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Alkyl- and Arylsubstituted Ketenedithioacetal Tetroxides: Diels-Alder Reactivity and Reductive Desulfonylation of the Adducts

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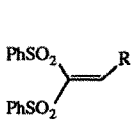
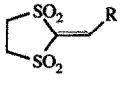
Abstract: The Diels-Alder reactivity of the representative alkyl and aryl-substituted ketenedithioacetal tetroxides of general formula **1** is reported. These dienophiles reacted under thermal conditions (refluxing toluene) with cyclopentadiene to afford predominantly the endo adduct. In the case of **1C** and **1D** the endo and exo adducts were formed with total stereoselectivity with respect to the biphenyl or binaphthyl residue as determined on the basis of n.O.e. experiments. Dienophiles **1A-D** failed to react with other dienes under similar reaction conditions but reacted efficiently in ether containing 5 M lithium perchlorate under sonication. Under these reaction conditions, the cycloaddition to quadricyclane, 1-methoxy-, 1- and 2-trimethylsilyloxy-1,3-butadiene and to the Danishefsky diene were investigated. In the cycloaddition to 1-trimethylsilyloxy-1,3-butadiene and to the Danishefsky diene the open chain adducts (*Z*)-**14** and **17** were obtained in high yield as primary adducts. Eventually, the former undergoes isomerization to (*E*)-**14**, while the latter is further hydrolyzed to **18**. The open-chain compound **19** was also obtained via base treatment of **12Ac**. The generation of a highly stabilized bis(phenylsulfonyl)-substituted carbanion is probably the driving force of these transformations. Reductive desulfonylation of **8Ac** unexpectedly afforded the norbornadiene **20**, possibly via a carbene intermediate. At variance, adduct exo-**8Dc** and **10Ac** upon reduction gave the hydrocarbon exo-**21** and **22**. Finally, reduction of **12Ac** occurred with concomitant reduction of the carbonyl group to give alcohol **23**.

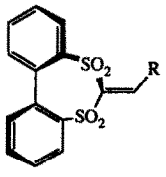
By virtue of the high activation imparted by the two geminal sulfonyl groups, the ketenedithioacetal tetroxide **1Aa**[2] has been shown to be a good dienophile.[3] So far, however, no work on the cycloadditivity properties of derivatives, differently substituted at the thio-residue and/or at the alkene carbon appears to have been done, despite the fact that alkyl- or aryl-substitution on the dienophile should enlarge the synthetic potentiality of these reagents. Here we report on the reaction of a few dienophiles of the general formula **1A-D**[2] with representative dienes and some transformations of the adducts. Dienophiles **1C** and **1D** are atropisomeric chiral molecules and the face selectivity associated to their cycloaddition is also reported.



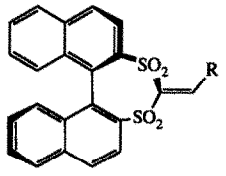
1A



1B



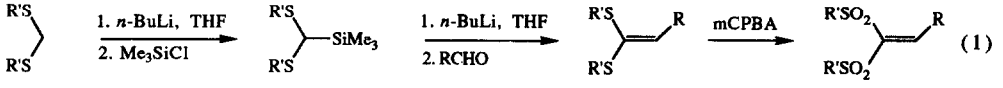
1C



1D

a R = H
b R = CH_3
c R = C_6H_5
d R = $CH{=}CH_2$

Preparation of the Dienophiles. The reagents investigated in this study were the substituted derivatives **1Ab**, **1Ac**, **1Bc**, **1Cc**, **1Db**, **1Dc**, and **1Dd**[2] which were all unknown and the unsubstituted ketenedithioacetals **1Aa**,[3] **1Ca**[4] and **1Da**[4] whose preparation has been reported elsewhere. All the reagents, except for **1Ac** and **1Bc**, were prepared from the respective methylenic dithioacetals, via the Peterson methodology as shown in equation (1).[5]



(1)

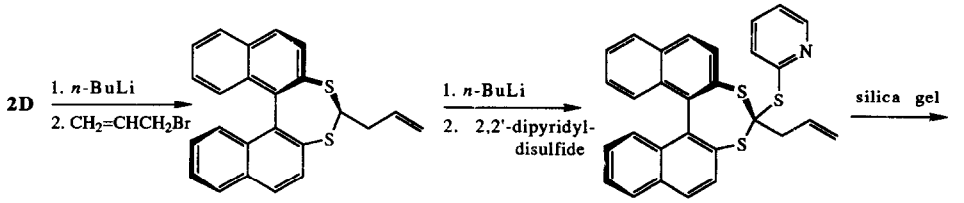
2 **3** **4** **1**

A: R' = Ph; **C**: R'-R' = 2,2'-biphenyl; **D**: R'-R' = 1,1'-binaphtho-2,2'-diyl
b: R = Me; **c**: R = Ph, **d**: R = CH=CH_2

Introduction of the trimethylsilyl group in the dithioacetal **2**, followed by treatment of the resulting silylated product **3** with *n*-butyllithium and the appropriate aldehyde, furnished the respective ketene dithioacetals **4**.[5] The latter were finally oxidized with *m*-chloroperbenzoic acid (*m*CPBA) in high overall yields to the dienophiles **1**. All the compounds obtained with this route were previously unknown. The methyl substituted derivatives were particularly reactive and care had to be paid to avoid decomposition. It should also be noticed that the unsubstituted derivatives **1Aa-1Da** could also be prepared in high yields via the same synthetic procedure.[4]

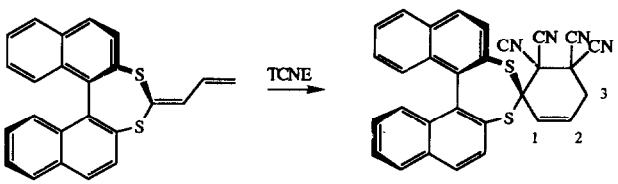
Dienophiles **1Ac** and **1Bc** were prepared via the reported Knövenagel condensation of benzaldehyde with bis(phenylsulfonyl)methane[6] and 1,3-dithiolane-*S*,*S*-tetroxide[7] respectively.

Compound **1Dd** was prepared, beside by the Peterson methodology from acrolein as described in equation (1) via the route engaging the use of 2,2'-bipyridyl disulfide,[8] albeit in lower overall yield. As described in equation (2), treatment of the anion of dinaphthodithiepine **2D** with allyl chloride generated the propenyl derivative **5** which was again submitted to treatment with base followed by quenching with 2,2'-dipyridyldisulfide to obtain the orthothiocarbonate **6**. The latter on silica gel was converted into the diene **4Dd**, identical in all respects to that obtained via the Peterson methodology.



(2)

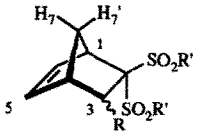
5 **6**



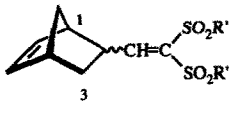
4Dd **7**

In order to confirm the structure by chemical means, **4Dd** was reacted with tetracyanoethylene (TCNE) to afford cycloadduct **7**. Diene **4Dd** is a chiral diene and may find useful applications as reported for similar compounds.[5,9] From the point of view of its cycloadditivity properties, it did not exhibit a high reactivity, failing to react under thermal conditions with standard dienophiles such as maleic anhydride and fumaric and maleic acid dimethyl esters.

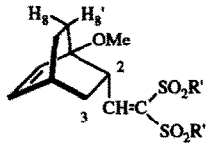
Cycloaddition to Cyclopentadiene. The cycloaddition of **1A-D** with cyclopentadiene afforded the expected Diels-Alder adducts **8**.



8Ac (R = Ph, R' = Ph)
8Bc (R = Ph, R'-R' = -CH_2CH_2-)
8Cc (R = Ph, R'-R' = 2,2'-biphenyl)
8Db (R = Me, R'-R' = 1,1'-binaphtho-2,2'-diyl)
8Dc (R = Ph, R'-R' = 1,1'-binaphtho-2,2'-diyl)



8Dd



9

(R'-R' = 1,1'-binaphtho-2,2'-diyl)

The results of the cycloaddition experiments are summarized in Table I.

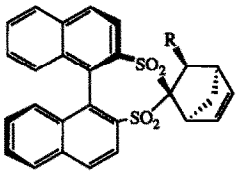
Table I. Reaction conditions, yields and diastereomeric ratio of the adducts of **1A-D** to cyclopentadiene.

#	Reagent	Reaction Conditions	Adduct	Yield (%)	Endo/exo Ratio	Diastereomeric Ratio[a] endo**8**:endo**8'**:exo**8**:exo**8'**
1	**1Ac**	Toluene, reflux, 24 h	**8Ac**	90	4 : 1	-
2	**1Bc**	Toluene, reflux, 24 h	**8Bc**	90	2 : 1	-
3	**1Cc**	Toluene, reflux, 12 h	**8Cc**	95	1.5 : 1	1.5 : - : 1 : -
4	**1Db**	$CDCl_3$, 20 °C, 12 h	**8Db**	98	4 : 1	4.0 : - : 1 : -
5	**1Dc**	Toluene, reflux, 12 h	**8Dc**	95	1.5 : 1	1.5 : - : 1 : -
6	**1Dd**	$CDCl_3$, 20 °C, 5 min	**8Dd**	90	6 : 2	4 : 2 : 1 : 1[b]

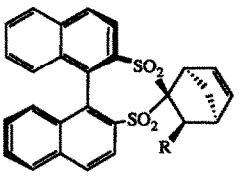
[a]Refers to the relative stereochemistry of the biphenyl or binaphthyl residue. [b]The stereochemistry of the adducts was not determined.

A general observation is that methyl or phenyl substitution leads to a dramatic drop of reactivity with respect to the unsubstituted derivatives **1Aa**[4] or **1Ca**[5] and **1Da**.[5] As an example, while the reaction of the parent system **1Aa** with cyclopentadiene proceeds at room temperature in chloroform, the same reaction employing **1Ac** required heating a toluene solution at reflux for 24 hours. Unexpectedly, under the reaction conditions which were effective for the cycloaddition of the phenyl derivative **1Ac**, the methyl substituted analog **1Ab** did not react. For what the stereoselectivity is concerned, the endo/exo ratio was in favour of the endo isomer (Table I) as determined by the coupling constants between the proton a to the R group and the vicinal bridgehead proton and decoupling experiments.

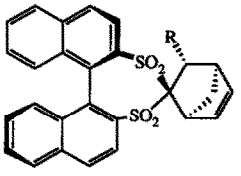
As indicated in Table I, in the case of **1Cc** and **1Db,c** only two, out of the four possible diastereoisomeric adducts indicated below for **8D**, were formed.



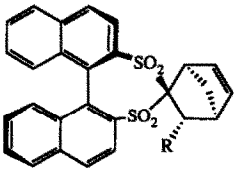
endo-**8D**
(major)



endo-**8D'**

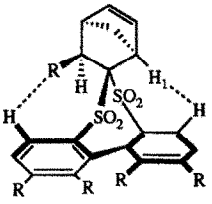


exo-**8D**
(minor)

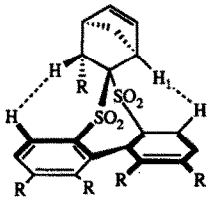


exo-**8D'**

The diastereoisomers were separated by flash chromatography and independently analyzed. The stereochemistry of the biphenyl or binaphthyl group with respect to the norbornene skeleton was assigned by n.O.e. measurements.[10] Substantial enhancements were observed between the protons in the phenyl or naphthyl group and the bridgehead and vicinal protons of the norbornene skeleton thus allowing the assignment of the configurations shown in structures **8**.[11]



endo-**8**
(major)



exo-**8**
(minor)

Hence, the reaction of **1Cc** and **1Db,c** with cyclopentadiene affords one single endo and one single exo diastereoisomers and it is therefore highly face selective.

To be noticed that the cycloadducts relative to **1C** did not show any interconversion, showing that the rotation around the two phenyl rings is not operating at ordinary temperatures even after prolonged time.

Finally, the cycloaddition of **1Dd** with cyclopentadiene did not lead to addition to the activated double bond but to the distal one leading to a mixture of at least four isomeric cycloadducts **8Dd** which were not further characterized. The cycloaddition to 1-methoxy-1,3-cyclohexadiene showed the addition again to the least activated double bond but it was highly regio- and stereoselective furnishing a single cycloadduct to which was assigned structure **9** on the basis of n.O.e. enhancement between H-2 and H-8'.

The addition of cyclopentadiene to the apparently least activated double bond of electron-poor dienes has been noticed also with capto-dative dienes.[12]

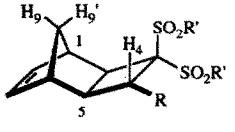
Cycloaddition in 5 M Lithium Perchlorate in Ether. The reaction of **1A-D** with other dienes did not occur under the reaction conditions used with cyclopentadiene. At variance, the cycloadditions were effectively performed in ether containing lithium perchlorate (5 M)[13] at room temperature for 12-24 hours. This appears to be the first case of catalysis of a sulfonyl alkene in a cycloaddition reaction.[12] The dienes investigated were quadricyclane and the open chain dienes 1-methoxy and 1-trimethylsilyloxy-1,3-butadiene, 2-trimethylsilyloxy-1,3-butadiene and 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (Danishefsky diene). Sonication proved beneficial to the reaction rate. The thick reaction mixture contained into screw capped vials, turned clear and transparent when placed into a ultrasonic bath. Control experiments showed that under sonication the rate of cycloaddition of **1Ac** to 1-methoxy1,3-butadiene was at least twice as fast.

Table II. Reaction conditions and yields in the cycloaddition of **1A-D** to dienes in 5 M lithium perchlorate in ether under sonication.

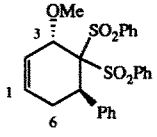
#	Reagent	Diene	Reaction Conditions	Adduct	Yield
1	**1Ab**	2-Trimethylsilyloxy-1,3-butadiene	1. 40-50 °C, 24 h; 2. H_3O^+	**12Ab**	95%
2	**1Ab**	Quadricyclane	40-50 °C, 12 h	**10Ab**	98%
3	**1Ac**	1-Methoxy-1,3-butadiene	40-50 °C, 24 h	**11**	90%
4	**1Ac**	1-Trimethylsilyloxy-1,3-butadiene	40-50 °C, 24 h	**14**[a]	90%
5	**1Ac**	2-Trimethylsilyloxy-1,3-butadiene	40-50 °C, 24 h	**12Ac**	90%
6	**1Ac**	Danishefsky diene	40-50 °C, 24 h	**17**	99%
7	**1Ac**	Quadricyclane	40-50 °C, 24 h	**10Ac**	99%
8	**1Bc**	Quadricyclane	40-50 °C, 12 h	**10Bc**	80%

[a]Ratio *E* : *Z* = *ca.* 2 : 1

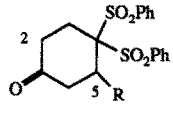
Reaction of **1Ab**, **1Ac** and **1Bc** with quadricyclane led to the normal cycloadducts **10Ab**, **10Ac** and **10Bc** respectively. The stereochemistry shown was assigned on the basis of the coupling constant of H-4 with the vicinal H-5. The size of the coupling constants is in agreement with the Karplus relation plus other literature data.[14]



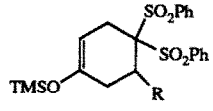
10Ab (R = Me, R' = Ph)
10Ac (R = Ph, R' = Ph)
10Bc (R = Ph, R'-R' = -CH_2CH_2-)



11



12Ab (R = Me)
12Ac (R = Ph)

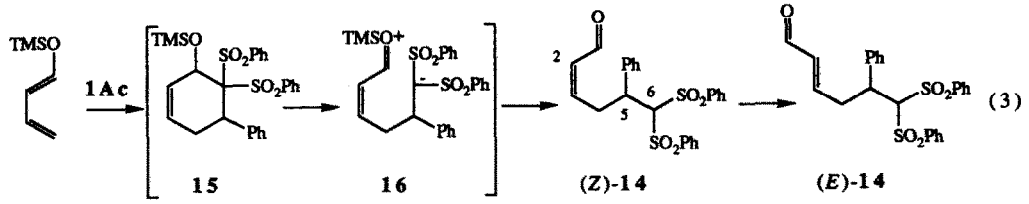


13Ab (R = Me)
13Ac (R = Ph)

The cycloaddition of **1Ac** to 1-methoxy-1,3-butadiene afforded cycloadduct **11**. The stereochemistry of the latter was assigned as shown because the coupling constant of the proton adjacent to the methoxy group with the vicinal vinyl proton, is very small (*ca.* 0 Hz) indicating a dihedral angle close to 90°. Furthermore, n.O.e. enhancement was observed between the methyl group and the proton a to the phenyl ring.

The cycloaddition of **1Ab** and **1Ac** to 2-trimethylsilyloxy-1,3-butadiene afforded the hydrolysis products **12Ab** and **12Ac**. The primary enolethers **13Ab** and **13 Ac** were hydrolyzed under the aqueous work up.

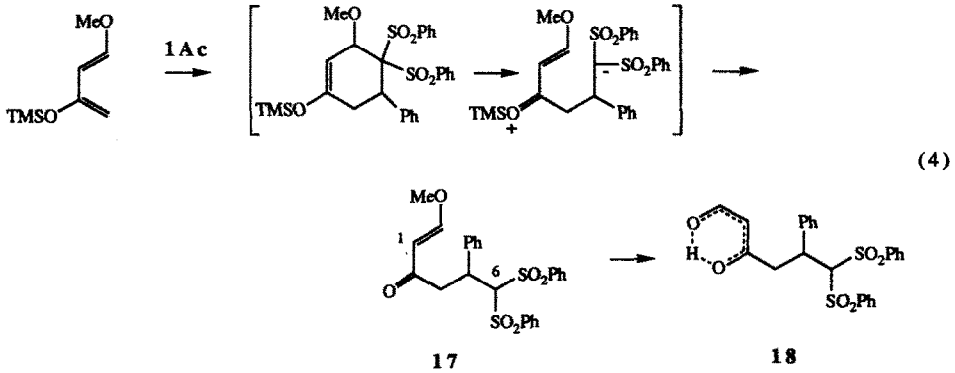
At variance with the previous cases, the cycloaddition of **1Ac** with 1-trimethylsilyloxy-1,3-butadiene led to the open chain adduct (*Z*)-**14** which on standing in chloroform solution slowly converted into the trans isomer (*E*)-**14** [equation (3)].



(3)

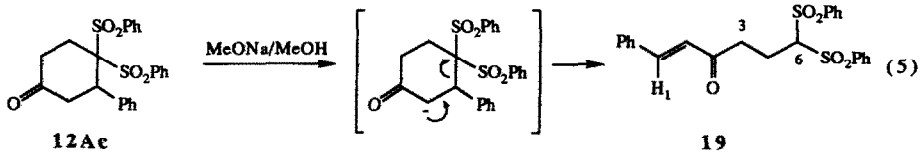
The fact that (*Z*)-**14** derives from the primary cycloadduct **15** is suggested by the observation that at the early stages of the reaction the (*Z*)-isomer was formed highly predominantly while in a dipolar mechanism leading directly to **16** both (*Z*)- and (*E*)-isomers would be expected. Furthermore, the other cases reported (entries 1 and 5 in Table II) show that the cycloaddition was effective under the employed conditions. A dipolar mechanism would have led to different products also in the cycloaddition to 2-trimethylsilyloxy-1,3-butadiene. Unfortunately, the reaction could not be followed by NMR because of the unusual reaction medium.

Cycloaddition to the Danishefsky diene afforded **17** via a similar reaction mechanism as shown in equation (4). Adduct **17** was not stable and converted on standing in chloroform solution with $T_{1/2}$ of *ca.* 24 hours to **18**, via hydrolysis of the enolether functionality.



(4)

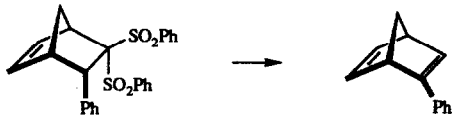
To corroborate the stability and the actual involvement of a doubly phenylsulfonyl substituted carbanion in the reactions so far described we have reacted compound **12Ac** with sodium methoxide in methanol. The reaction led in high yield to the open chain product **19** [equation (5)].



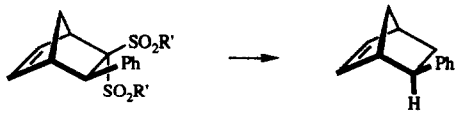
(5)

It is finally worth mentioning that under the same reaction condition simple enolethers such as 1-trimethylsilyloxy-cyclohexene did not react with **1Ac**. This observation supports the suggestion that the open chain derivatives observed in equations (3) and (4) are indeed derived from the primary Diels-Alder adducts.

Reductive Desulfonylation. Sodium amalgam reduction of the endo adduct **8Ac** afforded unexpectedly norbornadiene **20**[15] in quantitative yield [equation (6)]. The reaction was expected to give the norbornene **21** instead.



endo-**8Ac** **20** (6)

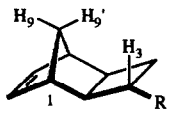


exo-**8Dc** exo-**21** (7)

(R'-R' = 1,1'-binaphtho-2,2'-diyl)

The formation of the norbornadiene **20** appears to be associated with the stereochemistry of the adduct. In other words, the insertion of the carbene into the vicinal C-H bond was effective only in an exo manner. Infact, the desulfonylation reaction performed under the same reaction conditions on the exo derivative **8Dc** afforded only the exo norbornene **21**.

The reductive desulfonylation of **10Ac** gave the expected tricyclic structure **22**, the respective cyclobutene being not formed. The reduction of **12Ac** gave alcohol **23**. In this case concomitant reduction of the ketone was observed.



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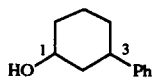

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Depending upon the products determined in this study, the substituted ketenedithioacetals tetroxides **1** may be viewed as synthons of substituted acetylenes or ethylenes in Diels-Alder or dipolar cycloadditions.

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Experimental Section

2*H*-dibenzo[*d*,*f*][1,3]dithiepine (2C). This compound was prepared as for the binaphthyl derivative **2D**[16] in quantitative yields: mp 102-3 °C (CH_2Cl_2/petroleum ether). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 4.37 (2 H, s), 7.38-7.64 (8 H, series of m). Anal. Calcd for $C_{13}H_{10}S_2$: C, 67.78; H, 4.37. Found: C, 67.47; H, 4.57.

2*H*-2-Trimethylsilyl-dibenzo[*d,f*][1,3]dithiepine (3C). A 1.6 M *n*-hexane solution of *n*-butyllithium (2.98 mL, 4.77 mmol) was added dropwise, under argon, to a cooled solution (-60 °C) of 2*H*-dibenzo[*d,f*][1,3]dithiepine (1.0 g, 4.34 mmol) in dry THF (10 mL). After stirring at -60 °C for 2 h, trimethylsilyl chloride (0.6 g, 4.77 mmol) was added dropwise and the reaction mixture was let warming to room temperature. After 12 h saturated ammonium chloride was added and the reaction mixture was extracted with dichloromethane (3 x 75 mL), dried (Na_2SO_4) and rotoevaporated to dryness to leave an oily residue: 1.28 g, 98% yield. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.17 (9 H, s), 4.13 (1 H, s), 7.30-7.75 (8 H, series of m). IR (KBr film, cm^{-1}) 3065 (w), 2950 (m), 1250 (s), 855 (s), 845 (s), 750 (s). Anal. Calcd for $C_{16}H_{18}S_2Si$: C, 63.52; H,5.99. Found: C, 63.76; H, 6.10.

2*H*-2-Trimethylsilyl-dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (3D). This compound was obtained with the same procedure described for the dibenzo-analog **3C** in 90% yield: mp 178-9 °C (CH_2Cl_2/petroleum ether); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.15 (9 H, s), 4.13 (1 H, s), 7.05-7.99 (12 H, series of m). IR (KBr, cm^{-1}) 3025 (w), 2950 (w), 1500 (w), 1205 (s), 855 (s), 845 (s), 820 (s), 750 (s). Anal. Calcd for $C_{16}H_{17}S_2Si_2$: C, 71.59; H, 5.50. Found: C, 71.29; H, 5.64. A small amount (8%) of the disubstituted trimethylsilyl derivative was also obtained: mp 206-8 °C (CH_2Cl_2/petroleum ether); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.28 (18 H, s), 7.03-8.20 (12 H, series of m). IR (KBr, cm^{-1}) 3000 (w), 1580 (m), 1500 (s), 1250 (s), 850 (s), 690 (s). Anal. Calcd for $C_{27}H_{30}S_2Si_2$: C, 77.45; H, 7.22. Found: C, 77.71; H, 6.90.

General Procedure for the Peterson Olefination. To a solution of 2*H*-2-trimethylsilyl-dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (1.0 g, 2.48 mmol) in 10 mL of dry THF was added dropwise at -45 °C a 1.6 M solution of *n*-butyllithium in *n*-hexane (1.62 mL, 2.60 mmol). After 2 h at -45 °C, the appropriate aldehyde was added and the reaction mixture was slowly let reaching room temperature. After 12 h the reaction mixture was washed with saturated ammonium chloride and water, dried ($MgSO_4$) and rotoevaporated. Generally, the crude product was directly submitted to the oxidation to the tetroxide. The ketenedithioacetal **4Ab** presented spectral data in agreement with those reported.[17]

2-Benzylidene-dibenzo[*d,f*][1,3]dithiepine (4Cc). 98% yield, oil; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.93 (1 H, s), 7.20-7.74 (13 H, series of m). IR (KBr film, cm^{-1}) 3050 (m), 2950 (m), 1595 (m), 1420 (s), 1060 (m), 770 (s), 750 (s).

2-Ethylidene-dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (4Db). 98% yield, mp 200-5 °C (CH_2Cl_2/EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.84 (3 H, d, *J* = 7.1 Hz), 5.95 (1 H, q, *J* = 7.1 Hz), 7.09-7.96 (12 H, series of m). IR (KBr, cm^{-1}) 3059 (w), 2900 (w), 1580 (w), 805 (s), 694 (s). Anal. Calcd for $C_{23}H_{16}S_2$: C, 77.48; H, 4.52. Found: C, 77.93; H, 5.02.

2-Benzylidene-dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (4Dc). 99% yield, mp 230-1 °C (CH_2Cl_2/EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.00 (1 H, s), 7.20-8.04 (17 H, series of m). IR (KBr, cm^{-1}) 3050 (w), 2920 (w), 1575 (w), 810 (s), 750 (s).

2-Butylidene-dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (4Dd).

Method A (via Peterson olefination). Diene **4Dd** was obtained following the general procedure described for the Peterson olefination in 96% yield, mp 240-5 °C (CH_2Cl_2/petroleum ether); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.14 (1 H, dt, *J* = 10.2 and 0.9 Hz), 5.21 (1 H, dt, *J* = 18.0 and 0.9 Hz), 6.51 (1 H, ddd, *J* = 10.5, 0.9 and 10.9 Hz), 6.85 (1 H, ddd, *J* = 18.0, 10.5 and 10.2 Hz), 7.15-8.20 (12 H, series of m, Ar). IR (KBr, cm^{-1}) 3075 (w), 2925 (w), 1605 (w), 1320 (s), 815 (s), 715 (s). Anal. Calcd for $C_{24}H_{16}S_2$: C, 78.22; H, 6.36. Found: C, 78.24; H, 6.37.

Method B (with 2,2'-dipyridyldisulfide). A 1.6 M solution of *n*-butyllithium in *n*-hexane (4.05 mL, 6.05 mmol) was added under argon to a cooled (-60 °C) solution of 2*H*-dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine **2D** (2.0 g, 6.05 mmol) in 15 mL of dry THF. After 2 h at -60 °C, allyl chloride (0.52 mL, 6.5 mmol) was added and the reaction mixture was slowly let reaching room temperature. After 12 h the reaction mixture was washed with saturated ammonium chloride and water, dried ($MgSO_4$) and rotoevaporated to obtain the propene **5** (2.02 g, 90% yield): mp 188-9 °C (CH_2Cl_2/EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.47 (1 H, m), 2.60 (1 H, m), 4.84 (1 H, dd, *J* = 7.6 and 6.6 Hz), 5.13 (1 H, d, *J* = 18.3 Hz), 5.11 (1 H, d, *J* = 10.3 Hz), 5.87 (1 H, m), 7.10-

7.95 (12 H, series of m, Ar). IR (KBr, cm^{-1}) 3050 (w), 2900 (w), 1570 (m), 815 (s), 745 (s). The propene **5** (1.26 g, 3.41 mmol) in THF (15 mL) was cooled to -70 °C and a 1.6 M solution of *n*-BuLi in *n*-hexane (2.18 mL, 7.0 mmol) was added dropwise under argon. After stirring for 5 h at -70 °C, 2,2'-dipyridyl-disulfide (0.77 g, 3.5 mmol) in 15 mL of dry THF was added dropwise and the reaction mixture was let reaching room temperature. After 12 h, saturated ammonium chloride was added and the reaction mixture was extracted with dichloromethane. After drying, the crude orthothiocarbonate was purified by flash chromatography eluting with dichloromethane to afford **6** as a crystalline solid (0.96 g, 85% yield): mp 202-5 °C (CH_2Cl_2/EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.01 (1 H, dd, J = 14.4 and 7.8 Hz), 3.50 (1 H, dd, J = 14.4 and 5.7 Hz), 5.05 (1 H, dd, J = 17.7 and 1.2 Hz), 5.11 (1 H, dd, J = 9.3 and 1.2 Hz), 6.09 (1 H, m), 7.11-8.00 (16 H, series of m, Ar). IR (KBr, cm^{-1}) 3050 (w), 1560 (s), 1410 (s), 1115 (s), 815 (s), 750 (s). A mixture of the orthothiocarbonate **6** (0.5 g, 2.0 mmol), silica gel (*ca.* 25 g, 230-400 mesh) and dichloromethane (*ca.* 25 mL) was stirred at room temperature for 3 days, filtered and rotoevaporated. The crude diene **4Dd** was purified by flash-chromatography eluting with n-hexane/dichloromethane 8:2 and recrystallized from dichloromethane - petroleum ether (0.19 g, 50% yield).

Adduct to 4Dd of TCNE (7). To a solution of **4Dd** (200 mg, 0.54 mmol) in chloroform (10 mL) was added at room temperature tetracyanoethylene (0.7 mg, 5.0 mmol). After 10 min the solvent was removed to afford a colorless solid; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.00-3.33 (2 H, m, H-3), 4.65 (1 H, m, H-2), 5.98 (1 H, m, H-1), 7.10-8.05 (12 H, series of m, Ar).

General Procedure for the Oxidation Reaction to the Tetroxides. A solution of *m*-chloroperbenzoic acid (70% pure, *ca.* 100 mmol) in dichloromethane (*ca.* 30 mL) was added under stirring at room temperature to the ketenedithioacetal (10 mmol) in dichloromethane (*ca.* 20 mL). The reaction mixture was slightly warmed to 40 °C for 12 h. The solution was cooled to room temperature and washed with saturated sodium metabisulfite, sodium bicarbonate and water. After drying (Na_2SO_4) and rotoevaporation of the solvent, the tetroxide was recrystallized from the appropriate solvent. In the preparation of **1Dd**, washing with metabisulfite and sodium bicarbonate led to degradation of the product. In this case it was necessary to eliminate the excess *m*CPBA via a rapid flash-chromatography eluting with dichloromethane.

1,1-Diphenylsulfonylpropene (1Ab). In this case 99% *m*-chloroperbenzoic acid was used: 90% yield, mp 182-4 °C (CH_2Cl_2-petrol ether); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.35 (3 H, d, J = 7.8 Hz), 7.49-8.03 (10 H, series of m, Ar), 7.93 (1 H, q, J = 7.8 Hz).

2-Benzylidene-dibenzo[*d,f*][1,3]dithiepine-*S,S'*-tetroxide (1Cc). 97% yield, mp 115-6 °C (CH_2Cl_2/petroleum ether); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.42-8.18 (13 H, series of m), 8.19 (1 H, s). IR (KBr, cm^{-1}) 2910 (w), 1335 (s), 1115 (s), 785 (m). Anal. Calcd for $C_{20}H_{14}O_4S_2$: C, 62.80; H, 3.69. Found: C, 62.88; H, 3.76.

2-Ethylidene-dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine-*S,S'*-tetroxide (1Db). 90% yield, mp 195-6 °C (CH_2Cl_2/petroleum ether); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.41 (3 H, d, J = 7.6 Hz), 7.18-7.47 (4 H, series of m), 7.51 (1 H, q, J = 7.6 Hz), 8.02-8.36 (8 H, series of m, Ar). IR (KBr, cm^{-1}) 3060 (m), 2915 (m), 1600 (m), 1320 (s), 1150 (s), 750 (s), 610 (s).

2-Benzylidene-dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine-*S,S'*-tetroxide (1Dc). 98%, mp 214-5 °C (CH_2Cl_2/petroleum ether); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.20-8.28 (17 H, series of m, Ar), 8.25 (1 H, s). IR (KBr, cm^{-1}) 3070 (w), 2925 (w), 1610 (m), 1315 (s), 1115 (s), 710 (s). Anal. Calcd for $C_{27}H_{18}O_4S_2$: C, 69.60; H, 3.75. Found: C, 69.18; H, 3.62.

2-Butylidene-dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine-*S,S'*-tetroxide (1Dd). 90%, mp 265 °C (CH_2Cl_2/EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.94 (2 H, m), 7.15-8.30 (14 H, series of m). IR (KBr, cm^{-1}) 3070 (w), 2925 (w), 1605 (w), 1320 (s), 1130 (s), 720 (s).

General Procedure for the Diels-Alder Reactions of 1A-D with Cyclopentadiene. A solution of dienophile **1A-D** (5 mmol) and cyclopentadiene (*ca.* 20 mmol) in the appropiate solvent was stirred for the period of time and the temperature indicated in Table I. After rotoevaporation of the solvent and of the excess of cyclopentadiene, the reaction mixture was purified by flash-chromatography eluting with dichloromethane.

endo-8Ac: 72% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.50 (1 H, d, J = 9.5 Hz, H-7), 3.56 (1 H, s, H-4), 3.62 (1 H, d, J = 9.5 Hz, H-7'), 4.21 (1 H, broad s, H-1), 4.97 (1 H, d, J = 3.2 Hz, H-3), 6.32 (2 H, m, H-5 and H-6), 7.05-8.10 (15 H, series of m, Ar).

exo-8Ac: 18% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.60 (1 H, dd, J = 8.9 and 2.2 Hz, H-7), 2.20 (1 H, d, J = 8.9 Hz, H-7'), 3.05 (1 H, broad s), 3.62 (1 H, broad s), 4.14 (1 H, d, J = 2.2 Hz, H-3), 6.21 (1 H, dd, J = 5.6 and 3.0 Hz), 6.52 (1 H, dd, J = 5.6 and 3.2 Hz), 7.20-8.00 (15 H, series of m, Ar).

endo-8Bc: 60% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.83 (2 H, narrow AB system, J_{AB} = 9.9 Hz, H-7 and H-7'), 3.00 (2 H, m), 3.33 (1 H, m, H-4), 3.68 (2 H, m), 3.70 (1 H, m, H-1), 4.67 (1 H, d, J = 2.4 Hz, H-3exo), 6.54 (1 H, dd, J = 5.4 and 3.3 Hz, H-5), 7.00 (1 H, dd, J = 5.4 and 3.0 Hz, H-6), 7.23-7.41 (5 H, m, Ar).

exo-8Bc: 30% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.93 (1 H, dd, J = 9.9 and 2.1 Hz, H-7), 2.68 (1 H, d, J = 9.9 Hz, H-7'), 3.08 (2 H, m), 3.36 (1 H, m, H-4), 3.42 (2 H, m), 3.75 (1 H, m, H-1), 3.94 (1 H, d, J = 2.4 Hz, H-3endo), 6.50 (1 H, dd, J = 5.4 and 2.7 Hz, H-5), 6.78 (1 H, dd, J = 5.4 and 3.0 Hz, H-6), 7.25-7.39 (5 H, m, Ar).

endo-8Cc: 57% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.72 (1 H, d, J = 9.0 Hz, H-7), 2.64 (1 H, d, J = 9.0 Hz, H-7'), 3.32 (1 H, m, H-4), 3.39 (1 H, m, H-1), 4.60 (1 H, d, J = 2.7 Hz, H-3exo), 6.47 (1 H, dd, J = 5.4 and 2.9 Hz, H-5), 6.49 (1 H, m, Ar), 6.97 (1 H, dd, J = 5.4 and 2.9 Hz, H-6), 7.20-8.25 (12 H, series of m, Ar).

exo-8Cc: 38% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.81 (1 H, d, J = 8.9 Hz, H-7), 3.19 (1 H, m, H-4), 3.28 (1 H, d, J = 8.9 Hz, H-7'), 3.40 (1 H, m, H-1), 4.24 (1 H, d, J = 2.5 Hz, H-3endo), 6.30 (1 H, dd, J = 5.3 and 2.9 Hz, H-5), 6.32 (1 H, m, Ar), 6.62 (1 H, dd, J = 5.3 and 2.8 Hz, H-6), 7.20-8.25 (12 H, series of m, Ar).

endo-8Db: 78% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.16 (3 H, d, J = 7.5 Hz, -CH_3), 1.36 (1 H, d, J = 9.9 Hz, H-7), 2.16 (1 H, d, J = 9.9 Hz, H-7'), 2.89 (1 H, m, H-4), 2.23 (1 H, m, H-1), 3.70 (1 H, qd, J = 7.5 and 3.3 Hz, H-3exo), 6.47 (2 H, m, H-5 and H-6), 7.20-8.20 (12 H, series of m, Ar).

exo-8Db: 20% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.42 (3 H, d, J = 7.2 Hz, -CH_3), 1.60 (1 H, d, J = 9.6 Hz, H-7), 2.62 (1 H, m, H-4), 2.69 (1 H, d, J = 9.6 Hz, H-7'), 3.03 (1 H, qd, J = 7.2 and 2.4 Hz, H-3endo), 3.23 (1 H, m, H-1), 6.05 (1 H, dd, J = 5.7 and 2.7 Hz, H-6), 6.47 (1 H, dd, J = 5.7 and 3.0 Hz, H-5), 7.20-8.20 (12 H, series of m, Ar).

endo-8Dc: 56% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.52 (1 H, d, J = 9.4 Hz, H-7), 2.33 (1 H, d, J = 9.4 Hz, H-7'), 3.26 (1 H, m, H-1), 3.49 (1 H, m, H-4), 5.05 (1 H, d, J = 3.2 Hz, H-3exo), 6.86 (1 H, dd, J = 5.1 and 2.9 Hz, H-5), 6.70 (1 H, dd, J = 5.1 and 3.4 Hz, H-6), 7.05-8.40 (17 H, series of m, Ar).

exo-8Dc: 39% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.86 (1 H, dd, J = 8.6 and 2.4 Hz, H-7), 3.19 (1 H, m, H-1), 3.34 (1 H, m, H-4), 3.37 (1 H, d, J = 8.6 Hz, H-7'), 4.31 (1 H, d, J = 2.4 Hz, H-3endo), 6.25 (1 H, dd, J = 5.4 and 2.4 Hz, H-5), 6.66 (1 H, dd, J = 5.4 and 3.4 Hz, H-6), 7.05-8.40 (17 H, series of m, Ar).

8Dd (major diastereoisomer): ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.20-1.40 (3 H, series of m, H-3endo, H-7 and H-7'), 2.22 (1 H, ddd, J = 13.1, 10.9 and 1.5 Hz, H-3exo), 2.97 (2 H, m, H-1 and H-4), 3.99 (1 H, m, H-2), 6.05 (1 H, dd, J = 9.0 and 5.1 Hz, H-5 or H-6), 6.30 (1 H, dd, J = 9.0 and 5.3 Hz, H-6 or H-5), 7.15-8.40 (13 H, series of m, H-8 and Ar).

9: 90% yield; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.10 (1 H, ddd, J = 13.2, 4.8 and 3.3 Hz, H-3endo), 1.20-1.82 (4 H, series of m, H-7, H-7', H-8 and H-8'), 2.17 (1 H, ddd, J = 13.2, 11.1 and 2.1 Hz, H-3exo), 2.47 (1 H, m, H-4), 3.31 (3 H, s, OCH_3), 4.09 (1 H, ddd, J = 11.1, 9.6 and 4.8 Hz, H-2), 6.26 (1 H, d, J = 8.4 Hz, H-6), 6.36 (1 H, dd, J = 8.4 and 6.3 Hz, H-5), 7.29 (1 H, d, J = 9.6 Hz, H-9), 7.14-8.34 (12 H, series of m, Ar).

General Procedure for the Cycloaddition Reactions in 5 M Lithium Perchlorate in Ether. A screw-capped, Pyrex test-tube was charged with anhydrous lithium perchlorate (1.5 g), the dienophile (5 mmol), the diene (20 mmol) and dry ethyl ether (3 mL) and placed into an ultrasonic bath for the reported period of time (Table II). During the sonication, the ultrasonic bath warmed to *ca.* 40-50 °C and the reaction mixture became homogeneous. The ether was removed by rotoevaporation,

dichloromethane (*ca.* 75 mL) was added and the solution was washed with water (3 x 50 mL). After drying (Na_2SO_4) and rotoevaporation of the solvent, the crude adducts were purified by flash-chromathography eluting with dichloromethane.

10Ab: 98% yield. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.22 (3 H, d, J = 7.2 Hz, CH_3), 1.45 (1 H, d, J = 10.5 Hz, H-9), 2.34 (1 H, t, J = 7.5 Hz, H-5), 2.36 (1 H, d, J = 10.5 Hz, H-9'), 2.73 (1 H, d, J = 7.5 Hz, H-2), 2.92 (1 H, broad s, H-6), 3.06 (1 H, dq, J = 7.5 and 7.2 Hz, H-4), 3.31 (1 H, broad s, H-1), 6.09 (2 H, m, H-7 and H-8), 7.55-8.05 (10 H, series of m, Ar).

10Ac: 99% yield. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.42 (1 H, dt, J = 9.9 and 0.3 Hz, H-9), 2.35 (1 H, dd, J = 9.9 and 0.3 Hz, H-9'), 2.77 (1 H, dd, J = 7.8 and 7.5 Hz, H-5), 2.89 (1 H, dd, J = 7.5 and 0.3 Hz, H-2), 2.96 (1 H, m, H-1 or H-6), 2.99 (1 H, m, H-1 or H-6), 4.59 (1 H, d, J = 7.8 Hz, H-4), 6.04 (1 H, dd, J = 5.4 and 3.0 Hz, H-7 or H-8), 6.11 (1 H, dd, J = 5.4 and 3.3 Hz, H-7 or H-8), 6.98-8.20 (15 H, series of m, Ar).

10Bc: 80% yield. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.53 (1 H, d, J = 10.5 Hz, H-9), 1.91 (1 H, d, J = 10.5 Hz, H-9'), 2.76 (1 H, broad s, H-6), 2.80 (2 H, m), 2.95 (1 H, broad s, H-1), 3.37 (1 H, m), 3.57-3.65 (3 H, series of m), 4.25 (1 H, m, H-4), 6.08 (1 H, dd, J = 6.1 and 2.4 Hz, H-7 or H-8), 6.11 (1 H, dd, J = 6.1 and 2.9 Hz, H-7 or H-8), 7.20-7.40 (5 H, series of m, Ar).

11: 90% yield, ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.46 (1 H, ddd, J = 19.2, 4.5 and 3.3 Hz, H-6 or H-6'), 3.02 (1 H, ddd, J = 19.2, 6.9 and 1.2 Hz, H-6 or H-6'), 3.35 (3 H, s, OCH_3), 4.38 (1 H, dd, J = 6.9 and 4.5 Hz, H-5), 4.66 (1 H, broad s, H-3), 5.86 (2 H, m, H-1 and H-2), 7.20-7.70 (15 H, series of m, Ar).

12Ab: 95% yield. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.09 (3 H, d, J = 10.2 Hz, CH_3), 2.24-2.76 (4 H, series of m), 2.87 (1 H, ddq, J = 13.2, 12.9 and 10.2 Hz, H-5), 3.06 (1 H, d, J = 12.9 Hz, H-6 or H-6'), 3.12 (1 H, d, J = 13.2 Hz, H-6 or H-6'), 7.58-8.18 (10 H, series of m, Ar).

12Ac: 90% yield. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.69-2.92 (4 H, series of m), 3.13 (1 H, d, J = 7.2 Hz, H-2 or H-6 or H-6'), 3.15 (1 H, d, J = 7.2 Hz, H-6 or H-6'), 4.27 (1 H, t, J = 7.2 Hz, H-5), 7.05-8.10 (15 H, series of m, 15 H).

(*Z*)-14: 35% yield. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.43 (1 H, m, H-4), 3.81 (1 H, m, H-4), 3.96 (1 H, m, H-5), 4.77 (1 H, d, J = 1.0 Hz, H-6), 5.78 (1 H, dddd, J = 11.1, 9.0, 1.2 and 1.1 Hz, H-2), 6.29 (1 H, ddd, J = 11.1, 6.2 and 6.0 Hz, H-3), 7.30-7.85 (15 H, series of m, Ar), 9.85 (1 H, d, J = 9 Hz, CHO).

(*E*)-14: 65% yield. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.03 (1 H, dddd, J = 16.2, 6.3, 3.0 and 1.6 Hz, H-4), 3.65 (1 H, dddd, J = 18.6, 16.2, 6.1 and 1.5 Hz, H-4), 3.93 (1 H, ddd, J = 18.6, 6.9 and 1.5 Hz, H-5), 4.75 (1 H, d, J = 1.5 Hz, H-6), 5.86 (1 H, dddd, J = 15.6, 8.1, 1.6 and 1.5 Hz, H-2), 6.50 (1 H, ddd, J = 15.6, 6.3 and 6.1 Hz, H-3), 7.30-7.80 (15 H, series of m, Ar), 9.28 (1 H, d, J = 8.1 Hz, CHO).

17: 99% yield. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.22 (1 H, dd, J = 18.0 and 2.7 Hz, H-4), 4.55 (1 H, ddd, J = 10.8, 2.7 and 2.6 Hz, H-5), 3.82 (1 H, dd, J = 18.0 and 10.8 Hz, H-4), 3.64 (3 H, s, OCH_3), 4.53 (1 H, d, J = 12.6 Hz, H-1 or H-2), 4.81 (1 H, d, J = 2.6 Hz, H-6), 7.10-7.94 (16 H, series of m, Ar and H-2 or H-1).

18: Obtained in quantitative yield from **17** in $CDCl_3$. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.25 (1 H, dd, J = 17.5 and 3.2 Hz, H-4), 3.82 (1 H, dd, J = 17.5, and 9.9 Hz, H-4), 4.59 (1 H, ddd, J = 9.9, 3.2 and 1.3 Hz, H-5), 4.82 (1 H, d, J = 1.3 Hz, H-6), 4.58 (1 H, d, J = 12.8 Hz, H-1 or H-2), 7.10-7.95 (16 H, series of m, Ar and H-2 or H-1).

Reaction of 12Ac with sodium methoxide (19): A solution of **12Ac** (100 mg, 0.025 mmol) in methanol (*ca.* 10 mL) containing sodium methoxide (13.8 mg, 0.25 mmol) was refluxed for 12 h. The reaction mixture was washed with saturated ammonium chloride and extracted with dichloromethane (3 x 50 mL), dried (Na_2SO_4) and rotoevaporated: 90 mg, 90% yield, mp 115 °C (CH_2Cl_2-petroleum ether). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.51 (2 H, q, J = 6.6 Hz, H-4), 3.18 (2 H, t, J = 6.6 Hz, H-3), 4.85 (1 H, t, J = 6.6 Hz, H-5), 6.63 (1 H, d, J = 16.2 Hz, H-1), 7.50 (1 H, d, J = 16.2 Hz, H-2), 7.30-7.94 (15 H, series of m, Ar). IR (KBr, cm^{-1}) 3050 (w), 2965 (w), 1685 (m), 1655 (m), 1610 (m), 1450 (s), 1375 (s), 1150 (m), 725 (s).

General Procedure for the Sodium Amalgam Reduction of the Diels-Alder Adducts. Sodium amalgam (6% by weight Na/Hg, 3.6 mmol) was added in small portions under argon to the heterogeneous mixture formed by the Diels-Alder

adduct (0.44 mmol), sodium dihydrogenphosphate (7.7 mmol) and methanol (*ca.* 10 mL) and stirred at room temperature for 12 h. Water was added and the organics were extracted with pentane (3 x 50 mL). After drying ($MgSO_4$) and rotoevaporation of the solvent the hydrocarbonic product was obtained virtually pure as determined by NMR.

exo-**21**: 90% yield, oil. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.05 (1 H, dt, J = 9.5 and 1.5 Hz), 1.22 (1 H, dt, J = 9.5 and 1.3 Hz), 1.40 (1 H, dt, J = 10.2 and 1.6 Hz), 1.48 (1 H, d, J = 10.2 Hz), 1.52 (1 H, m), 1.96 (1 H, m), 2.83 (1 H, m), 7.18 (2 H, m), 7.23 (5 H, m, Ar). MS (70 eV): 170 (80%, M^+), 142 (100%), 93 (40%), 77 (15).

22: 95% yield, oil. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.45 (1 H, d, J = 9.0 Hz, H-9 or H-9'), 1.90 (1 H, d, J = 9.0 Hz, H-9 or H-9'), 1.92 (1 H, m), 2.10-2.26 (3 H, series of m), 2.82 (1 H, m), 2.78 (1 H, m, H-1 or H-6), 2.83 (1 H, m, H-1 or H-6), 6.03 (1 H, dd, J = 5.7 and 3.0 Hz, H-7 or H-8), 6.09 (1 H, dd, J = 5.7 and 3.0, H-7 or H-8), 7.10-7.40 (5 H, m, Ar). ^{13}C-NMR ($CDCl_3$, 74.5 MHz) d 28.74, 33.57, 38.88, 40.55, 44.05, 44.25, 45.45, 125.41, 126.70, 128.17, 134.82, 135.66, 147.65.

23: 93% yield, oil. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.20-2.20 (10 H, series of m), 3.70 (1 H, m, H-3), 7.20-7.35 (5 H, series of m, Ar). IR (KBr, cm^{-1}) 3370 (m), 2925 (s), 1440 (m), 740 (s), 700 (s).

References and Notes

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(2) Througout the paper, the upper case letter referes to the thioresidue (**A**: Ph; **B**: -CH_2CH_2-; **C**: 2,2'-biphenyl; **D**: 1,1'-binaphtho-2,2'-diyl) and the lower case letter to the alkene substituent (**a**: R = H; **b**: R = Me; **c**: R = Ph; **d**: R = CH_2=CH_2).

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