2-Chloro-1,4-benzodithiin 1,1,4,4-Tetraoxide – A Conjunctive Dienophile for the Preparation of Tetrasubstituted Polycyclic Olefins

Ottorino De Lucchi, and Sergio Cossu

Dipartimento di Chimica, Università Ca′ Foscari di Venezia,
Dorsoduro 2137, I-30123 Venezia, Italy
Fax: (internat.) + 39-41/257-8517

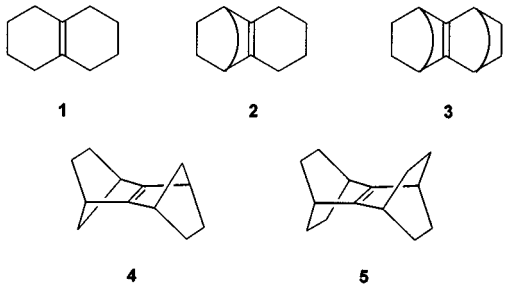
Received June 26, 1998

Keywords: Heterocycles / Cycloadditions / Diatomic carbon / Sulfones / Alkenes / Polycycles

2-Chloro-1,4-benzodithiin 1,1,4,4-tetraoxide **11** is a reactive dienophile that forms Diels-Alder adducts with a number of dienes. Adducts **17a–j** undergo facile dehydrochlorination to give 2,3-substituted 1,4-benzodithiin tetraoxides **18a–j**, which react further with another molecule of diene (the same or a different one) affording the "double" adducts **19–23**. Upon reductive desulfonylation with sodium amalgam, the latter are transformed to tetrasubstituted polycyclic olefins **24–27**. These olefins correspond to the cycloadducts that would theoretically have been formed by the cycloaddition of diatomic carbon with two molecules of diene, reacting in a Diels-Alder fashion.

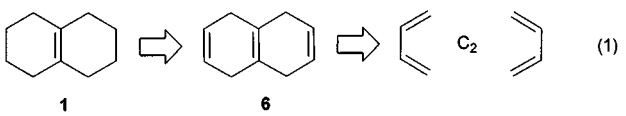
Introduction

Unsaturated polycyclic hydrocarbons of types **1−3** are molecules of interest both from the synthetic and theoretical points of view. They exhibit peculiar geometrical and electronic features, as in the case of sesquinorbornene **4**[1] or of tetrahydrosesquibarrelene **5**.[2] The molecules **4** and **5**, as well as many other tetrasubstituted olefins of this type, are difficult to prepare and a general method for the synthesis of members of this class of compounds is still lacking.



1 **2** **3** **4** **5**

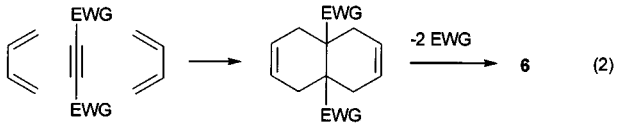
In principle, a very simple and rapid method would be a double Diels-Alder cycloaddition on a molecule composed of only two carbons, i.e. diatomic carbon C_2, followed by hydrogenation, as illustrated retrosynthetically for the simplest case of **1** in Eq. 1.



1 **6** (1)

The actual C_2 molecule has received attention, in particular with regard to theoretical,[3] spectroscopic,[4a] and kinetic aspects,[4b] and, more recently, its reactivity was also studied in some detail.[4c] Molecular C_2, generated by vaporizing carbon in an arc,[5] reacts with most classes of compounds[6] such as alcohols, ketones, aldehydes, alkanes, alkenes, and ethers, showing radical behavior.[1a][2][3][4][5][6][7] Research in this area has been further stimulated in recent years by the discoveries of the fullerenes, where C_2 has been postulated to play a role in their formation.[8] The uncertainties regarding the mechanism by which fullerenes are formed and a widely sought classical synthesis of C_{60} and other fullerenes[9] may well take advantage of chemical alternatives to C_2 and of newer syntheses of alkenes of the types **1−3**.

From a synthetic point of view, having established that dicarbon is too reactive to find useful applications and that a Diels-Alder reactivity is far even from any speculation, the alternative is to define reagents able to perform a double cycloaddition on the same carbon−carbon unit. In other words, to define a reagent able to perform as a synthon for diatomic carbon, mimicking its hypothetical reactivity in cycloaddition reactions. Indeed, such a "C_2-like" reagent would be an acetylene substituted with electron-withdrawing groups (EWG) that activate the Diels-Alder reaction[10] and that can be eliminated from the adducts with the formation of the requisite internal unsaturation, as shown in Eq. 2.

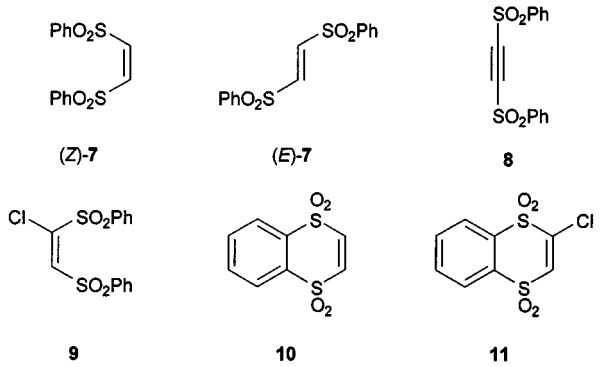


(2)

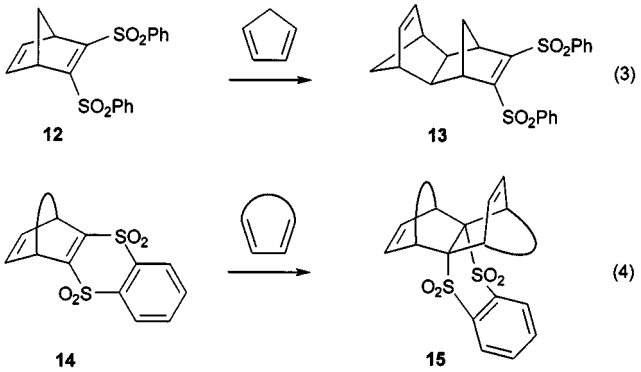
Most of the known and stable acetylenes bearing two electron-withdrawing groups, such as the dicarboxy,[11] or the dicyano derivatives,[12] do induce high activation, but the removal of the carboxy or cyano functionalities is not

  1434−193X/98/1212−2775 $ 17.50+.50/0

easy. Groups which exhibit good activating properties and which are also readily removable under mild conditions are arylsulfonyl functions, as exemplified by the bis(phenylsulfonyl)ethylenes (*Z*)- and (*E*)-**7**, which are known to act as acetylene equivalents in cycloaddition reactions.[13] Unfortunately, the related bis(phenylsulfonyl)acetylene **8** is unstable, although it can be generated and reacted in situ with a few dienes.[14] An alternative to bis(phenylsulfonyl)acetylene **8** is (*E*)-bis(phenylsulfonyl)chloroethylene **9**, for which we have already reported on the dienophilic reactivity and synthetic utility.[15]



The cycloadducts derived from **9**, once dehydrochlorinated, correspond to the cycloadducts of less stable bis(phenylsulfonyl)acetylene **8**,[15] hence **9** can be viewed as a synthetic equivalent of **8**. The adducts derived from **8** or **9** are not reactive in cycloaddition reactions with dienes. For example, 2,3-bis(phenylsulfonyl)norbornadiene **12** reacts with cyclopentadiene at the less activated double bond, giving the "wrong" adduct **13** (Eq. 3).[16]

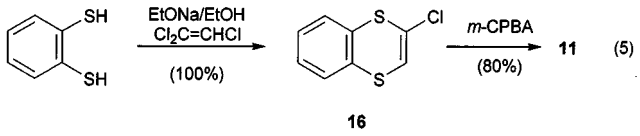


In view of the higher reactivity reported for **10**[17] compared with that of (*E*)- and (*Z*)-**7**, and also in view of the lesser steric hindrance provided by the benzodithiin tetraoxide group in **14** compared with that of the two phenylsulfonyl groups in **12**, it was thought that adducts **14** might also have been more reactive and able to offer the desired reactivity.[18] As shown in Eq. 4, this was indeed found to be the case, and herein we report in full on the chemistry of 2-chloro-1,4-benzodithiin 1,1,4,4-tetraoxide **11** and of its dehydrochlorinated adducts **14**, together with representative examples of syntheses of tetrasubstituted olefins.

Results and Discussion

Preparation of Dienophile 11

The preparation of dienophile **11** was carried out most conveniently by the reaction sequence shown in Eq. 5. Benzene-1,2-dithiol is available by numerous routes, some of which can be conducted on a large scale.[19] Treatment of the disodium salt of benzene-1,2-dithiol in ethanol with trichloroethylene affords 2-chloro-1,4-benzodithiin **16** in quantitative yield, by direct substitution of two chlorine atoms. Compound **16** can then be oxidized with *m*-chloroperbenzoic acid (*m*-CPBA) or alternatively with H_2O_2/AcOH to give **11** in 80% yield (Eq. 5).



Cycloaddition of 11 to Dienes

Compound **11**, employed as the dienophile in the cycloaddition reactions, exhibits sufficient reactivity to afford adducts with almost any diene. As standard practice, the simplest adduct **17a** with 1,3-butadiene was obtained by in situ generation of the diene from 3-sulfolene at 60°C, via retrocheleotropic SO_2 elimination. Adduct **17a** was formed in quantitative yield. The cycloaddition occurred at room temperature within a few hours with cyclopentadiene and furan to afford cycloadducts **17b** and **17c**, respectively, also in quantitative yields. A somewhat longer time was required for quadricyclane to form the adduct **17d**, but higher temperatures were avoided in this case to prevent retrocyclization of the quadricyclane to norbornadiene. As with most other C=C dienophiles, for less reactive dienes such as 1,3-cyclohexadiene, 1,3-cycloheptadiene, diphenylfulvene, norbornadiene, and anthracene, **11** also requires higher temperatures. In our hands, refluxing toluene proved to give the best results. Under these conditions, however, 1,3,5,7-cyclooctatetraene (COT) afforded only polymeric compounds and for this diene it was necessary to carry out the reaction under high pressure (15 kbar, 48 h, room temp.). Under these conditions, cycloadduct **17j** was obtained quantitatively. Adducts **17a–j** are depicted in Figure 1.

Experimental data for the synthesis of cycloadducts **17a–j** and *endo-exo* ratios, where appropriate, are summarized in Table 1.

Compound **11** adds to cyclic dienes according to the Alder rule, the *endo* adducts shown in the structures **17a–j** being the predominant or exclusive products. The *endo* structure was established by analysis of the ^{1}H-NMR data, especially upon consideration of the coupling constants between the protons α to the sulfonyl group and the vicinal bridgehead proton, as well as by measurement of NOE enhancements. NOE data were especially useful for the assignment of the configuration of the adducts with quadricyclane and norbornadiene, **17g** and **17h**, respectively.

Figure 1. Adducts of **11** to dienes

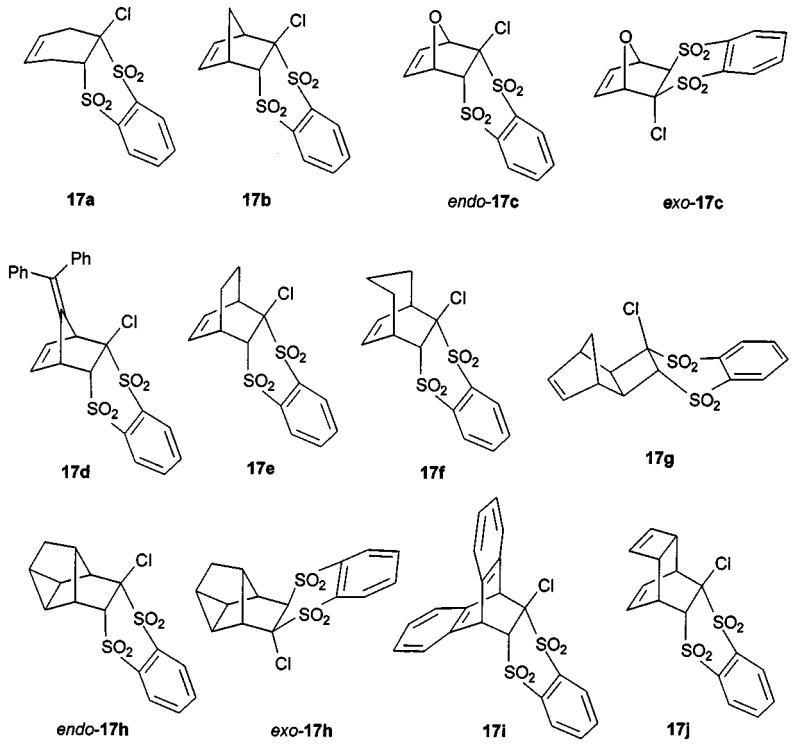


Table 1. Reaction conditions, and *endo/exo* ratios for the adducts of **11** with dienes

diene	adduct	solvent	temp. [°C]	time	*endo/exo* ratio
1,3-butadiene[a]	**17a**	neat	60	24 h	–
cyclopentadiene	**17b**	CH_2Cl_2	rt	5 h	100:0
furan	**17c**	CH_2Cl_2	rt	24 h	87:13
diphenylfulvene	**17d**	toluene	100	10 h	100:0
1,3-cyclohexadiene	**17e**	toluene	105	24 h	100:0
1,3-cycloheptadiene	**17f**	toluene	115	6 d	100:0
quadricyclane	**17g**	CH_2Cl_2	rt	7 d	0:100
norbornadiene	**17h**	toluene	120	72 h	60:40
anthracene	**17i**	toluene	110	24 h	–
1,3,5,7-cyclooctatetraene[b]	**17j**	CH_2Cl_2	rt	48 h	100:0

[b] Reaction carried out at high pressure (ca. 15 kbar).

The ^{1}H-NMR spectra of the adducts with 1,3-cyclohexadiene **17e** and with 1,3-heptadiene **17f** show broad signals for the vinyl protons. This fact can be attributed to a fluxional behaviour of these molecules in solution, as observed by Licini et al. in similar molecules.[20] In the case of the reaction with anthracene, the adduct **17i** could not be isolated because it spontaneously underwent dehydrochlorination to give **18i**.

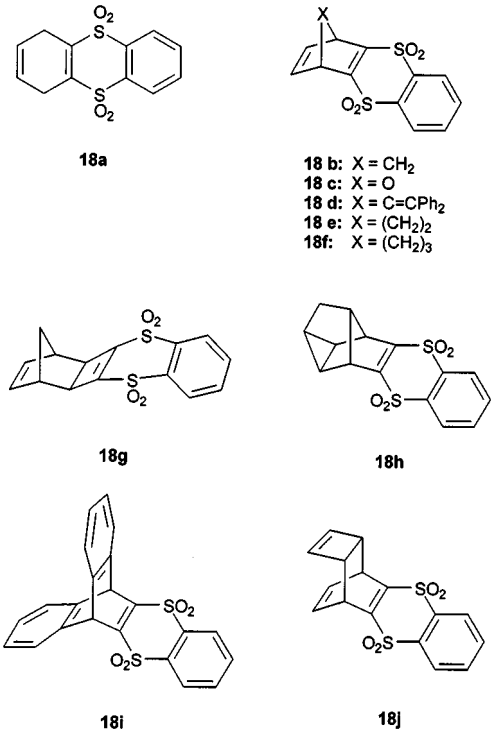
Dehydrochlorination of Adducts 17a–j

Cycloadducts **17a–j** (Figure 2) are readily dehydrochlorinated within a few minutes with triethylamine in acetonitrile, affording **18a–j** in very high yields as a result of a *syn*-coplanar elimination.[21] It should be noted that it was necessary to use strictly one equivalent of triethylamine and short reaction times in order to maximize yields. The adduct of **11** with 1,3-butadiene **18a** could not be isolated as it underwent spontaneous oxidation to thianthrene tetraoxide. Since it was considered as being of little practical use, it was not studied further. The adduct derived from furan **17c** resisted dehydrochlorination with triethylamine, even after prolonged reaction times and at reflux temperature. Eventually, it was found that **17c** could be dehydrochlorinated to **18c** in 70% yield with *n*-butyllithium.

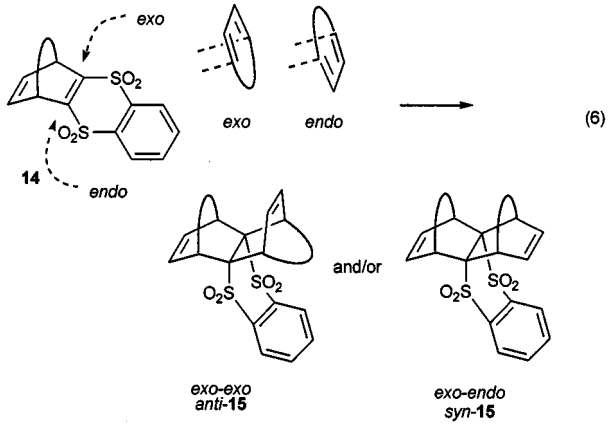
Cycloaddition of 18a–e to Dienes

Generally, compounds **18a–e** reacted with various dienes under rather mild reaction conditions to afford addition products to the bis(sulfonyl)-activated double bond. In principle, four possible stereoisomers can be formed, depending on the *exo* or *endo* approach to the diene, and on the *exo* or *endo* orientation of the diene (Eq. 6). Two out

Figure 2. Dehydrochlorinated adducts derived from **17a−j**

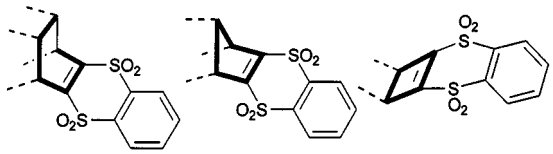


of the four possible stereoisomers are generally observed: the *exo-exo* and the *exo-endo* forms, as indicated in Eq. 6.



For the sake of simplicity, the *exo-exo* isomer is referred to as the *anti* isomer **15**, while the *exo-endo* isomer is classified as the *syn* isomer **15**. The substrates and dienes used, along with the experimental conditions and the *anti:syn* ratios obtained are reported in Table 2.

The possibility of introducing dienes in two independent steps allowed us to produce symmetrical and unsymmetrical polycycles amenable to reductive desulfonylation, facilitating the preparation of complex polycyclic olefins. The structures of the bis-adducts were elucidated by NMR spectrometry and confirmed in the case of **21c** by X-ray analysis.[22] The results are discussed in the appropriate section. Three types of dienophiles can be considered, as classified below. They are differentiated according to the size of the ring fused to the 1,4-benzodithiin moiety, which is six-membered in **18e**,**i**,**j**, five-membered in **18b−d**,**h**, and four-membered in **18g**.



In general, the reactivity increases with decreasing ring size. Thus, while all of the systems were reactive towards 1,3-butadiene (generated from 3-sulfolene at 60°C), only the four-membered ring **18g** and the five-membered rings **18b**,**d**,**h** reacted with cyclopentadiene and furan.

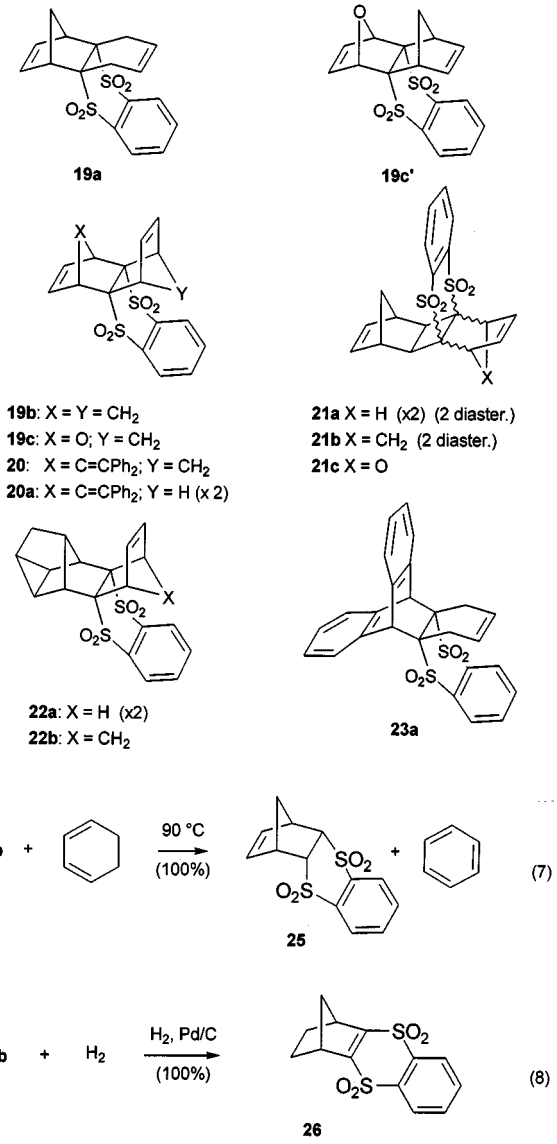
The reaction invariably takes place at the *exo* side of the dienophile **18** (Eq. 6), in line with expectation, while the orientation of the incoming diene is in most cases *exo* (Eq. 6), i.e. contrary to the Alder rule, giving rise predominantly or exclusively to *anti*-type adducts. Thus, 1,3-butadiene reacts with **18b**,**d**,**g**,**h**,**i** to afford adducts **19a** and **21a−23a** (Table 2) resulting from cycloaddition to the *exo* side of **18**. Cyclopentadiene reacts with **18b**,**d**,**h** within a few hours at 80°C affording **19b**, **20**, and **22b** as purely *anti* adducts, while reaction with **18g** affords a mixture of *anti* **21b** and *syn* **21b′** in an equimolar ratio. Furan reacts with **18b** and **18g** at room temperature affording the *anti*-isomers **19c** and **21c** and the isomer *syn*-**19c′**. By monitoring the reaction by ^{1}H-NMR, we established that **19c′** represents the kinetic product and it is the first and only compound formed after

Table 2. Reaction conditions and *anti/syn* ratios for the adducts of **18b**, **18d**, **18g**, and **18h** with dienes

substrate	diene	adduct	solvent	temp. [°C]	time	*anti/syn* ratio
18b	1,3-butadiene[a]	**19a**	neat	60	24 h	−
	cyclopentadiene	**19b**	CH_2Cl_2	80	12 h	100:0
	furan	**19c**,**19c′**	CH_2Cl_2	rt	7 d	50:50
18d	cyclopentadiene	**20**	CH_2Cl_2	80	5 h	100:0
	1,3-butadiene[a]	**20a**	neat	60	24 h	−
18g	1,3-butadiene[a]	**21a**	neat	60	24 h	−
	cyclopentadiene	**21b**	CH_2Cl_2	80	7 h	50:50
	furan	**21c**	CH_2Cl_2	rt	7 d	100:0
18h	1,3-butadiene[a]	**22a**	neat	60	10 h	−
	cyclopentadiene	**22b**	CH_2Cl_2	80	12 h	100:0
18i	1,3-butadiene[a]	**23a**	neat	60	10 h	−

[a] Generated in situ from 3-sulfolene at 60°C.

Figure 3. Bis-adducts of **18b−j** with dienes



short reaction times, while **19c** is formed during the time required to fully consume the reactants. The stereochemistry of addition to dienophile **18g**, i.e. the one example of a four-membered ring system studied, requires further comment. The products of the additions of cyclopentadiene and furan, **21b** and **21c**, have been identified as having the stereochemistry that arises from a below plane attack, i.e. at the non-substituted part of the cyclobutene ring, whereas 1,3-butadiene does not appear to be selective in this respect and its reaction affords equal proportions of the adducts arising from attack at either side.[18]

Reactions of **18b** with other dienes were also studied. For example, reaction of **18b** with 1,3-cyclohexadiene at 90°C affords, completely selectively, only the *endo* hydrogenated compound **25** (Eq. 7). The structure of product **25** was confirmed by an independent cycloaddition of 1,4-benzodithiin 1,1,4,4-tetraoxide **10** to cyclopentadiene.

This result is indicative of an electronic interaction between the dienophile and the sulfonyl-activated alkene, with formation of a charge-transfer complex that does not evolve into a Diels-Alder adduct, but rather to the hydrogenated product and benzene. Indeed, the ability of cyclohexadienes to act as hydrogenating agents is known.[23] It should be noted that hydrogenation under standard reaction conditions, i.e. with hydrogen gas and Pd/C catalyst, gives rise to the product **26**, hydrogenated at the unsubstituted side (Eq. 8). Such behaviour is similar to that observed with the bis(phenylsulfonyl) derivative **12**.[24]

Structure Determinations

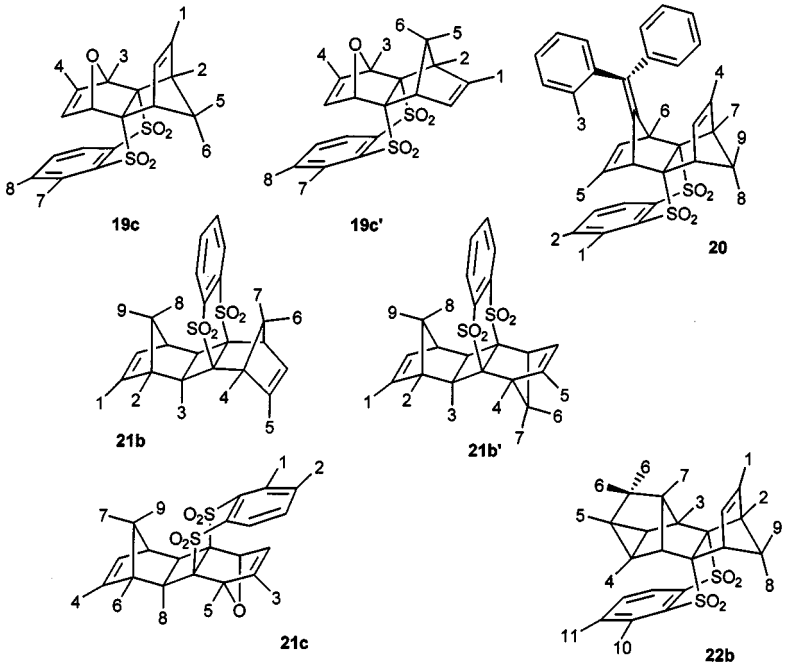
The structures of compounds **19c**, **19c′**, **20**, **21b**, **21b′**, **21c**, and **22** were largely determined using ^{1}H-NMR techniques, e.g. by monodimensional differential NOE spectroscopy and by decoupling experiments. The results of the NOE experiments were corroborated on the basis of the theoretically determined atom distances in the structures of all four possible stereoisomers, minimized with a Spartan program at the PM3 level.

In **19c**, the vinylic H4 (δ = 6.17) is easily differentiated from H1 (δ = 6.40) because the latter is coupled with the apical H6 (δ = 3.16) and with the bridgehead H2 (δ = 3.78). In addition, H1 shows an NOE with H5 (δ = 1.89). Strong NOE interactions are also observed between H2 and the other bridgehead H3 (δ = 4.89), between the vinylic H4 and the aromatic H7 (δ = 7.98−8.02) and the bridgehead H3, thus indicating the *endo* orientation of the aromatic ring relative to the 7-oxa-substituted bicyclic moiety, as shown in Figure 4. On the basis of similar considerations, vinylic H1 (δ = 6.57), vinylic H4 (δ = 6.33), bridgehead H2 (δ = 3.66), bridgehead H3 (δ = 5.28), apical H5 (δ = 3.16), and apical H6 (δ = 1.61) can be assigned in the case of **19c′**, Particularly diagnostic for the differentation of **19c′** from **19c** is the strong NOE interaction between the bridgehead H3 and apical H6.

In compound **20**, the AA′BB′ system of the bis(phenylsulfonyl)-substituted aromatic ring allows its differentiation from the apical phenyl rings. The vinylic H4 (δ = 6.45) is coupled with the apical H8 (part of an AB system at δ = 3.38) and with the bridgehead H7 (δ = 3.70), while the vinylic H5 (δ = 6.15) is coupled only with the bridgehead H6 (δ = 3.86). H8 is coupled with the vicinal H9 (part of AB system at δ = 1.98), which shows an NOE with the vinylic H4. Informative NOE interactions are observed between aromatic H3 (δ = 6.90−7.05) and vinylic H4, confirming their adjacent positions, and between aromatic H1 (AA′BB′ system at δ = 8.00−8.05) and vinylic H5, indicating that the bis(phenylsulfonyl)-substituted aromatic ring is orientated *endo* to the apical substituted norbornene system.

In **21b**, the coupling of H3 (δ = 1.60) with H9 (δ = 0.90) permits discrimination between the two apical systems composed of H9, H8 (δ = 1.18), and H7 (δ = 2.05), and H6 (δ = 2.54), respectively, as AB systems. Proton H9 gives an AB system with the vicinal H8, which is also coupled with the vinylic H1 (δ = 5.99). Consequently, the remaining vi-

Figure 4. ChemDraw representations with arbitrary numbering of **19c**, **19c′**, **20**, **21b**, **21b′**, **21c** and **22** based on PM3 computations



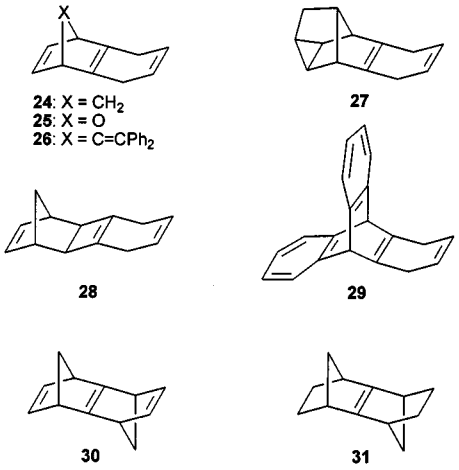
nylic system is H5 (δ = 6.58), which is coupled with H7 and with H4 (δ = 3.92). Proton H2 (δ = 3.41) is coupled with H8 and H9. Diagnostic interactions between H3 and vinylic H5 are revealed by NOE experiments.

For the second isomer **21b′**, similar considerations lead to the following assignments: H6 (δ = 1.55), H8 (δ = 1.66), H7 (δ = 2.10), H3 (δ = 2.28), H9 (δ = 3.11), H4 (δ = 3.53), H2 (δ = 3.66), H5 (δ = 5.89), H1 (δ = 6.17), H11 (δ = 7.68−7.73) and H10 (δ = 7.90−7.95). Furthermore, a strong NOE interaction between H3 and the apical H7 is consistent with the proposed structure.

In **21c**, the bridgehead H6 (δ = 3.64) is coupled with both the apical H7 (δ = 2.93) and H9 (δ = 1.69), and shows a strong NOE with the vinylic H4 (δ = 6.16) and with H8 (δ = 2.42). Proton H5 (δ = 5.10) exhibits NOE interactions with H3 (δ = 6.18) and with H8. Particularly informative in this case is the reciprocal interaction between aromatic H1 (δ = 7.95) and the vinylic H3.

The structure of **22b** is assigned on the basis of the strong NOE′s observed between H7 (δ = 3.08) and the vinylic H1 (δ = 6.47), and between aromatic H10 (δ = 8.09−8.16) and H4 (δ = 0.76).

Figure 5. Polycyclic olefins obtained by reductive desulfonylation



Reductive Desulfonylation

The reduction of compounds **19a**, **19b**, **20a**, **21a**, **22a**, **22b**, **23a** with sodium amalgam (6%) in buffered methanol gave the polycyclic hydrocarbons **24−31**.

The generation of compounds **24−29**, which contain the 1,4-cyclohexadiene moiety, proved to be particularly efficient. These polycyclic olefins appear to be more stable than olefins generated by more complex substrates. On being left to stand in air or upon mild oxidation, they are transformed into the corresponding aromatic hydrocarbons, thus providing an alternative to the use of benzyne in cycloaddition reactions.[18] Triene **30** is rather reactive[25] and yields are poor. Sesquinorbornene **31** is more stable,[12] although it is very volatile and care had to be taken in order to avoid loss by evaporation. Substrates incorporating furan are also very sensitive.[26] In these cases, the products could be observed in the ^{1}H-NMR spectra of the crude reaction mixtures, albeit in a rather impure state. Because of the poor yields and the instability of these compounds, we did not proceed further with their purification.

We thank the *Regione Veneto, Department for Industry and Energy,* for financial support in purchasing the Varian Unity 400 NMR spectrometer. This work was supported by the *CNR* (Rome).

Experimental Section

General: Melting points are uncorrected. − ^{1}H- and ^{13}C-NMR spectra were recorded on Varian VXR 300 and Varian Unity 400 spectrometers. The NOED′S measurements were obtained on a Varian Unity 400 spectrometer. The lines of the selected signals were cyclically saturated for 0.05 s over a total time of 10 s, with the appropriate attenuation of the decoupling power. − IR spectra were recorded over the range 4000−600 cm^{-1} on Perkin-Elmer 983 or Bruker FT-IR spectrophotometers. − Microanalytical determinations were performed on a Perkin-Elmer 2400 analyzer. − Commercial high purity reagents and solvents were employed without further purification.

2-Chloro-1,4-benzodithiin (**16**): 1,2-Benzenedithiol (5.0 g, 35.21 mmol) was added to a solution of EtONa (1.61 g, 70.42 g atom of sodium metal in 150 ml of EtOH). The reaction mixture was stirred at room temp. for 10 min., trichloroethylene (4.65 g, 35.21 mmol) was added, and the stirred mixture was refluxed for a further 5 h under nitrogen. Water (150 ml) was then added and the ethanol was removed under reduced pressure. The residue was extracted with diethyl ether (3 × 100 ml), the combined extracts were washed with water, and dried over sodium sulfate. Rotary evaporation of the ether gave a pale-yellow oil (6.97 g, 98.6% yield). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.50 (s, 1 H), 7.22−7.28, 7.32−7.38 (m, 4 H, Ar). − IR (film): $\tilde{\nu}$ = 3051 cm^{-1}, 2921, 1611, 1567, 1440, 1426, 1255, 810, 776. − $C_8H_5ClS_2$: calcd. C 47.88, H 2.51; found C 47.60, H 2.80.

2-Chloro-1,4-benzodithiin 1,1,4,4-Tetraoxide (**11**): A mixture of **16** (6.8 g, 33.88 mmol), AcOH (70 ml), H_2O_2 (25 ml of a 35% solution), and sulfuric acid (1 ml) was stirred at 60°C for 2 h and then at reflux temperature for an additional 3 h. After cooling to room temp., water was added. The colorless crystalline solid that separated was washed several times with water, dried, and recrystallized from ethanol (6.5 g, 72.5% yield); m.p. 175−177°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (s, 1 H), 7.85−7.98, 8.12−8.27 (m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$, 2 C atoms omitted): δ = 125.58, 126.21, 134.16, 134.45, 135.54, 138.70. − IR (KBr disc): $\tilde{\nu}$ = 3027 cm^{-1}, 1580, 1560, 1358, 1305, 1231, 1175, 1120, 713, 783. − $C_8H_5ClO_4S_2$: calcd. C 36.29, H 1.90; found C 36.00, H 2.11.

4a-Chloro-1,4,4a,10a-tetrahydrothianthrene 5,5,10,10-Tetraoxide (**17a**): A mixture of **11** (3.0 g, 10.17 mmol) and 3-sulfolene (3.6 g, 30.51 mmol) was heated at 60°C for 24 h. The excess 3-sulfolene was then removed by sublimation and the solid residue was recrystallized from dichloromethane/diethyl ether (3.11 g, 96% yield); m.p. 207−209°C (CH_2Cl_2/Et_2O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.85−3.24 (m, 4 H), 4.67 (m, 1 H), 5.68−5.77 (m, 1 H), 5.88−5.97 (m, 1 H), 7.83−7.96, 8.04−8.09, 8.15−8.19 (each m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.45, 31.46, 64.88, 79.71, 120.18, 123.16, 125.72, 125.92, 131.81, 134.01, 135.26, 138.03. − IR (KBr disc): $\tilde{\nu}$ = 3087 cm^{-1}, 3047, 2958, 1429, 1385, 1338, 1321, 1163, 1153, 820, 688, 656. − $C_{12}H_{11}ClO_4S_2$: calcd. C 45.21, H 3.48; found C 44.98, H 3.60.

4a-Chloro-1,4,4a,10a-tetrahydro-1,4-methanothianthrene 5,5,10,10-Tetraoxide (**17b**): A mixture of **11** (6.5 g, 24.55 mmol), cyclopentadiene (1.62 g, 24.55 mmol), and dichloromethane (50 ml) was stirred at room temp. for 5 h. The colorless solid that precipitated was collected by filtration, washed several times with diethyl ether, and recrystallized from dichloromethane/diethyl ether (8.0 g, 98% yield); m.p. 271−272°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (dt, *J* = 9.6 and 1.5 Hz, 1 H), 2.20 (d, *J* = 9.6 Hz, 1 H), 3.63 (br s, 1 H), 3.66 (br s, 1 H), 4.55 (d, *J* = 3.3 Hz, 1 H), 5.73 (m, 1 H), 5.83 (m, 1 H), 7.80−7.87, 8.00−8.04, 8.10−8.13 (each m, 4 H, Ar). − ^{13}C NMR (100 MHz, 1:1 mixture of [D_6]DMSO/$CDCl_3$): δ = 46.58, 46.97, 57.05, 71.11, 88.83, 124.76, 124.92, 132.96, 133.41, 133.46, 135.55, 135.92, 136.47. − IR (KBr disk): $\tilde{\nu}$ = 3005 cm^{-1}, 2927, 1437, 1336, 1311, 1149, 1120, 897, 787, 768. − $C_{13}H_{11}ClO_4S_2$: calcd. C 47.20, H 3.35; found C 46.68, H 3.31.

4a-Chloro-1,4,4a,10a-tetrahydro-1,4-oxathianthrene 5,5,10,10-Tetraoxide (**17c**): A mixture of **11** (0.25 g, 0.85 mmol), furan (0.5 g, 8.5 mmol), and dichloromethane (2 ml) containing a few crystals of hydroquinone was placed in a screw-capped Pyrex test tube. The tube was purged with nitrogen, sealed, and the contents were stirred at room temp. for 24 h. The solvent was removed from the reaction mixture by rotary evaporation, leaving a colorless solid (0.3 g, quantitative yield of an 87:13 mixture of *endo/exo* isomers). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 1 H), 4.62 (d, *J* = 4.5 Hz, 2 H), 5.28 (t, *J* = 1.2 Hz, 1 H), 5.31 (br s, 1 H), 5.39 (m, 1 H), 5.44−5.48 (m, 1 H), 5.68 (s, 1 H), 6.07 (m, 1 H), 6.16 (m, 1 H), 6.71 (m, 1 H), 6.83 (m, 1 H), 7.84−7.91, 7.97−8.02, 8.08−8.13 (each m, 8 H, Ar). − ^{13}C NMR (100 MHz, solution in 1:1 [D_6]DMSO/$CDCl_3$): δ = 60.51, 71.78, 74.76, 76.24, 80.15, 82.40, 85.14, 88.56, 124.82, 125.46, 125.65, 125.86 (2 C), 126.25, 126.56, 133.73, 133.97, 134.27, 134.38, 135.34 (2 C), 135.65, 136.53, 137.61. − IR (KBr disc): $\tilde{\nu}$ = 3089 cm^{-1}, 2952, 1574, 1436, 1340, 1321, 1178, 1151, 1132, 875, 769, 728. − $C_{12}H_9ClO_5S_2$: calcd. C 43.31, H 2.73; found C 43.25, H 2.90.

11-Benzylidene-4a-chloro-1,4,4a,10a-tetrahydro-1,4-methanothianthrene 5,5,10,10-Tetraoxide (**17d**): A mixture of **11** (0.3 g, 1.02 mmol), diphenylfulvene (0.292 g, 1.27 mmol), and benzene containing a few crystals of hydroquinone was heated at 100°C for 10 h. After cooling to room temp., a colorless solid precipitated, which was filtered off and washed with diethyl ether (0.49 g, 97% yield); m.p. 272−273°C (CH_2Cl_2/Et_2O). − ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.14 (br s, 2 H), 4.73 (d, *J* = 3.3 Hz, 1 H), 5.92−6.10 (m, 2 H), 7.00−7.23 (m, 4 H, Ar), 7.25−7.50 (m, 6 H, Ar), 7.80−7.90 (m, 2 H, Ar), 7.95−8.20 (m, 2 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 49.12, 58.78, 78.29, 89.17, 126.51, 126.57, 127.67, 127.81, 127.86, 127.99, 128.26, 128.35, 128.58, 128.89, 129.20, 134.29, 134.34, 134.37, 137.90, 138.66, 139.26. − $C_{26}H_{19}ClO_4S_2$: calcd. C 63.09, H 3.87; found C 62.98, H 3.70.

4a-Chloro-1,4,4a,10a-tetrahydro-1,4-ethanothianthrene 5,5,10,10-Tetraoxide (**17e**): A mixture of **2** (0.4 g, 1.51 mmol), cyclohexadiene (0.35 g, 4.5 mmol), and a few crystals of hydroquinone in toluene (3 ml) was placed in a screw-capped Pyrex test tube. The tube was purged with nitrogen, sealed, and the contents were heated to 105°C for 24 h under stirring. After cooling to room temp., diethyl ether was added and the white compound that precipitated was collected by filtration, washed with diethyl ether, and recrystallized from dichloromethane/diethyl ether (0.49 g, 95% yield); m.p. 264−265°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35−1.61 (m, 2 H), 1.80−1.95 (m, 1 H), 2.33−2.44 (m, 1 H), 3.47−3.55 (m, 2 H), 4.09−4.25 (m, 1 H), 5.48−6.70 (m, 2 H), 7.77−7.90, 8.00−8.25 (both m, 4 H, Ar). − IR (KBr disc): $\tilde{\nu}$ = 3003 cm^{-1}, 2974, 1463, 1430, 1362, 1332, 1266, 1244, 1234, 1161, 1140, 1130, 1111, 867, 780, 766, 741. − $C_{14}H_{13}ClO_4S_2$: calcd. C 48.76, H 3.80; found C 48.62, H 4.04.

4a-Chloro-1,4,4a,10a-tetrahydro-1,4-propanothianthrene 5,5,10,10-Tetraoxide (**17f**): A mixture of **2** (0.3 g, 1.02 mmol), 1,3-cycloheptadiene (0.12 g, 1.27 mmol), and toluene containing a few crystals of hydroquinone was heated at 115°C for 6 days. After cooling to room temp., a colorless solid precipitated, which was filtered off and washed with diethyl ether; 0.34 g (87% yield); m.p. 160−162°C (CH_2Cl_2/Et_2O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.57−2.20 (m, 6 H), 3.40−3.54 (m, 2 H), 4.50 (br s, 1 H), 6.00−6.34

(m, 2 H), 7.84−7.92, 8.15−8.24 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, [D$_6$]DMSO/CDCl$_3$ in 1:1 ratio, 3 aliphatic C atoms were undetectable at 25°C and were omitted): δ = 23.80, 59.63, 70.83, 76.55, 123.97, 124.50, 125.72, 133.18, 133.52, 134.00, 135.57, 136.73, 141.30. − IR (KBr disc): ṽ = 3089 cm^{-1}, 3080, 2947, 2927, 1340, 1319, 1171, 1153, 791, 760. − $C_{15}H_{15}ClO_4S_2$: calcd. C 50.21, H 4.21; found C 50.44, H 4.43.

(1α,4a,4aβ,4bα,10aα,10b)-4b-Chloro-1,4,4a,4b,10a,10b-hexahydro-1,4-methanobenzo[b]benzo[3,4]cyclobuta[1,2-e][1,4]dithiin 5,5,10,10-Tetraoxide (**17g**): A mixture of **11** (0.9 g, 3.05 mmol), quadricyclane (0.85 g, 9.27 mmol), and a few crystals of hydroquinone in dichloromethane (3 ml) was placed in a screw-capped Pyrex test tube. The tube was purged with nitrogen, sealed, and the contents were stirred at room temp. for 7 days. Diethyl ether was then added and the colorless compound that precipitated was collected by filtration and washed with diethyl ether (1.03 g, 95% yield); m.p. 210−212°C (CH_2Cl_2/Et_2O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63 (dt, *J* = 10.5, 1.5 Hz, 1 H), 1.93 (d, *J* = 10.5 Hz, 1 H), 2.10−2.23 (m, 1 H), 2.73 (d, *J* = 7.2 Hz, 1 H), 3.11 (br s, 1 H), 3.20 (br s, 1 H), 3.96 (dd, *J* = 5.1, 1.5 Hz, 1 H), 6.06 (br s, 2 H), 7.89−7.97, 8.18−8.26 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.15, 42.90, 43.41, 43.67, 44.41, 68.89, 79.90, 127.81, 128.57, 133.14, 134.42, 134.71, 135.71, 137.04, 137.77. − IR (KBr disc): ṽ = 3070 cm^{-1}, 2989, 2931, 1385, 1340, 1323, 1174, 1190, 1130, 1101, 773, 748, 723. − $C_{15}H_{13}ClO_4S_2$: calcd. C 50.49, H 3.67; found C 50.58, H 3.57.

3b-Chloro-1,2,3,3a,3b,9a,10,10a-octahydro-2,3,10-methenobenzo[b]pentaleno[1,2-e][1,4]dithiin 4,4,9,9-Tetraoxide (stereoisomer) (**17h**): A mixture of **11** (0.9 g, 3.05 mmol), norbornadiene (0.85 g, 9.27 mmol), and a few crystals of hydroquinone in toluene (3 ml) was placed in a screw-capped Pyrex test tube. The tube was purged with nitrogen, sealed, and the contents were heated to 120°C for 72 h under stirring. After cooling to room temp., diethyl ether was added and the colorless compound that precipitated was collected by filtration, washed with diethyl ether, and dried; 1.02 g (94% yield, 60:40 mixture of *endo/exo* isomers). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42−1.46 (m, 2 H, *endo* isomer), 1.53−1.62 (m, 7 H, 3-*endo* and 4-*exo* isomers), 1.86−1.92 (m, 2 H, *exo* isomer), 2.36 (s, 1 H, *endo* isomer), 2.70 (s, 1 H, *endo* isomer), 2.84 (br s, 1 H, *endo* isomer), 2.87 (s, 1 H, *exo* isomer), 2.96 (s, 1 H, *exo* isomer), 4.20 (s, 1 H, *exo* isomer), 4.45 (d, *J* = 4.2 Hz, 1 H, *endo* isomer), 7.84−7.94, 8.12−8.26 (both m, 8 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$, 6:4 mixture of *endo/exo* isomers, 2 aliphatic C omitted): δ = 12.25, 14.15, 14.26 (2 C), 15.20, 18.28, 28.39, 32.89 (2 C), 39.98, 42.74, 47.15, 50.50, 57.64, 79.24, 79.54, 126.07, 126.20, 126.43, 127.43, 128.55, 134.07, 134.10, 134.42, 134.47, 134.60, 134.80, 135.54. − IR (KBr disc): ṽ = 3089 cm^{-1}, 2949, 2929, 2875, 1336, 1321, 1169, 1151, 1111, 810, 771, 758, 694. − $C_{15}H_{13}ClO_4S_2 \cdot 0.1\ CH_2Cl_2$ of a 6:4 mixture of *endo/exo* isomers: calcd. C 49.64, H 3.67; found C 49.49, H 3.64.

2-Chloro-3,10-dithiahexacyclo[10.6.6.0^{2,11}.0^{4,9}.0^{13,18}.0^{19,24}]tetracosa-4(9),5,7,13(18),14,16,19(24),20,22-nonaene 3,3,10,10-Tetraoxide (**17i**) *and* (**18i**): A mixture of **11** (0.5 g, 1.89 mmol), anthracene (0.6 g, 3.37 mmol), and toluene (5 ml) containing a few crystals of hydroquinone was placed in a screw-capped vessel and stirred at 110°C under nitrogen for 24 h. The reaction mixture was subsequently chromatographed on a silica gel column, eluting with dichloromethane. The solid collected was found to be a 1:1 mixture of **17i** and **18i**. The former was not completely characterized as it invariably contained traces of **18i** formed by spontaneous dehydrochlorination. The process was shown to be complete after 2 days at room temp. in the solid state.

(**17i**): Selected signals ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.27 (d, *J* = 2.1 Hz, 1 H), 5.04 (d, *J* = 2.1 Hz, 1 H), 5.16 (s, 1 H), 6.62 (t, *J* = 7.5 Hz, 1 H, Ar), 6.78 (t, *J* = 7.5 Hz, 1 H, Ar), 6.85 (d, *J* = 7.5 Hz, 1 H, Ar), 7.18−7.30 (m, 3 H, Ar), 7.40 (m, 1 H, Ar), 7.60 (d, *J* = 7.5 Hz, 1 H, Ar), 7.80 (d, *J* = 7.5 Hz, 1 H, Ar).

2-Chloro-3,10-dithiapentacyclo[10.4.2.0^{2,11}.0^{4,9}.0^{13,16}]octadeca-4(9),5,7,14,17-pentaene 3,3,10,10-Tetraoxide (**17j**): A dichloromethane solution (2 ml) of **11** (0.2 g, 0.76 mmol) and COT (83 mg, 0.80 mmol) was placed in a screw-capped Teflon vessel, which was purged with helium and sealed. The vessel was then placed in a high-pressure apparatus and was exposed to a pressure of 15 Kbar for 24 h at room temp. After concentration of the solution under reduced pressure, the colorless solid obtained was washed with cold diethyl ether and dried (98%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40−2.60 (m, 1 H), 3.00−3.10 (m, 1 H), 3.50−4.20 (several m, 3 H), 5.60−5.80 (t, *J* = 15.0 Hz, 2 H), 5.95−6.05 (t, *J* = 15.0 Hz, 2 H), 7.80−8.00, 8.05−8.25 (both m, 4 H, Ar). − $C_{16}H_{13}O_4S_2$: calcd. C 57.64, H 3.93; found C 57.41, H 3.71.

General Procedure for the Dehydrochlorination of **17a−j** *with Triethylamine:* A chloroform (15 ml) solution of adduct **17a−i** (mixture of *endo* and *exo* isomers, 5.37 mmol) and triethylamine (5.37 mmol) was heated under reflux for 10 min. After cooling to room temp., the reaction mixture was concentrated and the residue was purified by passage through a short silica gel column (eluant: dichloromethane). The dehydrochlorinated compounds **18a−i** were obtained as colorless solids, which were recrystallized from the solvent indicated.

1,4-Dihydro1,4-methanothianthrene 5,5,10,10-Tetraoxide (**18b**): Yield: 95%; m.p. 184−185°C (EtOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (dt, *J* = 7.4, 1.5 Hz, 1 H, 7-H or 7′-H), 2.47 (dt, *J* = 7.4, 1.5 Hz, 1 H, 7-H or 7′-H), 4.52 (m, 2 H, 1-H and 4-H), 7.07 (t, *J* = 2.1 Hz, 2 H, 5-H and 6-H), 7.80−7.87, 8.07−8.14 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.90, 71.97, 124.81, 133.62, 138.47, 141.26, 154.65. − IR (KBr): ṽ = 3084 cm^{-1}, 3008, 1325, 1315, 1161, 1147, 1135, 768, 690. − $C_{13}H_{10}O_4S_2$: calcd. C 53.04, H 3.42; found C 53.21, H 3.71.

3,10-Dithiatetracyclo[10.2.1.0^{2,11}.0^{4,9}]pentadeca-2(11),4(9),5,7,13-pentaen-15-yliden(diphenyl)methane 3,3,10,10-Tetraoxide (**18d**): Yield: 98%; m.p. 235−237°C (CH_2Cl_2/Et_2O). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.05 (t, *J* = 1.6 Hz, 2 H), 7.00−7.15, 7.17−7.40 (each m, 14 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.78, 116.62, 124.91, 127.73, 128.43, 129.53, 133.73, 137.87, 137.89, 138.53, 141.67, 153.75, 159.37. − $C_{26}H_{18}O_4S_2$: calcd. C 68.10, H 3.96; found C 68.32, H 4.02.

1,4-Dihydro-1,4-ethanothianthrene 5,5,10,10-Tetraoxide (**18e**): Yield: 97%; m.p. 324−325°C (CH_2Cl_2/Et_2O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61−1.77 (m, 4 H), 4.59 (s, 2 H), 6.53 (s, 2 H), 7.77−7.79, 8.06−8.12 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.71, 35.90, 124.84, 133.30, 133.60, 138.34, 146.66. − IR (KBr): ṽ = 3091 cm^{-1}, 2947, 2877, 1317, 1153, 1026, 766, 735, 702. − $C_{14}H_{12}O_4S_2$: calcd. C 54.53, H 3.92; found C 54.34, H 3.73.

1,4-Dihydro-1,4-Propanothianthrene 5,5,10,10-Tetraoxide (**18f**): Yield: 95%; m.p. 253−254°C (CH_2Cl_2/Et_2O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.55−1.90 (several m, 6 H), 3.91 (quintet, *J* = 3.9 Hz, 2 H), 6.36−6.42 (m, 2 H), 7.75−7.84, 8.06−8.14 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.78, 30.88, 34.08, 109.49, 124.99, 132.32, 133.58, 147.23. − IR (KBr): ṽ = 3091 cm^{-1}, 2924, 2862, 1431, 1321, 1153, 1117, 762, 702, 609. − $C_{15}H_{14}O_4S_2$: calcd. C 55.88, H 4.38; found C 56.02, H 4.12.

(1α,4a,4aβ,10bβ)-1,4,4a,10b-Tetrahydro-1,4-methanobenzo[b]benzo[3,4]cyclobuta[1,2-e][1,4]dithiin 5,5,10,10-Tetraox-

ide (**18g**): Yield: 94%; m.p. 173−175°C (CH_2Cl_2/Et_2O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.78 (s, 2 H), 3.10 (s, 2 H), 3.37 (s, 2 H), 6.28 (t, *J* = 1.9 Hz, 2 H), 7.80−7.87, 8.02−8.10 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.68, 40.20, 50.25, 124.87, 133.60, 135.70, 139.53, 148.57. − IR (KBr): $\tilde{\nu}$ = 3068 cm^{-1}, 2983, 2895, 1435, 1385, 1325, 1149, 1111, 773, 742, 694. − $C_{15}H_{12}O_4S_2$: calcd. C 56.24, H 3.78; found C 56.02, H 3.85.

1,2,3,3a,10,10a-Hexahydro-2,3,10-methenobenzo[b]pentaleno[1,2-e][1,4]dithiin 4,4,9,9-Tetraoxide (**18h**): Yield: 90%; m.p. 237−238°C (CH_2Cl_2/Et_2O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.81 (t, *J* = 1.5 Hz, 2 H), 1.98 (m, 2 H), 2.05−2.10 (m, 1 H), 2.56 (br s, 2 H), 3.58 (m, 2 H), 7.79−7.86, 8.08−8.14 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.00, 27.92, 31.97, 50.14, 57.29, 124.77, 133.50, 138.79, 149.24. − IR (KBr): $\tilde{\nu}$ = 3078 cm^{-1}, 3016, 2941, 2871, 1306, 1163, 1124, 806, 766, 756. − $C_{15}H_{12}O_4S_2$: calcd. C 56.24, H 3.78; found C 56.10, H 3.80.

3,10-Dithiapentacyclo[10.4.2^{2,11}.0^{4,9}.0^{13,16}]octadeca-2(11),4(9),5,7,14,17-hexaene 3,3,10,10-Tetraoxide (**18j**): Yield: 95%; m.p. 210−220°C (CH_2Cl_2/Et_2O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 3.80 (br s, 2 H), 4.55 (br s, 2 H), 5.30−5.80 (m, 2 H), 6.65 (t, *J* = 4.5 Hz, 2 H), 7.75−7.90, 8.05−8.20 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.51, 39.71, 124.86, 126.48, 126.82, 132.87, 133.08, 133.57. − $C_{16}H_{12}O_4S_2$: calcd. C 57.82, H 3.64; found C 57.70, H 3.80.

3,10-Dithiahexacyclo[10.6.6.0^{2,11}.0^{4,9}.0^{13,18}.0^{19,24}]tetracosa-2(11),4(9),5,7,13(18),14,16,19(24),20,22-decaene 3,3,10,10-Tetraoxide (**18i**): Obtained by spontaneous dehydrochlorination of **17i**. Yield: 0.74 g, 96%; m.p. 357−358°C (CH_2Cl_2/Et_2O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 5.99 (s, 2 H), 7.08−7.14 (m, 4 H, Ar), 7.49−7.55 (m, 4 H, Ar), 7.72−7.80 (m, 2 H, Ar), 8.02−8.11 (m, 2 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.73, 124.42, 124.92, 126.46, 133.66, 141.91, 151.60. − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3012, 2961, 1450, 1430, 1310, 1257, 1157, 1133, 1115, 881, 771, 755, 740, 720. − $C_{22}H_{14}O_4S_2$: calcd. C 65.01, H 3.47; found C 64.90, H 3.55.

Dehydrochlorination of **17c** *with n-Butyllithium. − 1,4-Dihydro-1,4-oxathianthrene 5,5,10,10-Tetraoxide* (**18c**): At −78°C under argon, a solution of *n*BuLi (0.94 ml, 1.6 M in hexanes) was added dropwise over a period of 20 min to a stirred solution of **17c** (0.5 g, 1.5 mmol) in THF (50 ml). The reaction mixture was allowed to warm to 0°C over a period of ca. 1 h, and was then quenched with water and extracted with CH_2Cl_2. The solid residue was purified by flash chromatography (eluant CH_2Cl_2); yield: 70%; m.p. 164−165°C (CH_2Cl_2/Et_2O). − ^{1}HNMR (300 MHz, $CDCl_3$): δ = 5.56 (t, *J* = 1.0 Hz, 2 H), 7.01 (t, *J* = 0.7 Hz, 2 H), 7.89−7.95, 8.15−8.21 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.93, 78.34, 126.57, 134.68, 138.76, 149.96. − $C_{12}H_8O_5S_2$: calcd. C 48.64, H 2.72; found C 48.49, H 3.06.

Reaction of **18b**, **18d**, **18g**, **18h** *with Cyclopentadiene. − General Procedure:* A mixture of **18b** (**18d**, **18g**, or **18h**) (5 mmol), freshly distilled cyclopentadiene (0.77 g, 10 mmol), and toluene (3 ml) was placed in a screw-capped vessel. The vessel was purged with argon, sealed, and the contents were stirred at 80°C for the time indicated in Table 2. After cooling to room temp., diethyl ether (3 ml) was added and the solid that precipitated was washed with diethyl ether (3 ml), filtered off, dried by suction, and finally recrystallized from the solvent indicated.

(1α,4a,4aβ,10aβ,11R,13S*)-1,4,12,13-Tetrahydro-11H-4a,10a-[1′,3′]-endo-cyclopenta-1,4-methanothianthrene 5,5,10,10-Tetraoxide* (**19b**): Yield: 98%; m.p. 257−258°C (CH_2Cl_2/Et_2O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15 (d, 1/2 AB system, *J* = 10.5 Hz, 1 H), 1.98 (dt, 1/2 AB system, *J* = 10.5 and 1.2 Hz, 1 H), 3.10 (dt, 1/2 AB system, *J* = 10.5 and 1.2 Hz, 1 H), 3.35 (br s, 2 H), 3.40 (d, 1/2 AB system, *J* = 10.5 Hz, 1 H), 3.70 (t, *J* = 1.9 Hz, 2 H), 6.00 (br s, 2 H), 6.50 (t, *J* = 1.9 Hz, 2 H), 7.80−7.87, 7.98−8.05 (both m, 4 H, Ar). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.41, 40.47, 44.40, 50.54, 80.20, 116.93, 125.88, 133.84, 134.85, 136.76. − $C_{18}H_{16}O_4S_2$: calcd. C 59.98, H 4.47; found C 60.30, H 4.60.

11-Benzylidene-1,4,12,13-tetrahydro-11H-4a,10a[1′,3′]-endo-cyclopenta-1,4-methanothianthrene 5,5,10,10-Tetraoxide (1α,4a,4aβ,10aβ,11R,13S*)* (**20**): Yield: 98%; m.p. 262−264°C (CH_2Cl_2/Et_2O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.98 (dt, 1/2 AB system, *J* = 10.5 and 1.2 Hz, 1 H), 3.38 (d, 1/2 AB system, *J* = 10.5 Hz, 1 H), 3.70 (t, *J* = 1.7 Hz, 2 H), 3.86 (t, *J* = 1.7 Hz, 2 H), 6.15 (t, *J* = 1.7 Hz, 2 H), 6.45 (t, *J* = 1.2 Hz, 2 H), 6.90−7.05, 7.15−7.35, 7.60−7.70, 7.95−8.00, 8.01−8.05 (each m, 14 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.84, 53.10, 55.30, 85.70, 118.57, 124.51, 127.80, 128.02, 128.36, 133.21, 138.47, 139.99, 141.29, 141.58, 148.36. − $C_{25}H_{22}O_4S_2$: calcd. C 66.64, H 4.92; found C 66.70, H 5.00.

2,9-Dithiaheptacyclo[8.6.4.0^{1,10}.0^{3,8}.0^{11,16}.11^{2,15}.11^{7,20}]docosa-3(8),4,6,13-pentaene 2,2,9,9-Tetraoxide (**21b** and **21b′**): Yield: 98%; 1:1 mixture of *syn/anti* isomers.

21b: ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (dt, 1/2 AB system, *J* = 10.5 and 1.2 Hz, 1 H), 1.18 (d, 1/2 AB system, *J* = 10.5 Hz, 1 H), 1.60 (s, 2 H), 2.05 (dt, 1/2 AB system, *J* = 10.5 and 1.2 Hz, 1 H), 2.54 (d, 1/2 AB system, *J* = 10.5 Hz, 1 H), 3.41 (s, 2 H), 3.92 (t, *J* = 1.8 Hz, 2 H), 5.99 (s, 2 H), 6.58 (t, *J* = 1.0 Hz, 2 H), 7.75−7.80, 8.08−8.13 (both m, 4 H). − **21b′**: ^1H NMR (300 MHz, $CDCl_3$): δ = 1.55 (dt, 1/2 AB system, *J* = 10.5 and 1.2 Hz, 1 H), 1.66 (d, 1/2 AB system, *J* = 10.5 Hz, 1 H), 2.10 (d, 1/2 AB system, *J* = 10.5 Hz, 1 H), 2.28 (s, 2 H), 3.11 (d, 1/2 AB system, *J* = 10.5 Hz, 1 H), 3.53 (t, *J* = 1.8 Hz, 2 H), 3.66 (s, 2 H), 5.89 (t, *J* = 1.0 Hz, 2 H), 6.17 (s, 2 H), 7.68−7.73, 7.90−7.95 (both m, 4 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 1:1 mixture of **21b** and **21b′**): δ = 23.57, 24.39, 29.89 (2 C), 38.07, 38.91, 43.94, 44.39, 47.93, 48.84, 55.37 (2 C), 123.81 (2 C), 124.48 (2 C), 133.31 (2 C), 142.21 (2 C). − $C_{20}H_{18}O_4S_2$ (1:1 mixture of **21b** and **21b′**): calcd. C 62.15, H 4.69; found C 61.97, H 4.60.

2,9-Dithianonacyclo[8.7.4.0^{1,10}.0^{3,8}.0^{11,16}.0^{12,14}.0^{13,17}.11^{8,21}]-docosa-3(8),4,6,19-tetraene 2,2,9,9-Tetraoxide (**22b**): Yield: 98%; m.p. 278−279°C (CH_2Cl_2/Et_2O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.76 (d, *J* = 5.1 Hz, 2 H), 1.26−1.30 (m, 3 H), 1.77 (d, *J* = 9.3 Hz, 1 H), 2.61 (m, 2 H), 3.08 (m, 1 H), 3.20 (d, *J* = 5.1 Hz, 1 H), 3.71 (t, *J* = 1.8 Hz, 2 H), 6.47 (t, *J* = 1.8 Hz, 2 H), 7.73−7.79, 8.09−8.16 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.33, 19.56, 39.26, 48.52, 51.16, 53.43, 123.80, 133.40, 141.39. − $C_{20}H_{18}O_4S_2$: calcd. C 62.16, H 4.69; found C 62.35, H 4.79.

Reaction of **18b** *and* **18g** *with Furan. − General Procedure:* A mixture of **18b** (or **18g**) (3.12 mmol), furan (0.5 g, 15.5 mmol), and dichloromethane (2 ml) was placed in a screw-capped vessel. The vessel was then purged with argon, sealed, and the contents were stirred at room temp. for the time indicated in Table 2. The solid that precipitated was washed with cold diethyl ether (3 × 1 ml), collected on a sintered glass funnel, and dried by suction.

(1α,4a,4aβ,10aβ,11R,13S*)-11H-4a,10a[1′,3′]-1,4,12,13-Tetrahydro-endo-cyclopenta-1,4-oxathianthrene 5,5,10,10-Tetraoxide* (**19c and 19c′**): Yield: 97%; 1:1 mixture of isomers. **19c**: ^1H NMR (300 MHz, $CDCl_3$): δ = 1.89 (d, 1/2 AB system, *J* = 9.3 Hz, 1 H), 3.16 (d, 1/2 AB system, *J* = 9.3 Hz, 1 H), 3.78 (br s, 2 H), 4.89 (br s, 2 H), 6.17 (br s, 2 H), 6.40 (br s, 2 H), 7.74−7.80, 7.98−8.02 (both m, 4 H, Ar). − **19c′**: ^1H NMR (300 MHz, $CDCl_3$): δ = 1.61 (d, 1/2 AB system, *J* = 9.3 Hz, 1 H), 3.16 (d, 1/2 AB system, *J* =

9.3 Hz, 1 H), 3.66 (br s, 2 H), 5.29 (br s, 2 H), 6.33 (br s, 2 H), 6.57 (br s, 2 H), 7.69−7.73, 7.91−7.96 (both m, 4 H, Ar). − ^{13}C NMR (100 MHz, $CDCl_3$, 1:1 mixture **19c** and **19c′**, 4 C atoms omitted): δ = 46.89, 51.90, 55.17, 71.99, 82.48, 82.95, 124.53, 124.82, 133.58, 133.65, 133.90, 137.76, 140.49, 141.23, 145.60. − $C_{17}H_{16}O_5S_2$: calcd. C 56.03, H 4.43; found C 56.24, H 4.50.

21-Oxa-2,9-dithiaheptacyclo[8.6.4.0^{1,10}.0^{3,8}.0^{1,16}.11^{2,15}.11^{7,20}]-docosa-3(8),4,6,13,18-pentaene 2,2,9,9-Tetraoxide (**21c**): Yield: 97%; m.p. >320°C (CH_2Cl_2/Et_2O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.69 (dt, 1/2 AB system, *J* = 10.8 and 1.8 Hz, 1 H), 2.42 (s, 2 H), 2.93 (d, 1/2 AB system, *J* = 10.8 Hz, 1 H), 3.64 (t, *J* = 1.2 Hz, 2 H), 5.21 (t, *J* = 1.2 Hz, 2 H), 6.15−6.19 (m, 4 H), 7.69−7.76, 7.88−7.95 (both m, 4 H, Ar). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.35, 46.45, 49.06, 71.73, 85.63, 124.23, 133.53, 137.18, 138.11, 140.20. − $C_{19}H_{16}O_5S_2$: calcd. C 58.75, H 4.15; found C 58.65, H 4.00.

(1α,4α,4aβ,10aβ,11R,13S*)-1,1,4,4,12,12,13,13-Octahydro-11H-4a,10a[1′,3′]-endo-cyclopenta-1,4-methanothianthrene 5,5,10,10-Tetraoxide:* A mixture of **19b** (1.0 g, 2.8 mmol) and 5% palladium on charcoal (10 mg) in ethyl acetate (20 ml) was stirred under hydrogen at room temp. for 4 h. The crude reaction mixture was then filtered through a short silica gel column, eluting with dichloromethane. The solvent was removed from the filtrate under reduced pressure, affording 0.97 g a colorless solid (97%); m.p. >275°C (CH_2Cl_2/Et_2O). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.22−1.68 (several m, 6 H), 1.75−1.90 (several m, 4 H), 2.30 (d, 1/2 AB system, *J* = 13.2 Hz, 1 H), 2.93 (s, 2 H), 3.13 (s, 1 H), 3.28 (d, 1/2 AB system, *J* = 13.2 Hz, 1 H), 7.76−7.80 (m, 2 H, Ar), 8.07−8.15 (m, 2 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.39, 26.46, 36.86, 43.26, 43.37, 44.16, 81.69, 123.65, 133.54, 140.71. − $C_{18}H_{20}O_4S_2$: calcd. C 59.32, H 5.53; found C 59.47, H 5.71.

Reductive Desulfonylation of **19a**, **19b**, **20a**, **21a**, **22a**, **22b**, **23a** *with Sodium Amalgam in Buffered MeOH. − General Procedure:* In a typical procedure, a mixture of the appropriate adduct (2.37 mmol) and NaH_2PO_4 (1.0 g, 8.3 mmol) in dry methanol (25 ml) was purged with nitrogen. Under efficient stirring, sodium amalgam was added in portions (6%, ca. an 8:1 molar ratio of sodium to substrate). The mixture was kept stirring at room temp. and the reaction was monitored by TLC, eluting with *n*-hexane. After ca. 12 h, the conversion was virtually complete. Water was then added and the mixture was extracted with pentane (3 × 50 ml). The combined extracts were washed with brine, dried over sodium sulfate, and the solvent was removed by rotart evaporation. All compounds were characterized by comparison of their spectral data with those reported in the literature.[12][18][25]

[1] P. D. Bartlett, A. A. M. Roof, R. Subramanyam, W. J. Winter, *J. Org. Chem.* **1984**, *49*, 1875. K. R. Kopecky, A. J. Miller, *Can. J. Chem.* **1984**, *62*, 1840. P. D. Bartlett, A. J. Blakeney, M. Kimura, W. H. Watson, *J. Am. Chem. Soc.* **1980**, *102*, 1383.

[2] A. Menzek, M. Krawiec, W. H. Watson, M. Balci, *J. Org. Chem.* **1991**, *56*, 6755. S. F. Nelsen, D. L. Kapp, *ibid.* **1985**, *50*, 1341.

[3] [3a] P. von Ragué Schleyer, P. Maslak, J. Chandrasekhar, R. S. Grav, *Tetrahedron Lett.* **1993**, *40*, 6387. − [3b] P. S. Skell, L. M. Jackman, S. Ahmed, M. L. McKee, P. B. Shevlin, *J. Am. Chem. Soc.* **1989**, *111*, 4422. − [3c] B. H. Lengsfield, D. H. Phillips, J. C. Schug, *J. Chem. Phys.* **1981**, *74*, 5176. − [3d] K. Jug, B. M. Bursian, *Theor. Chim. Acta* **1979**, *52*, 341. − [3e] K. Kirby, B. Liu, *J. Chem. Phys.* **1979**, *70*, 893. − [3f] S. R. Langhoff, M. L. Sink, R. H. Pitchard, C. W. Kern, S. J. Strickel, M. J. Boyd, *J. Chem. Phys.* **1977**, *67*, 1051. − [3g] W. A. Lathan, W. J. Hehre, J. Pople, *J. Chem. Soc.* **1971**, *93*, 808.

[4] [4a] E. A. Ballik, D. A. Ramsay, *Astrophys. J.* **1963**, *137*, 84. − [4b] L. Pasternack, A. P. Baronavski, J. R. McDonald, *J. Chem. Phys.* **1980**, *73*, 3508. − [4c] M. Douay, R. Nietmann, R. F. Bernath, *Mol. Spectrosc.* **1988**, *131*, 261.

[5] P. S. Skell, L. Wescott Jr., J. P. Golstein, R. R. Engel, *J. Am. Chem. Soc.* **1965**, *87*, 2829.

[6] P. S. Skell, J. Havel, M. J. McGlinchey, *Acc. Chem. Res.* **1973**, *6*, 97.

[7] K. P. Huber, G. Herzberg, in *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules*, Van Nostrand Reinhold Co., New York, **1979**.

[8] H. Schwarz, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1412; *Angew. Chem.* **1993**, *105*, 1475. T. Belz, H. Werner, F. Zemlin, U. Klengler, M. Wasemann, B. Tesche, E. Zeitler, A. Reller, R. Schlögl, *ibid.* **1994**, *33*, 1866; *106*, 1919.

[9] F. Diederich, Y. Rubin, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101; *Angew. Chem.* **1992**, *104*, 1123.

[10] From the outset, only disubstituted acetylenes were considered in view of the fact that the cycloaddition of the second molecule of diene was expected to necessitate of high activation.

[11] R. V. Williams, C.-L. A. Sung, H. A. Kurtz, T. M. Harris, *Tetrahedron Lett.* **1988**, *29*, 19. O. De Lucchi, G. Modena, *Tetrahedron* **1984**, *40*, 2585. J. D. Slee, E. LeGoff, *J. Org. Chem.* **1970**, *35*, 3897. J. R. Edman, H. E. Simmons, *J. Org. Chem.* **1968**, *33*, 3808.

[12] O. De Lucchi, N. Piccolrovazzi, G. Licini, G. Modena, G. Valle, *Gazz. Chim. It.* **1987**, *117*, 401. O. De Lucchi, N. Piccolrovazzi, G. Modena, *Tetrahedron Lett.* **1986**, *27*, 4347. C. D. Weis, *J. Org. Chem.* **1963**, *28*, 74.

[13] O. De Lucchi, D. Fabbri, S. Cossu, G. Valle, *J. Org. Chem.* **1991**, *56*, 1888. S. Cossu, O. De Lucchi, D. Fabbri, G. Licini, L. Pasquato, *Org. Prep. Proc. Int.* **1991**, *23*, 573. O. De Lucchi, V. Lucchini, G. Modena, L. Pasquato, *J. Org. Chem.* **1984**, *49*, 596.

[14] L. Pasquato, O. De Lucchi, L. Krotz, *Tetrahedron Lett.* **1991**, *32*, 2177.

[15] S. Cossu, O. De Lucchi, *Gazz. Chim. It.* **1990**, *120*, 569.

[16] U. Azzena, S. Cossu, O. De Lucchi, G. Melloni, *Gazz. Chim. It.* **1989**, *119*, 357.

[17] J. Nakayama, Y. Nakamura, M. Hoshino, *Heterocycles* **1985**, *23*, 1119. E. Wenkert, C. A. Broka, *Finn. Chem. Lett.* **1984**, 126.

[18] S. Cossu, O. De Lucchi, *Tetrahedron* **1996**, *54*, 14247. O. De Lucchi, S. Cossu, *J. Chem. Soc., Chem. Commun.* **1992**, 1089.

[19] O. De Lucchi, F. Fabris, in *Encyclopedia of Reagents for Organic Synthesis*, (Ed.: L. A. Paquette), Wiley Publishers, USA, **1995**, vol. 1, p. 256. M. Tiecco, *Synthesis* **1988**, 749. I. Degani, R. Fochi, *Synthesis* **1976**, 471. S. Hunig, E. Fleckestein, *Liebigs Ann. Chem.* **1970**, *738*, 192.

[20] E. Cecchet, F. Di Furia, G. Licini, G. Modena, *Tetrahedron: Asymmetry* **1996**, *7*, 369.

[21] For the X-ray structure determinations of **18g** and **18h**, see: K. Peters, E.-M. Peters, S. Cossu, O. De Lucchi, *Zeit. Krist.* **1996**, *211*, 429; *ibid.* **1996**, *211*, 431.

[22] K. Peters, E.-M. Peters, S. Cossu, O. De Lucchi, *Zeit. Krist.* **1998**, *213*, 254.

[23] A. M. Felix, E. P. Heimer, T. J. Lambros, C. Tzougraki, J. Meienhofer, *J. Org. Chem.* **1978**, *43*, 4194.

[24] U. Azzena, S. Cossu, O. De Lucchi, G. Melloni, *Gazz. Chim. It.* **1989**, *119*, 357.

[25] O. De Lucchi, G. Licini, L. Pasquato, *J. Chem. Soc., Chem. Commun.* **1985**, 418. L. A. Paquette, H. Künzer, K. E. Green, O. De Lucchi, G. Licini, L. Pasquato, G. Valle, *J. Am. Chem. Soc.* **1986**, *108*, 3453.

[26] S. Mirsadeghi, B. Rickborn, *J. Org. Chem.* **1985**, *50*, 4340.

[98288]