geminal to the bromine atom and the endo proton of the juxtaposed double bond.

Diene **6** is stable if kept at −20 °C but gradually decomposes at room temperature. In our case, we stored the dibromo derivative **9** and prepared diene **6** just before use.

Diene **6** was reacted with a number of dienophiles in the aim of determining its reactivity and chemical behavior. The reaction with maleic anhydride gives two isomeric products barely distinguishable by TLC to which structures **13** and **13′** were assigned (eq 5).





13 (X = O) **13'** (X = O)
14 (X = N-Ph) **14'** (X = N-Ph)

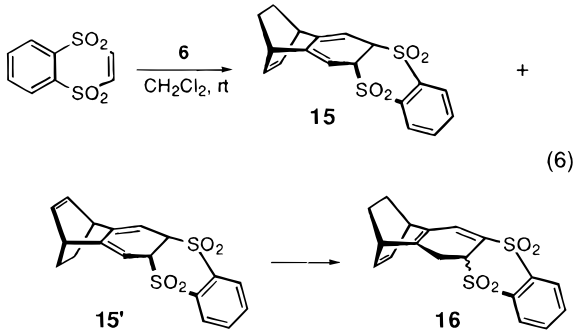
No NMR evidences attributable to the primary adduct **12** could be observed, even running the reaction in a NMR tube while monitoring continuously.

The reaction carried out with *N*-phenylmaleimide followed an identical course. However, while the adducts **13** and **13′** of the reaction with maleic anhydride were formed in a 1:1 ratio, in the case of *N*-phenylmaleimide, **14** and **14′** were formed in a 4:1 ratio. The assignment of the stereochemistry of these adducts by NMR is complicated by the large distance of the diagnostic protons. Indeed, no NOE interactions could be observed between the protons of the ethane bridge and the ones α to the anhydride functions. Several attempts at chromatographic separation of the two diastereoisomers **13**/**13′** and **14**/**14′** failed, both because of the close R_f values and because of the poor stability of the adducts on chromatographic adsorbents. Eventually, the adducts

(2) De Lucchi, O.; Cossu, S. *J. Chem. Soc., Chem. Commun.* **1992**, 1089.
(3) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553.
(4) Elix, J. A.; Sargent, M. V.; Sondheimer, F. *J. Am. Chem. Soc.* **1970**, *92*, 962.
(5) Parakka, J. P.; Sadanandan, E. V.; Cava, M. P. *J. Org. Chem.* **1994**, *59*, 4308.
(6) Diels, O.; Alder, K. *Ann.* **1931**, *486*, 236.
(7) Talma, A. G.; Goorhuis, J. G. M.; Kellog, R. M. *J. Org. Chem.* **1980**, *45*, 2544.
(8) Le Goff, E.; LaCount, R. B. *Tetrahedron. Lett.* **1965**, *32*, 2787.
(9) Akgun, E.; Mahmood, K.; Mathis, C. A. *J. Chem. Soc., Chem. Comunn.* **1994**, 761.
(10) Giannis, A.; Sandhoff, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 218.
(11) Davidson, R. S.; Gunther, W. H. H.; Waddington-Feather, S. M.; Lytghoe, B. *J. Chem. Soc.* **1964**, 4907.
(12) Paolucci, G.; Cacchi, S.; Cagliotti, L. *J. Chem. Soc.* **1979**, 1129.
(13) McKillop, A.; Taylor, R. J. K.; Watson, R. J.; Lewis, N. *Synthesis* **1994**, 31. Gorgues, A.; Le Coq, A. *J. Chem. Soc., Chem. Commun.* **1979**, 767.
(14) Wenkert, E.; Broka, A. *Finn. Chem. Lett.* **1984,** 126. Nakayama, J.; Nakamura, Y.; Hoshino, M. *Heterocycles* **1985**, *23*, 1119.

derived from phenylmaleimide could be separated on deactivated (MeOH) silica gel, though with substantial loss of material (see Experimental Section).

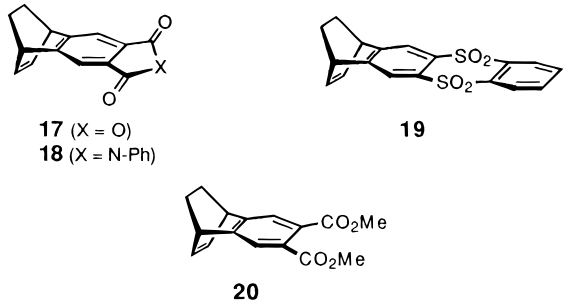
The cycloaddition of **6** with 1,4-benzodithiin-*S,S*-tetraoxide[14] leads to a product composition analogous to that of the former cases in a 1:1 ratio (eq 6). In addition, small amounts of a third component (as a mixture of two diastereoisomers) was observed. As with the former adducts, the chromatographic separation of the two isomeric adducts proved impossible. Column chromatography led to isolation of almost exclusively the third component that was clearly formed in the column at the expenses of **15** and **15′**. After isolation, structure **16** could be assigned on the basis of spectroscopic data. It is present as a 2.5:1 mixture of diastereoisomers not distinguishable by TLC but clearly evident in the ^{1}H NMR spectrum.



(6)

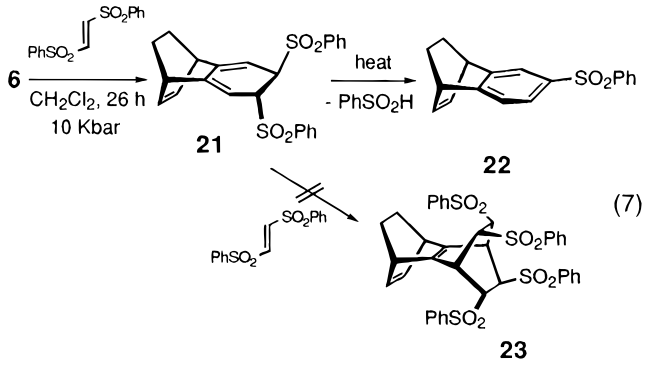
The structural assignment of **16** is based on the presence of a well resolved AB system that couples with the proton α to the sulfonyl group. A sharp singlet accounting for the vinylic proton is also present in the olefinic region.

It should also be noted that during manipulation of the dienic adducts **13**/**13′**, **14**/**14′,** and **15**/**15′**, small quantities of the aromatic compounds **17**−**19** were produced. They form by air oxidation of the diene functions as reported elsewhere.[2] In the cases of the adducts to maleic anhydride **17** and *N*-phenylmaleimide **18**, samples of these compounds could be obtained by dichlorodicyanoquinone (DDQ) oxidation[15] of **13**/**13′** and **14**/**14′** and fully characterized.



The related aromatic compound **20** could be obtained by direct cycloaddition of DMAD to diene **6**, corroborating the trend of reactivity of this diene.

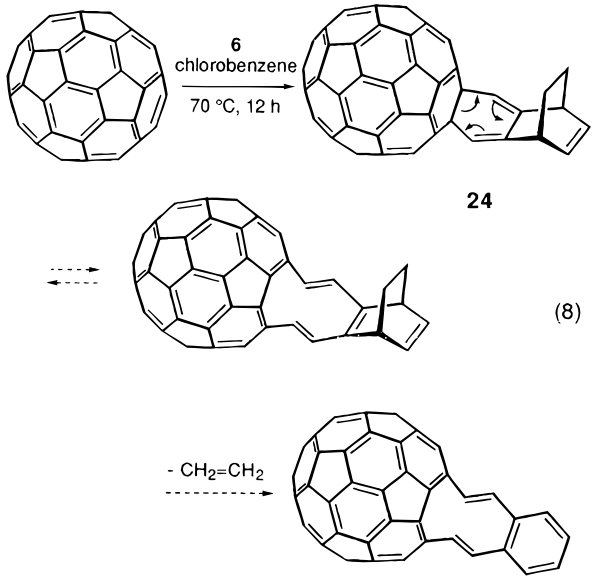
While, with *cis*-locked dienophiles so far described, the reaction of **6** affords two diastereoisomers; with *trans* dienophiles the product composition should be limited to a single product. This is indeed the case with (*E*)-1,2-bis(phenylsulfonyl)ethylene (eq 7).[16] The cycloaddition with this dienophile occurs at a pressure of *ca*. 10 kbar during a few hours at 50 °C and leads to product **21**.



(7)

In an attempt to produce the double adduct **23**, the reaction was carried out at a temperature of 100 °C. Instead of the desired double adduct **23**, the aromatic product **22**, derived from elimination of phenylsulfinic acid, was formed. The steric hindrance of the two sulfonyl groups and the need of a very definite configuration of the double adduct may be responsible of the lack of reactivity of **21**.

The reaction of **6** with fullerene-C_{60} was also investigated.[17] It was hoped that the diene produced could give Cope rearrangement and could be locked in the opened fullerene structure by aromatization (*via* ethylene extrusion) as shown in eq 8. The product would constitute an all sp^2-carbon molecule.



(8)

The reaction of diene **6** with fullerene-C_{60} in chlorobenzene at 70 °C gave two compounds in a 8:1 ratio (HPLC), of which the major one exhibited ^{1}H NMR data in agreement with the dienic structure **24**. The compound proved, however, not to be stable at room temperature, giving products that could not be reconciled with the forcasted behavior of eq 8.

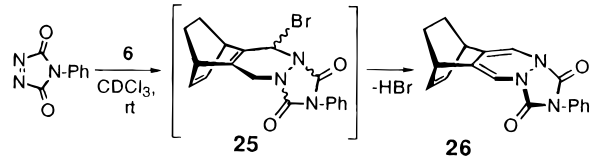
Because in the totality of cases so far discussed no double adducts were ever observed, we decided to test

(15) Lee, H. G. *J. Org. Chem.* **1988**, *53*, 4587.

(16) De Lucchi, O.; Lucchini, V.; Modena, G.; Pasquato, L. *J. Org. Chem.* **1984**, *49*, 596.

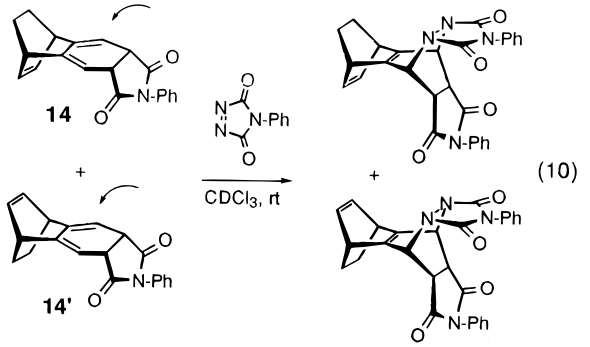
(17) Hirsch, A. *Chemistry of Fullerenes*; Georg Thieme Verlag: Stuttgart 1994.

the reaction of diene **6** with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), which is consisdered one of the strongest dienophiles known. The two major objectives of this sequence were to detect the bromo derivative and verify the double addition product. None of these considerations held true. Even if the cycloaddition reaction was instantaneous and could be carried out below rt, the bromo compound **25** could not be detected and, while the diene **26** formed in good yield, it reacted with more PTAD to give complex reaction mixtures from which no double adduct could be isolated.



(9)

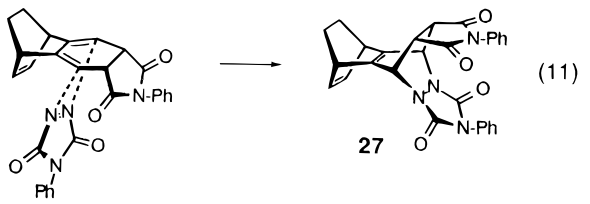
Therefore, we turned our attention to the reaction of PTAD with **14**/**14′**. The cycloaddition of a 4:1 mixture of diene gives a 4:1 mixture of adducts to which was assigned the structures indicated in eq 10 on the basis of "obvious" steric considerations.



(10)

Although both ^{1}H NMR and ^{13}C NMR provide the chemical shift, multiplicity, and integration for the assigned structure, no indication of the relative stereochemistry could be gained by NOESY or similar techniques. We resorted to diffractometric analysis of the major compound. Crystallization from acetone/water gave crystals with a cell lattice made out of four molecules in two different conformations. The two conformers are shown in Figure 1.

The determination of structure **27** allows for the assignment of structure **14** to the major adduct in the reaction of *N*-phenylmaleimide with **6** (eq 10). However, more important is the configuration of the adduct which is different from both those forecasted in eq 10. Indeed, the X-ray structure[18] shows that the double bond of the major adduct is on the same side of the *N*-phenylmaleimide and that the geometry of the maleimide moiety is as drawn in structure **27**. That is to say that the cycloaddition has occurred contrasterically, following the trajectory drawn in eq 11.



(11)

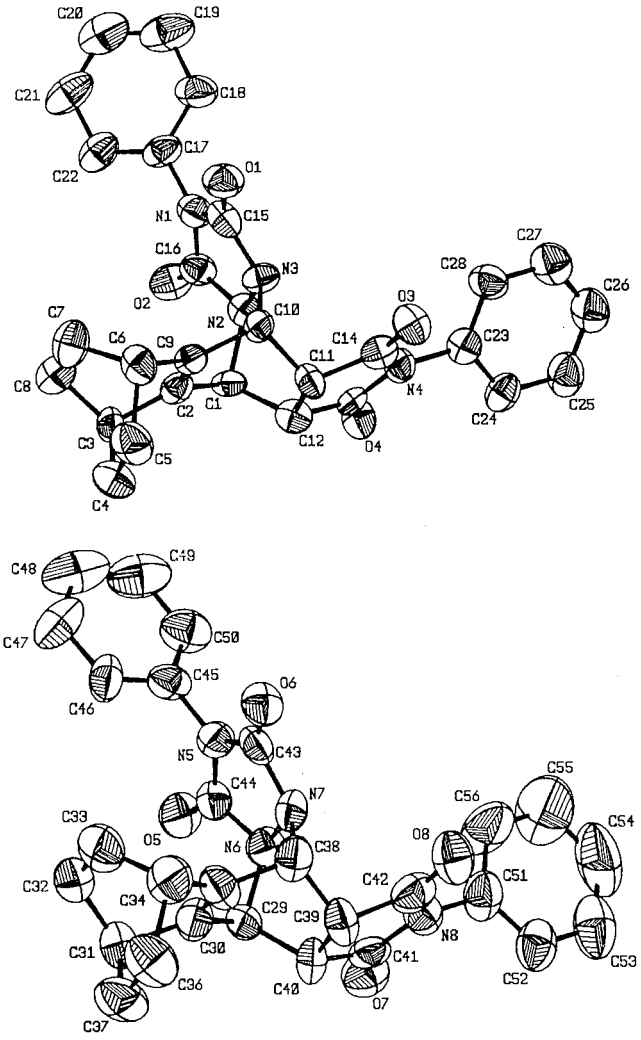


Figure 1. ORTEP representation of the two different conformations present in the cell of adduct **27**. Hydrogen atoms are omitted.

Electronic factors are hence predominant with respect to the steric ones in a reaction that one might predict was governed only by steric reasons. Such a consideration has to be kept in mind in the development of routes to polycylic olefins of type **1** and **2**.

Experimental Section

5-Methylene-6-(bromomethylene)bicyclo[2.2.2]octa-2-ene (6 and 6′). A solution of potassium *tert*-butoxide (180 mg, 1.48 mmol) in Et_2O (20 mL) was added dropwise during 5 min to a solution of **9** (0.2 g, 0.685 mmol) in Et_2O (10 mL) while stirring at −78 °C. After stirring for 30 min at rt, the reaction was quenched with H_2O (50 mL). The organic phase was separated, washed with H_2O (3 × 50 mL), dried (Na_2SO_4), and concentrated at reduced pressure to afford a pale red oil: 101 mg (70% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, mixture of isomers in 9:1 ratio) δ 1.39−1.43 (4 H, m, both isomers), 1.44−1.67 (4 H, m, both isomers), 3.23−3.28 (2 H, m, both isomers), 3.65 (1 H, m, minor isomer), 3.85−3.92 (1 H, m, major isomer), 4.72 (1 H, s, minor isomer), 4.78 (1 H, s, major isomer), 5.01 (1 H, s, major isomer), 5.18 (1 H, s, minor isomer), 6.18 (1 H, d, J = 11.6 Hz, major isomer), 6.26 6.35 (5 H, m, both isomers). ^{13}C-NMR ($CDCl_3$, 100 MHz, only major isomer) δ 24.13, 25.23,

(18) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

37.54, 42.10, 97.76, 98.26, 102.55, 110.08, 131.96, 134.34. IR (neat oil) ν 3051, 2954, 2930, 2869, 1460, 881, 702.

2,3-Bis(hydroxymethyl)bicyclo[2.2.2]octa-2,5-diene (8). From 7a. A 1.0 M cyclohexane solution of DIBALH (250 mL) was added, during 10 min, to a stirred solution of **7a** (5.0 g, 22.5 mmol) in Et_2O (20 mL) previously cooled at −78 °C. After 2 h the solution was stirred for additional 24 h at rt and then quenched with 10% HCl at 0 °C. Water (100 mL) was added, and the crude reaction mixture was extracted with Et_2O in a Soxhlet apparatus for 96 h. The ethereal solution, dried (Na_2SO_4) and concentrated, furnished 3.60 g of a pale yellow oil (96% yield). **From 11.** A solution of $NaBH_4$ (25 mg, 0.66 mmol) in dry MeOH (*ca*. 1 mL) was added to a well stirred solution of **11** (145 mg, 0.894 mmol) cooled at 0 °C under nitrogen. The solution was stirred at rt for 4 h, quenched with 10% HCl, and extracted with Et_2O (3 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated at reduced pressure giving a pale yellow oil: 114 mg (77% yield). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.20−1.50 (4 H, m), 1.55−1.70 (2 H, bs, OH, exchanges with D_2O), 3.65 (2 H, bs), 4.12 (1 H, d, 1/2 AB system, J = 12.0 Hz), 4.23 (1 H, d, 1/2 AB system, J = 12.0 Hz), 6.27−6.48 (2 H, m). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 25.26, 40.11, 60.16, 134.53, 141.00. IR (neat oil) ν 3347, 2943, 2869, 1345, 1095, 1004, 691.

2,3-Bis(bromomethyl)bicyclo[2.2.2]octa-2,5-diene (9). A solution of PBr_3 (2.59 g, 9.57 mmol) in Et_2O (20 mL) was added dropwise to a stirred solution of **8** (10.71 mmol) and pyridine (0.7 mL, 8.69 mmol) in Et_2O (20 mL) cooled at 0 °C. The resulting mixture was stirred for additional 12 h at rt, diluted with Et_2O (40 mL), and washed with brine (2 × 40 mL) and then with $NaHCO_3$ (2 × 40 mL, saturated solution), dried (Na_2SO_4), and concentrated at reduced pressure to give a red oil: 1.43 g (46% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.41 (2 H, ddd, 1/2 AB system, J = 9.0, 2.4, 1.6 Hz), 1.48 (2 H, ddd, 1/2 AB system, J = 9.0, 2.4, 1.6 Hz), 3.62 (2 H, bs), 4.11 (2 H, d, 1/2 AB system, J = 4.0 Hz), 4.15 (2 H, d, 1/2 AB system, J = 4.0 Hz), 6.34−6.37 (2 H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 25.86, 28.95, 41.91, 133.84, 139.92. IR (neat oil) ν 3055, 2948, 2870, 1199, 691, 621.

2-*endo*-3-*exo*-2,3-Bis(tosyloxymethyl)bicyclo[2.2.2]octa-5-ene. Tosylate of 10. A suspension of $LiAlH_4$ (1.93 g, 50.85 mmol), $AlCl_3$ (5.30 g, 39.75 mmol), and dry THF (50 mL) was heated at 55 °C. To this suspension a solution of **7a** (3.77 g, 16.96 mmol) in dry THF (20 mL) was cautiously added during 1 h, and the resulting mixture was stirred for additional 2 h. After cooling to 0 °C, the reaction was quenched with 10% HCl, diluted with H_2O (50 mL), and extracted in a Soxhlet apparatus with Et_2O for 48 h. The organic solution was dried (Na_2SO_4) and concentrated at reduced pressure giving 1.71 g of a colorless oil which was diluted with pyridine (10 mL) and treated with *p*-TsCl (4.07 g, 21.4 mmol) at −20 °C while stirring under nitrogen. After 12 h at 0 °C the crude reaction mixture was mixed with H_2O (20 mL) and extracted with CH_2Cl_2 (5 × 30 mL). The combined organic phases were washed with H_2O (5 × 50 mL), dried (Na_2SO_4), and concentrated at reduced pressure to furnish the bistosylate in 74% yield, mp 131−2 °C (EtOH). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.96−1.50 (6 H, series of m), 2.45 (6 H, s), 2.50 (2 H, bs), 3.58 (2 H, d, J = 7.6 Hz), 3.86 (1 H, t, J = 9.6 Hz), 3.93−4.00 (1 H, m), 5.92 (1 H, d, J = 7.2 Hz), 6.26 (1 H, d, J = 7.2 Hz), 7.33−7.37, 7.73−7.79 (10 H, series of m, Ar). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 18.32, 21.66, 24.70, 30.05, 30.80, 39.39, 41.33, 71.32, 72.95, 127.85, 127.87, 129.89, 129.95, 131.62, 132.85, 132.91, 135.56, 144.83, 144.93. IR (KBr) ν 3042, 2947, 2872, 1354, 1171, 853, 817, 668.

Diels−Alder Adduct of 6 and Maleic Anhydride (13/13′). A solution of **6** (75 mg, 0.36 mmol) and maleic anhydride (35 mg, 0.37 mmol) in CH_2Cl_2 (3 mL) in a screw-capped Pyrex test tube was purged with nitrogen, sealed, and stirred at rt monitoring by TLC (eluent: mixture of AcOEt-light petroleum ethereum ether in 1.5/8.5 ratio). After 60 h the crude reaction mixture was purified by chromatography on MeOH-deactivated silica gel column (eluent: mixture of AcOEt-light petroleum ether in 1.5/8.5 ratio) affording colorless crystals consisting in a mixture of *endo*−*exo* isomers in 1:1 ratio (25 mg, 31% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, mixture of *endo*−*exo* isomers in 1:1 ratio) δ 1.41−1.67 (8 H, series of m, both isomers), 3.25 (4 H, bs, both isomers), 3.85 (2 H, bs, one isomer), 3.93 (2 H, bs, one isomer), 5.43 (2 H, bs, one isomer), 5.47 (2 H, bs, one isomer), 6.24−6.29 (4 H, m, both isomers). ^{13}C-NMR ($CDCl_3$, 100 MHz, mixture of *endo*−*exo* isomers in 1:1 ratio) δ 24.93, 25.26, 38.33, 38.37, 40.83, 41.39, 106.09, 106.32, 132.55, 132.78, 139.80, 140.43, 172.64 (C═O, both isomers). IR (KBr) ν 2958, 2927, 2855, 1864, 1849, 1769, 1384, 1261, 803, 689.

Diels−Alder Adduct of 6 and *N*-Phenylmaleimide (14/14′). A solution of **6** (0.39 g, 1.84 mmol) and *N*-phenylmaleimide (0.32 g, 1.84 mmol) in CH_2Cl_2 (6 mL) containing a few crystals of hydroquinone in a screw-capped Pyrex test tube was purged with nitrogen, sealed, stirred at rt, and monitored by TLC. After 96 h the solvent was removed at reduced pressure, and the residue was purified by flash chromatography on MeOH-deactivated silica gel column (eluent AcOEt/*n*-hexane in 1:1 ratio). A colorless solid was collected consisting of a mixture of isomers in 4:1 ratio: 0.176 (32% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, mixture of isomers in 4:1 ratio) δ 1.41−1.67 (8 H, series of m, both isomers), 3.22 (4 H, bs, both isomers), 3.78 (2 H, bs, minor isomer), 3.88 (2 H, bs, major isomer), 5.52 (2 H, bs, major isomer), 5.57 (2 H, bs, minor isomer), 6.23−6.32 (4 H, m, both isomers), 7.24−7.55 (10 H, series of m, Ar, both isomers). ^{13}C-NMR ($CDCl_3$, 100 MHz, major isomer, one C missing) δ 25.57, 38.55, 41.30, 108.31, 126.53, 128.49, 128.99, 132.86, 139.56, 177.70. ^{13}C-NMR ($CDCl_3$, 100 MHz, minor isomer, one C missing) δ 25.21, 30.91, 40.79, 108.65, 126.44, 129.01, 132.68, 139.00, 177.70. IR (KBr, mixture of isomers in 4:1 ratio) ν 3050, 2937, 2865, 1707, 1394, 1197, 690.

Diels−Alder Adduct of 6 to 1,4-Benzodithiin-*S*,*S*′-tetraoxide (15/15′ and 16). The procedure previously described for the preparation of **14**/**14′** was employed starting from **6** (40 mg, 0.19 mmol) and 1,4-benzodithiin-*S*,*S*′-tetraoxide (43 mg, 0.19 mmol) in CH_2Cl_2 (2 mL). The reaction was monitored by TLC (eluent: mixture of AcOEt/*n*-hexane in 1/9 ratio). After 72 h the crude reaction mixture was concentrated at reduced pressure and diluted with Et_2O (4 mL). The ethereal solution, separated and slowly concentrated, furnished a mixture of *endo*−*exo* isomers in 45/55 ratio as a pale yellow solid. Chromatography on silica gel column eluting with a mixture of AcOEt/light petroleum ether gave a small amount of **15**/**15′** in 1:9 ratio. ^{1}H-NMR ($CDCl_3$, 200 MHz, mixture of isomers in 45/55 ratio) δ 1.40−1.85 (8 H, m, both isomers), 3.42 (4 H, bs, both isomers), 4.81 (2 H, dd, J = 3.0, 1.5 Hz, major isomer), 4.85 (2 H, dd, J = 3.0, 1.5 Hz, minor isomer), 5.58−5.63 (4 H, m, both isomers), 6.22−6.33 (4 H, m, both isomers), 7.67−8.19 (8 H, series of m, Ar, both isomers). Further elution furnished **16**: Major isomer (17% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.20−1.45 (4 H, m), 3.29 (1 H, dd, 1/2 AB system, J = 10.4, 5.8 Hz), 3.53 (1 H, dd, 1/2 AB system, J = 10.4, 0.8 Hz), 3.64 (2 H, bs), 4.98 (1 H, dd, J = 5.8, 0.8 Hz), 6.26−6.40 (2 H, m), 7.31 (1 H, s), 7.75−7.81, 7.93−8.03 (4 H, series of m, Ar). ^{13}C-NMR ($CDCl_3$, 100.57 MHz) δ 24.11, 24.90, 39.77, 41.80, 53.41, 59.02, 123.80, 125.22, 131.60, 132.04, 133.82, 133.89, 134.51, 139.00, 147.52. IR (KBr) ν 3054, 2959, 2933, 2869, 1318, 1128, 1106, 803, 707, 692. Minor isomer (7% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.22−1.60 (4 H, series of m), 3.30 (1 H, dd, 1/2 AB system, J = 21.6, 12.8 Hz), 3.53 (1 H, dd, 1/2 AB system, J = 21.6, 1.6 Hz), 3.62−3.70 (2 H, m), 5.06 (1 H, dd, J = 12.8, 1 6 Hz), 6.25−6.41 (2 H, m), 7.36 (1 H, s), 7.74−7.82, 7.94−8.02 (4 H, series of m, Ar).

Oxidation of 14/14′ with DDQ (18). A solution of **14/14′** (20 mg, 0.088 mmol of a mixture of isomers in 1/1 ratio) and DDQ (20 mg, 0.088 mmol) in $CDCl_3$ (0.5 mL) in a NMR tube was allowed to stand at rt and monitored by ^{1}H-NMR. After 7 days the resulting mixture was diluted with $CHCl_3$ and filtered. The solution was concentrated at reduced pressure affording to a colorless solid: 18 mg (92% yield), mp 105 °C ($CDCl_3$). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.45 (2 H, d, 1/2 AB system, J = 8.0 Hz), 1.68 2 H, d, 1/2 AB system, J = 8.0 Hz), 4.21 (2 H, bs), 6.51−6.58 (2 H, m), 7.74 (2 H, s, Ar). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 24.54, 40.79, 119.10, 133.90, 149.50, 153.64, 178.61. IR (KBr) ν 2961, 2923, 2851, 1847, 1778, 1384, 1261, 800, 740, 709.

Oxidation of 15/15′ with DDQ (19). Similarly as before, starting from **15/15′** (15 mg, 0.049 mmol of a mixture of isomers in 4/1 ratio), DDQ (12 mg, 0.050 mmol), and $CDCl_3$ (0.5 mL), after 5 days at rt there was obtained pale yellow crystals: 14 mg (quantitative yield), mp 130 °C dec. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.40−1.70 (4 H, series of m), 4.20 (2 H, bs), 6.52−6.58 (2 H, m), 7.27−7.52 (5 H, series of m) Ar), 7.72 (2 H, s, Ar). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 25.12, 41.07, 117.98, 118.42, 126.55, 127.81, 129.03, 129.52, 131.73, 134.35, 151.88. IR (KBr) ν 3050, 2927, 2871, 2859, 1720, 1712, 1383, 753, 690.

1,4-Dihydro-1,4-ethano-6,7-bis(methoxycarbonyl)naphthalene (20). A solution of **6** (53 mg, 0.25 mmol) and dimethyl acetylenedicarboxylate (35 mg, 0.25 mmol) in $CDCl_3$ (0.5 mL) in a NMR tube was purged with nitrogen and immersed in an ultrasonic bath. When the reaction was complete (^{1}H-NMR), the crude reaction mixture was purified by flash chromatography on MeOH-deactivated silica gel (elutant: AcOEt/*n*-hexane in 15/85 ratio) to afford a pale yellow oil: 50 mg (74% yield). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.35−1.65 (4 H, series of m), 3.85 (6 H, s), 4.05 (2 H, bs), 6.45−6.55 (2 H, m), 7.55 (2 H, s, Ar). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 25.15, 40.13, 52.48, 122.99, 129.91, 134.43, 147.74, 168.57. IR (neat oil) ν 3053, 2952, 2870, 1725, 1294, 1260, 1201, 855, 786, 699.

Diels−Alder Adduct of 6 and (*E*)-Bis(phenylsulfonyl)-ethylene (21 and 22). A solution of **6** (210 mg, 0.995 mmol) and (*E*)-1,2-bis(phenylsulfonyl)ethylene (0.61 mg, 1.99 mmol) in CH_2Cl_2 (*ca*. 2 mL) in a screw-capped Teflon tube was degassed by immersion in a ultrasonic bath for 20 min, sealed, and exposed to 10 kbar in a high pressure apparatus at 100 °C for 48 h. The crude reaction mixture was added to CH_2Cl_2 (*ca*. 4 mL) and the unreacted dienophile removed by filtration. The organic solution was concentrated and purified by flash chromatography (eluent: AcOEt/*n*-hexane 2:8 ratio) eluting in the order **21** and **22**. **21** (5% yield): ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.00−1.40 (4 H, series of m), 2.85−3.00 (2 H, m), 4.50−4.70 (2 H, m), 5.35−5.40 (2 H, m), 5.65−5.70 (1 H, m), 5.80−5.95 (1 H, m), 7.20−7.85 (10 H, series of m). **22**: colorless oil (50 mg, 20% yield). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.30−1.60 (4 H, m), 4.03 (2 H, bs), 6.45−6.51 (2 H, m), 7.25−7.40, 7.42−7.63, 7.67−7.84, 7.85−8.08 (8 H, series of m, Ar). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 25.14, 30.91, 40.23, 40.30, 121.53, 123.21, 125.14, 127.57, 129.14, 132.83, 134.14, 134.89, 138.02, 142.17, 145.57, 150.23. IR (neat oil) ν 3055, 2957, 2870, 1446, 1306, 1147, 1094, 829, 724, 688.

Diels−Alder Adduct of 6 to Fullerene-C_{60} (24). A solution of **6** (40 mg, 0.19 mmol), fullerene-C_{60} (50 mg, 0.069 mmol), and chlorobenzene (10 mL) was heated for 2 h at 70 °C and for additional 12 h at 60 °C, while stirring. The solvent was removed at reduced pressure, and the residue was diluted with toluene and purified by HPLC, eluting two different products plus unreacted fullerene-C_{60} (54%). The second compound eluted was concentrated (40 °C, 16 mmHg) and recrystallized from toluene/*n*-hexane. The crystalline compound was separated and washed with *n*-hexane (2 × 3 mL) and with MeOH (2 × 3 mL), affording red crystals: 53 mg (41% yield). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.65−1.80 (2 H, m), 2.00−2.15 (2 H, m), 3.60 (2 H, bs), 6.14 (2 H, s), 6.48−6.58 (2 H, m).

Diels−Alder Adduct of 6 and PTAD (26). A solution of **6** (50 mg, 0.237 mmol) and PTAD (41 mg, 0.234 mmol) in $CDCl_3$ (0.5 mL) in a NMR tube was purged with nitrogen, sealed, and monitored by ^{1}H-NMR. After a few minutes the crude reaction mixture was concentrated at reduced pressure, and the residue was purified by flash chromatography on deactivated silica gel, eluting with a mixture of AcOEt/*n*-hexane in 2:8 ratio, which afforded a colorless solid: 52 mg (73% yield), mp 143−5 °C dec. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.40−1.68 (4 H, series of m), 3.25 (2 H, bs), 6.31−6.34 (2 H, m), 7.36−7.54 (5 H, m, Ar). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 25.41, 34.58, 110.61, 123.22, 125.63, 128.29, 129.16, 131.12, 132.44, 142.51. IR (KBr) ν 3092, 3048, 2934, 2867, 1763, 1720, 1412, 1337, 1261, 797, 756, 740, 689.

Diels−Alder Adducts of 15/15′ with PTAD (27). The procedure described for the preparation of **26** was employed starting from a mixture in 4:1 ratio of **15/15′** (60 mg, 0.20 mmol), PTAD (35 mg, 0.20 mmol) and $CDCl_3$ (0.5 mL). After 12 h the crude reaction mixture was purified by flash chromatography on MeOH-deactivated silica gel eluting with a 2:8 mixture AcOEt/*n*-hexane. The minor adduct and **27** were eluted in the order. Minor adduct (45% yield), mp 183−5 °C ($CDCl_3$/*n*-pentane). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.20−1.50 (4 H, m), 3.68 (2 H, t, J = 1.6 Hz), 3.78 (2 H, bs), 5.62 (2 H, t, J = 1.6 Hz), 6.30−6.50 (2 H, m), 7.20−7.70 (10 H, series of m, Ar). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 24.72, 38.78, 41.88, 54.56, 125.38, 125.81, 128.73, 128.98, 129.19, 129.23, 130.71, 131.09, 134.72, 141.01, 157.33, 173.53. IR (KBr) ν 3067, 2957, 2942, 1716, 1409, 1386, 1262, 776, 765, 746, 691. **27**: (45% yield), mp 160−1 °C ($CDCl_3$/*n*-pentane), 173−5 °C (acetone/water). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.30−1.60 (4 H, m), 3.14 (2 H, t, J = 1.6 Hz), 3.90 (2 H, bs), 5.57 (2 H, t, J = 1.6 Hz), 6.30−6.55 (2 H, m), 7.20−7.53 (10 H, series of m, Ar). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 25.18, 38.70, 43.52, 55.46, 125.76, 126.28, 128.51, 128.92, 129.20, 129.37, 130.72, 131.42, 134.82, 141.76, 157.61, 173.59. IR (KBr) ν 3067, 2955, 2942, 2870, 1716, 1409, 1384, 1262, 833, 776, 765, 746, 691.

Supporting Information Available: Copies of NMR spectra (42 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.

JO951434T