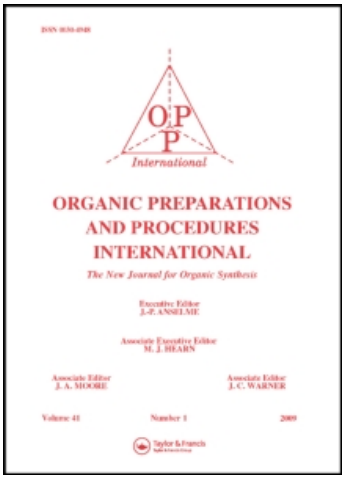

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1,2-*bis*(ARYLSULFONYL)ALKENES. A REVIEW

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INTRODUCTION 573
1. UNSUBSTITUTED 1,2-*bis*(ARYLSULFONYL)ALKENES 573
   a. Synthesis 573
   b. Reactivity 574
   c. Synthetic Applications 576
   d. Halogen-Substituted 1,2-*bis*(Arylsulfonyl)alkenes 581
   e. Benzodithiin-*S*,*S*-tetraoxide 581
   f. Chiral 1,2-*bis*(Arylsulfonyl)alkenes 582
2. SUBSTITUTED 1,2-*bis*(ARYLSULFONYL)ALKENES 584
   a. Monosubstituted 1,2-*bis*(Arylsulfonyl)alkenes 584
   b. Disubstituted 1,2-*bis*(Arylsulfonyl)alkenes 584
   c. Disubstituted Benzodithiin Derivatives 587
REFERENCES 589

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INTRODUCTION

1,2-*bis*(Arylsulfonyl)alkenes are becoming popular reagents in organic synthesis.[1] Their utility stems from the strong electron-withdrawing ability of the two sulfonyl groups which activate the double bond in Diels-Alder and Michael reactions, from the reasonably simple preparation and from the high crystallinity which usually characterizes molecules containing these functional groups. Furthermore, the synthetic versatility of the products, which includes a simple and high yielding transformation into alkenes or replacement of the two arylsulfonyl groups by hydrogen atoms (characteristics which are shared by very few others electron-deficient alkenes), contributes to their utility. The aryl substituent is most commonly the phenyl group, however, because the tolyl group behaves quite similarly, no distinction between the two reagents have been made throughout this review.

1. UNSUBSTITUTED 1,2-*bis*(ARYLSULFONYL)ALKENES

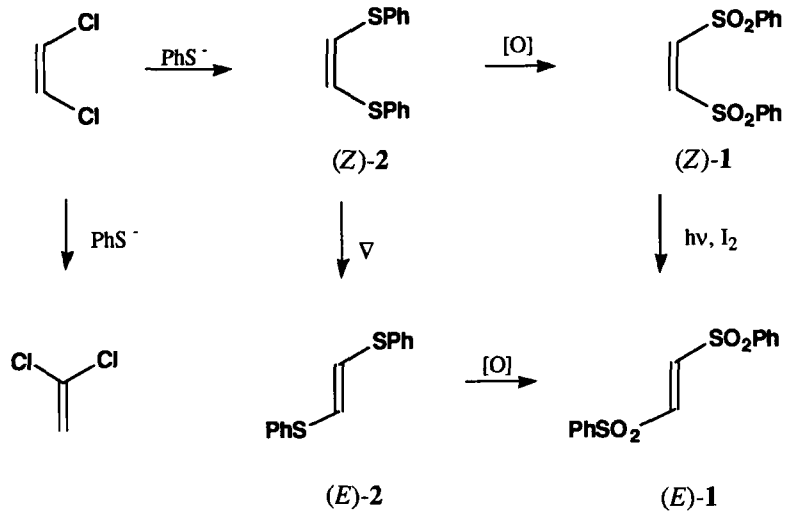
a. Synthesis

The parent compounds (*Z*)- and (*E*)-1,2-*bis*(phenylsulfonyl)ethylenes **1**[2] are readily available by oxidation of the corresponding thioethers **2** which, in turn, are prepared through a number of routes (Scheme 1). The more efficient preparation of (*Z*)-**2** is from (*Z*)-1,2-dichloroethylene,[3] but for large quantities, the use of the cheaper 1,1-dichoroethylene is preferable,[4] albeit the reaction is not as clean. The use of the mixture of the (*Z*)- and (*E*)-1,2-dichloroethylenes is also possible, but the (*E*)-isomer is unreactive under standard conditions. In fact, as shown by Truce and coworkers,[4] the substitution of the chlorine atoms with the thio-residue occurs by an elimination-addition mechanism which is accomplishable only with the (*Z*)- and 1,1-dichloro alkenes where a *trans* elimination is possible. Under more drastic reaction conditions (DMF, 70-90°C), the *trans*-1,2-dichloroethylene also affords the substitution product (*E*)-**2** (57% (*E*), 14% (*Z*)).[5] In these cases an addition-elimination mechanism may be operative.

From the above mentioned reactions, the isomer (*Z*)-**2** is obtained stereospecifically. The

latter, on oxidation with peracetic acid, affords high yields of the *bis*-sulfone (*Z*)-**1**. The

Scheme 1



preparation of the (*E*)-isomer of **1** is accomplished by iodine catalyzed photorearrangement of (*Z*)-**1**. No special photochemical apparatus is required for this reaction. When a concentrated solution of (*Z*)-**1** in dichloromethane, containing a few crystals of iodine, is exposed to the sunlight into a standard Pyrex flask for a few hours, crystals of the (*E*)-isomer separate because of the higher insolubility of the latter.[2] Grams quantities of the reagents are hence rapidly and quite inexpensively obtained. The reagents **1** are indefinitely stable at room temperature, provided that the (*Z*)-isomer is kept shaded from direct light in dark bottles. It should be mentioned that other, seemingly less practical methods for obtaining **1** and/or **2** are also possible.[6]

X-Ray structure analysis of the two isomers (Fig. 1 and 2)[7] shows that the crowding nature of the phenylsulfonyl groups in the (*Z*)-isomer leads to a puckering of the double bond. As it will be shown later on this paper, this fact may have implications on the reactivity of this molecule.

b. Reactivity

The very different solubility of the two isomers makes them easy to be recognized and separated when needed, and helps in the performance of the cycloadditions reactions. As an empirical observation, it was noted that, generally, the more soluble (*Z*)-isomer of **1** affords in dichloromethane quite unsoluble adducts; conversely, the more insoluble (*E*)-adduct of **1** leads to more soluble products. Therefore, a cycloaddition reaction of the *cis* isomer is completed when no more precipitate is observed, while a cycloaddition of the (*E*)-isomer is completed when dissolution of the crystals continues at room temperature.

The choice of the solvent for carrying out the cycloaddition reaction of **1** is often crucial. For

example, it was reported that the (*E*)-isomer was not reactive towards furan even in refluxing benzene.[8] In dichloromethane, the cycloaddition occurs smoothly at room temperature in quantitative yields.[2,9] Even the (*Z*)-isomer is reactive with furan and gives the adduct in a dichloromethane

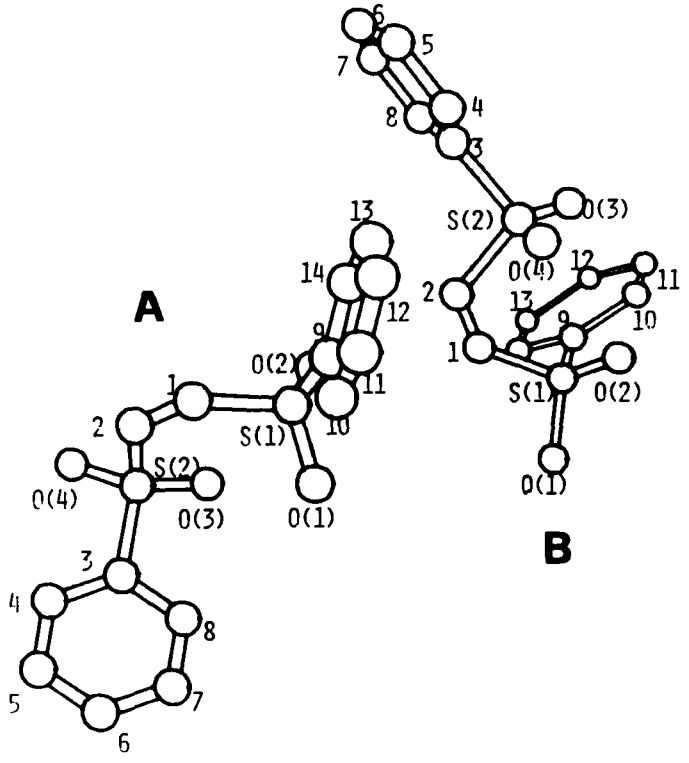


Fig. 1. X-ray Structure of Compound (*Z*)-**1** with the two conformations composing the crystal lattice. (From Ref. 7).

solution at room temperature.[9] The reason for this apparent discrepancy may lie in the reversibility of the reaction. Indeed, heating the reaction mixture to speed up the reaction is detrimental to the product yield because it increases the retro-process. The success of the reaction run in dichloromethane may be due to the mentioned insolubility of the adduct, which helps in removing product from the equilibrium.

Generally, in cycloaddition reactions, the (*E*)-isomer is more reactive than the (*Z*)-isomer. This fact is observed in the rate of reaction with standard dienes and in the fact that a few dienes (1,3-cycloheptadiene and cyclooctatetraene as examples) reacted only with the former. The difference in reactivity may be attributed to steric factors, as shown by the X-ray structures (Figs. 1 and 2). The bulky nature of the phenylsulfonyl groups in the *cis* isomer, beside puckering the double bond and blocking the approach of a diene, may not allow a correct orbital alignment for an efficient electronic activation. It should be noted that in the case of the (*Z*)-isomer, forcing of the reaction conditions

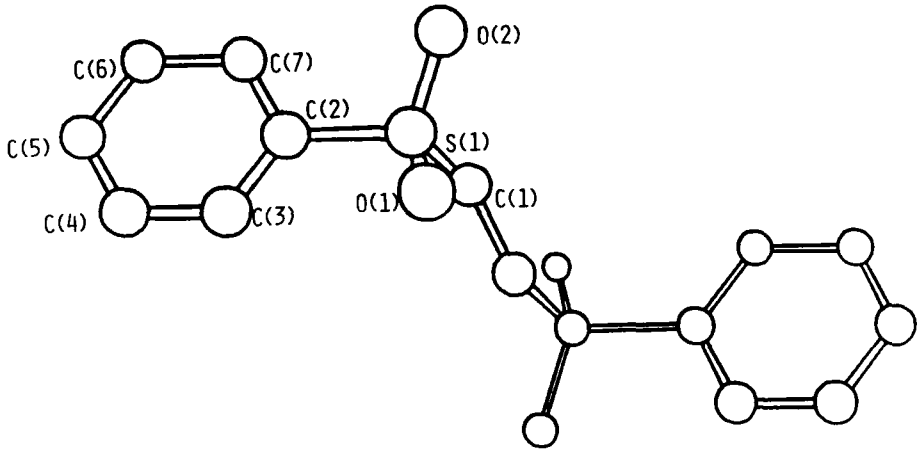


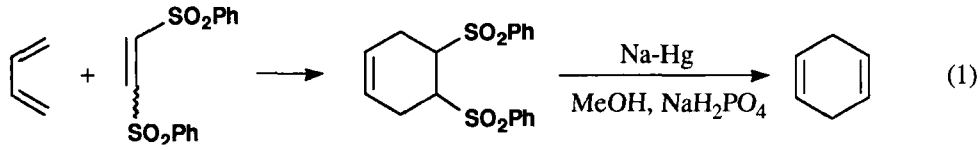
Fig. 2. X-ray Structure of Compound (*E*)-**1**. (From Ref. 7)

may cause the interconvertion to the thermodynamically more stable and more reactive (*E*)-isomer.

An order of reactivity between the isomers of **1**, and of other dienophiles towards cyclopentadiene and dimethylanthracene has been reported.[10] The reaction of (*E*)-**1** with cyclopentadiene in dioxane is two orders of magnitude faster than that of the (*Z*)-isomer. Under these conditions, even the (*E*)-isomer is twice as reactive as maleic anhydride.[10] This higher reactivity may differ substantially with other dienes. Indeed, there have been cases in which **1** failed to react with substrates where maleic anhydride gives adducts in high yields, such as styrene,[11] homobarrelene[12] and other polycyclic dienes.[14] Steric factors may be responsible. The study of the transmission of electronic effects by the arylsulfonyl groups and experiments on the mechanism of the cycloaddition reaction of **1** have been reported.[15]

c. Synthetic Applications

The cycloaddition reactions of the (*Z*)- and (*E*)-isomers have been reviewed recently.[1] A few highlights and other examples, not included in the recent compilation, will be given here. Most commonly, reagents **1** are utilized as synthetic equivalents of acetylene in cycloaddition reactions[16] through the cycloaddition-desulfonylation sequence illustrated in Eq. 1.

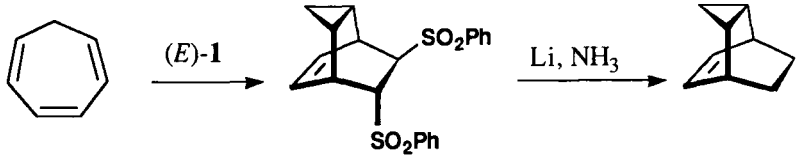


(1)

So far, the use of sodium amalgam (from 1.5 to 6%) in methanol (with or without tetrahydrofuran) buffered with suspended sodium dihydrogen phosphate is the best method to transform a β-disulfonyl derivative into an alkene. Although the reaction mixture is heterogeneous, the reduction usually proceeds smoothly and, at the end of the reaction, the hydrocarbon product is isolated cleanly by extraction with pentane or light petroleum. Sonication is also effective in the reduction step. Control experiments in standard desulfonylations showed that reactions carried out under sonication are at least three times faster. The use of magnesium in methanol which would be safer and in particular avoids the use of mercury, affords a mixture of saturated and unsaturated hydrocarbons as shown in the example of Eq. 2.[17]

(2)

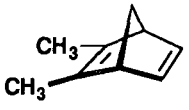
Other conditions, or the use of different buffers, also lead to mixtures of the saturated and unsaturated adducts. In the course of the study aimed at defining the best reduction conditions, it was shown that lithium or sodium metal in liquid ammonia effectively reduces *bis*arylsulfonyl adducts solely to the saturated adduct as shown in Eq. 3.[18] In this case, (*E*)-**1** can be viewed as synthetic equivalent of ethylene in cycloaddition reactions.



(3)

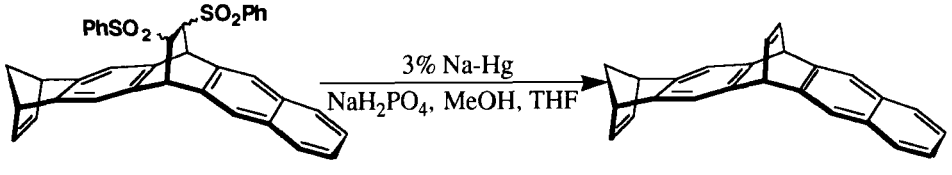
Photochemical routes have been proved to be only partially successful. Unpublished results from our laboratory have shown that the same substrates of Eq. 2 can be desulfonylated on irradiation of a solution containing aromatic amines as electron donors.[19]

2,3-Dimethylnorbornadiene **3** is an example of a simple molecule which can be prepared *via* the route of Eq. 1.[20]



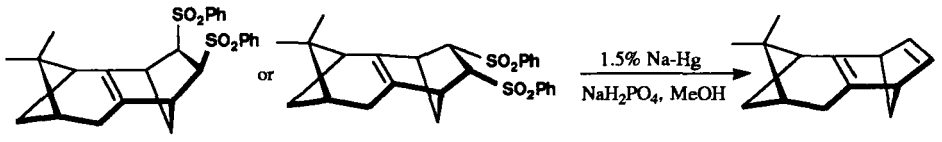
3

Several isomeric etheno-bridged 2,3-norbornadienonaphthacenes have been prepared *via* the standard cycloaddition-desulfonylation sequence. One example is shown in Eq. 4.[21]



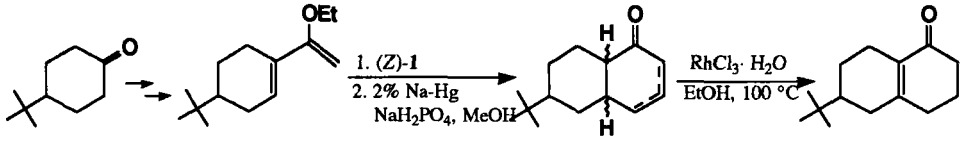
(4)

Another application of the same sequence is in the synthesis of the norbornadiene shown in Eq. 5 which is an interesting chiral ligand.[22]



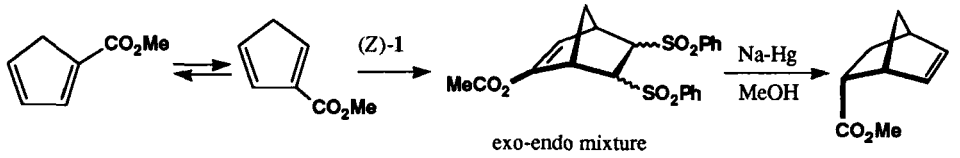
(5)

Similarly, cycloaddition of (*Z*)-**1**, followed by reduction and isomerization of the double bond, is a regiocontrolled cyclohexenone annulation route from a ketone as shown in Eq. 6.[23]



(6)

1-Methoxycarbonylcyclopentadiene reacts with (*Z*)-**1** to give a mixture of the two sulfones shown in Eq. 7 which arise from a prior [1,5] sigmatropic rearrangement of the diene under the reaction conditions.[24] Both adducts were desulfonylated with sodium amalgam in methanol to the partially saturated compound **4**. The reduction potential of the reducing agent is therefore sufficient to cause hydrogenation of the more electrophilic double bond.

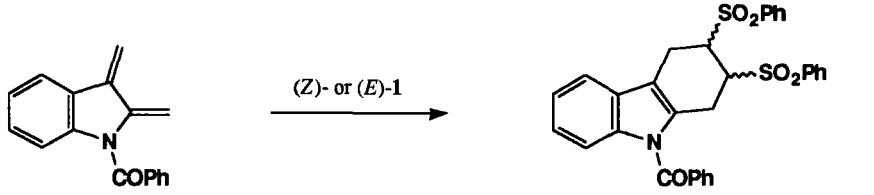


exo-endo mixture

(7)

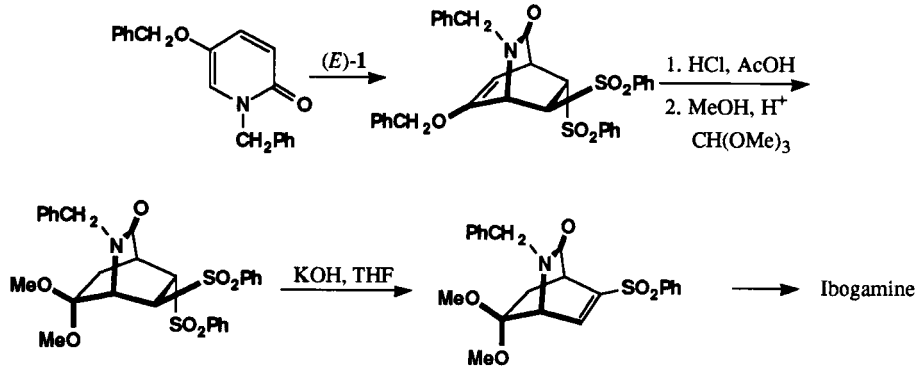
4

The recently reported cycloadducts of (*Z*)- and (*E*)-**1** to *N*-benzoylindole-2,3-quinodimethane (Eq. 8) may be useful for the preparation of natural products containing the carbazole ring system.[25]



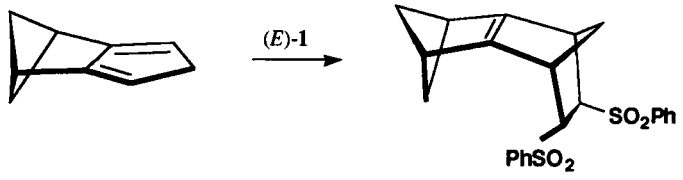
(8)

More rarely, the adducts of **1** to dienes have been treated with bases to yield the vinyl sulfone.[18] An example is illustrated in the Eq. 9. The vinyl sulfone thus obtained was further reacted with nucleophiles in a short and stereoselective synthesis of ibogamine.[26]



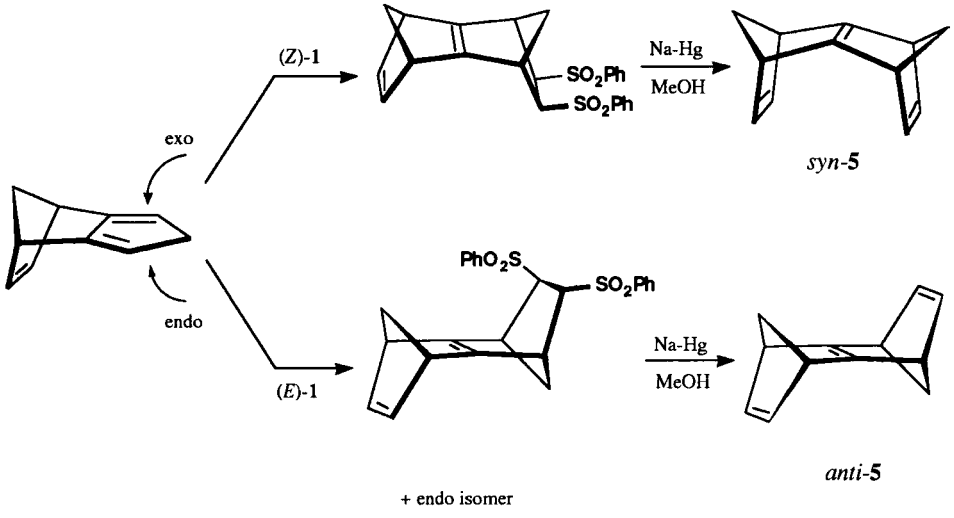
(9)

In the case of addition to 1,2,3,5-tetrahydro-1,3-methanopentalene, the resulting cycloadduct was too unstable for further manipulations (Eq. 10).[27]

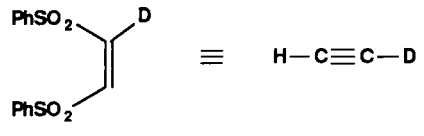


(10)

It should be recalled that both the *syn*- and the *anti*-sesquinorbonatrienes **5** are available *via* cycloaddition of (*Z*)- and (*E*)-**1**. In this fortunate case, the cycloaddition of the two isomers of **1** to



(11)

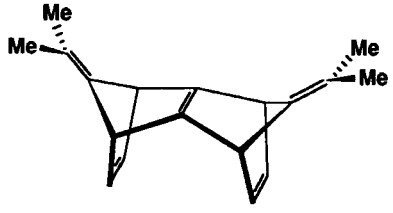


8,9-dehydroisodicyclopentadiene affords the two adducts derived from the attack of the dienophile to the top and the bottom of the diene, eventually allowing the preparation of both isomeric trienes (Eq. 11).[28] Further studies on these molecules have recently been published.[29,30]

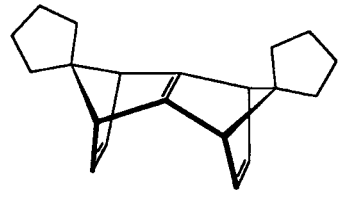
The availability and the use of the monodeuteriated (*Z*)-**1** as a synthetic equivalent of monodeuterioacetylene in cycloaddition reactions has also been demonstrated.[30]

High pressure is a valuable and efficient method to increase reactivity.[31] Cycloaddition reactions, otherwise inefficient at ambient pressure, are smoothly obtained at 10-12 kbar. This special activating technique was used by Paquette and his coworkers to prepare a number of molecules of the sesquinorbornene family.

Examples are the preparations of alkylidene derivatives of *syn*-sesquinorbornatriene, *e.g.* **6**,[32] and of the first shelf-stable *syn*-sesquinorbornatriene **7**[33] *via* high pressure cycloaddition of (*Z*)-**1** to the appropriate isodicyclopentadiene. In the preparation of **6**, a pressure of 9 kbar was sufficient in order for the reaction to occur at room temperature while for the preparation of **7**, 16 kbar were required.

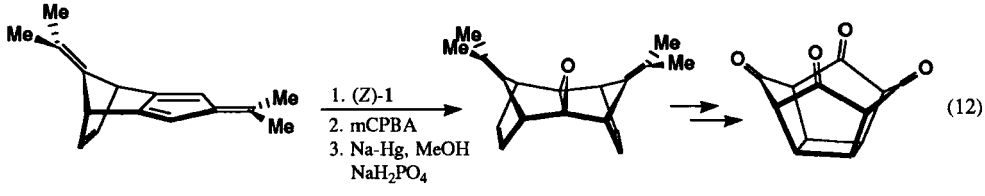


6



7

An interesting application of this activation technique associated with the sequence of reactions shown in Eq. 1 is the synthesis of [4]peristylane molecules, examplified in Eq. 12 by the preparation of the C_{4v} tetraketone **8**.[34] Furthermore, studies on the facial selectivity of the Diels-Alder reaction of (*Z*)-**1** under high pressure conditions with substituted isodicyclopentafulvenes have been reported.[35]



(12)

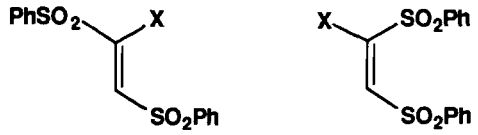
8

In the context of high pressure activation, it is worth noting that the rate of cycloaddition of **1** to poorly reactive dienes is drastically enhanced if carried out in 5M lithium perchlorate in ether.[36,37] The reason for this activation has been rationalized as a microscopic high pressure given by the molecules of the salt to the reagents.[36] As an example, the reaction of (*Z*)-**1** with 1,3-cyclohexadiene occurs overnight in refluxing toluene or overnight at room temperature in 5M lithium perchlorate in

ether. Because of the poor solubility of isomer of **1** in ether, sonication has proved useful to further activate the cycloaddition reactions in this medium.[37]

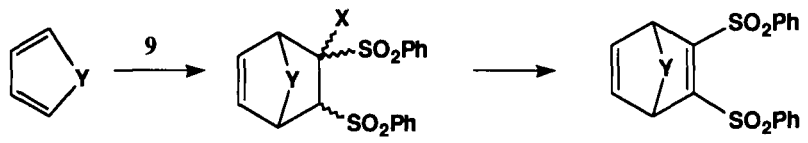
d. Halogen-Substituted 1,2-*bis*(Arylsulfonyl)alkenes

Compounds in which one vinyl hydrogen is replaced by a halogen atom (chlorine especially but also bromine can be used) such as **9**[38] have been proved to be useful synthetic equivalents of the insufficiently stable *bis*(arylsulfonyl)acetylenes *via* the synthetic sequence illustrated in Eq. 13.[39]

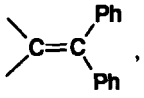


X = Cl, Br

(*Z*)-**9** (*E*)-**9**

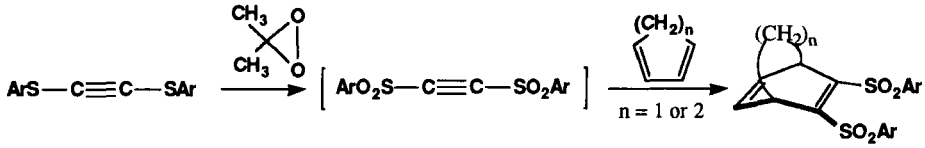


(13)

X = Cl, Br
Y = -O-, -(CH_2)-, -$(CH_2)_2$-,  , etc.

The *bis*(arylsulfonyl)alkenes obtained in this way are especially good Michael acceptors.[39] In contrast, the cycloadditivity properties of substituted 1,2-*bis*(arylsulfonyl)alkenes appear to be drastically reduced as will be described also in the section dealing with disubstituted 1,2-*bis*(arylsulfonyl)alkenes.

bis(Arylsulfonyl)acetylenes **10** has been eventually obtained *via* oxidation of the corresponding sulfides with dimethyldioxirane and the stability properties have been clearly demonstrated (Eq. 14).[40]



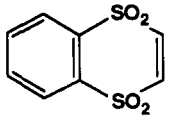
(14)

10

e. Benzodithiin-*S*,*S*-tetraoxide

A dienophile closely resembling (*Z*)-**1** is the benzodithiin-*S*,*S*-tetraoxide **11**, in which, the cyclic geometry of this molecule allows a more favorable arrangement so that it has been proved to

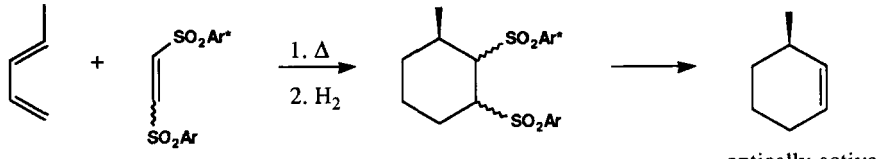
be more reactive than (*Z*)-or (*E*)-**1**. However, no further reports on its use were published after the independent communication by two research groups on its high potential.[41] Dienophile **11** is readily prepared in a number of routes described in the original papers[41] or by the same procedure described for (*Z*)-**1** starting from 1,2-benzenedithiol and (*Z*)-1,2-dichloroethylene.[37] The higher reactivity of **11** with respect of **1** is shown by the milder reaction conditions needed to carry out the cycloaddition with common dienophiles and by the time required to complete the reaction.



11

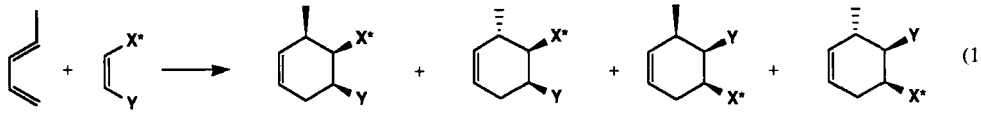
f. Chiral 1,2-*bis*(Arylsulfonyl)alkenes

To translate the results obtained in standard cycloadditions to asymmetric synthesis, a few strategies have been put forward. For example, an asymmetric variant to Eq. 1 should permit to perform the reaction illustrated in Eq. 15 eventually leading to a chiral hydrocarbon. Thus the ability of **1** to be included into the cavities of cyclodextrins has been examined.[42] This study was aimed at defining if a chiral environment generated by the cyclodextrins, will lead to chiral adducts when the *trans* isomer of **1** is used. Induced circular dichroism confirming the formation of the inclusion complexes was observed in aqueous solutions, but up to now, it has been impossible to separate the crystal complexes.



optically active (15)

On planning for a chiral acetylene equivalent of the type of (*Z*)- and (*E*)-**1**, able to perform the synthetic transformation illustrated in Eq. 15, it should be taken into consideration that the



(16)

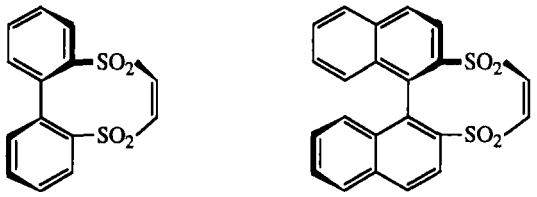
12 2 diastereoisomers 2 diastereoisomers 2 diastereoisomers 2 diastereoisomers

standard introduction of a chiral auxiliary would lead to a dienophile of type **12** which, in principle, can afford 8 stereoadducts as indicated in Eq. 16. On the other hand, a C_2-symmetrically chiral reagent of type **13** can lead to half the number of possibilities (Eq. 17).

(17)

13 2 diastereoisomers 2 diastereoisomers

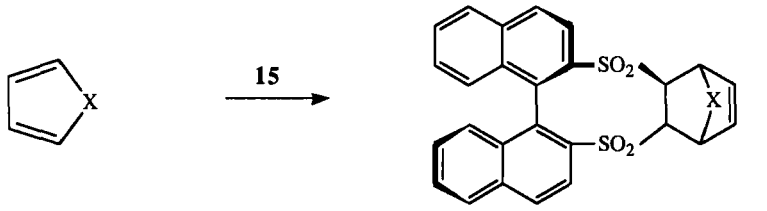
It is quite obvious that the chance to obtain a higher diastereoselection increases with a decrease in the number of possible stereoadducts. With this in mind, we have devised compounds **14** and **15** which present minimum structural diversity from (Z)-**1** in order to maintain the chemical properties associated with the achiral reagent.[43,44]



14 **15**

These compounds are atropisomeric reagents with C_2 symmetry, whose chirality is intrinsic to the shape of the molecule and not provided, as usual, by asymmetric carbon or sulfur atoms. While the resistance of **15** to racemization is expected based on the similarity with other binaphthyl compounds, the stability of **14** to racemization[45] is noteworthy. Both reagents are readily available from the respective dibenzo or 1,1'-dinaphtho-2,2'-dithiols which in turn are available *via* a number of routes.[46]

The cycloaddition reactions have been performed mostly on the binaphthyl derivative **15**, although a few reactions carried out with **14** have shown identical behaviour.[47] The reaction of **15** with symmetrical dienes leads to the expected cycloadducts (Eq. 18).[44]



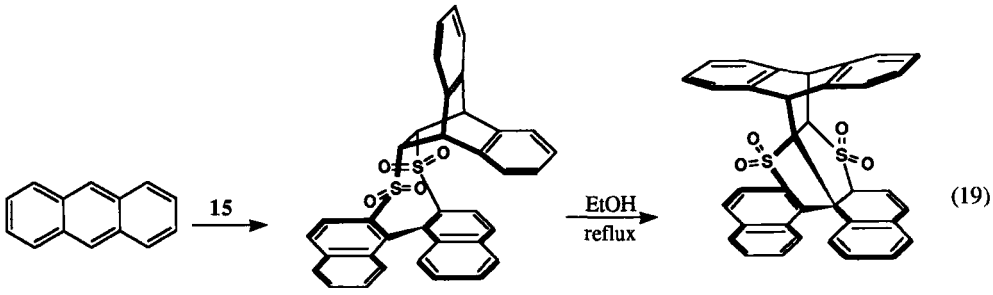
(18)

X = -O-, -(CH_2)-, -$(CH_2)_2$-,

In a few cases, the primary cycloadduct rearranges to more complicated structures as in the case of the adduct to anthracene (Eq. 19).[44]

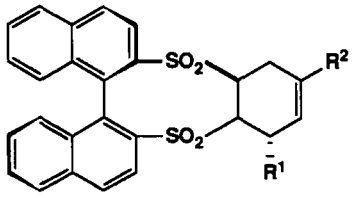
In the reaction with unsymmetrical dienes, the reaction affords, a single diastereoisomer in nearly all the cases so far investigated.[44]

Out of the possible four stereoisomers, the actual cycloadduct is the one which arises from the least sterically demanding approach. As expected the adducts can be desulfonylated under the same

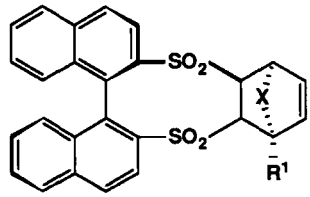


(19)

reaction conditions used for derivatives of (*Z*)- and (*E*)-**1**. Although this study has so far been performed on the racemic substrates, a number of possibilities have been advanced for the preparation of the reagents **14** and **15** in optically active form.[45,47]



R^1 = OMe R^2 = OTMS
R^1 = OMe R^2 = H
R^1 =OTMS R^2 = H
R^1 = Me R^2 = H
R^1 = H R^2 = OTMS



R^1 = OMe X = O
R^1 = OMe X = $(CH_2)_2$

2. SUBSTITUTED 1,2-*bis*(ARYLSULFONYL)ALKENES

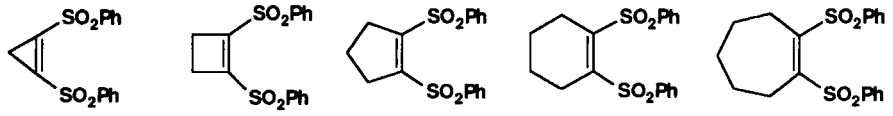
a. Monosubstituted 1,2-*bis*(Arylsulfonyl)alkenes

Monosubstituted alkyl- or aryl-substituted 1,2-*bis*(arylsulfonyl)alkenes have been reported infrequently and with only a few synthetic applications.[48] Reagents of this type present drastically reduced reactivity. In our experience, the introduction of a single methyl group is sufficient to completely suppress reactivity with standard dienes under reaction conditions where the unsubstituted derivatives undergo cycloaddition in high yield.[49]

b. Disubstituted 1,2-*bis*(Arylsulfonyl)alkenes

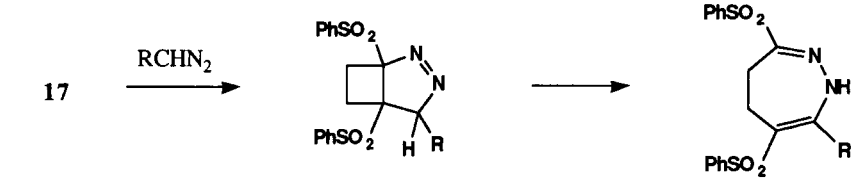
Disubstituted 1,2-*bis*(arylsulfonyl)alkenes display varying reactivity in relation to the substitution pattern. They can be prepared *via* different routes.[50] For the cyclic examples, except for the three membered ring **16** which has not been reported so far, the cyclobutene **17**[51] has been reported to be formed in the oxidation of the corresponding sulfide[51,52] and the higher homologues

bearing from five- to seven-membered ring *via* a simple procedure involving bisarylsulfenylation of the cyclic ketone.[53]



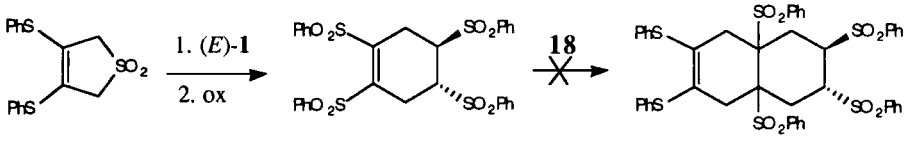
16 **17**

As already anticipated, the cycloadditivity properties of these molecules are poor. Except for the four-membered molecule **17** which cycloadds to cyclopentadiene and furan,[51] no cycloaddition to larger ring compounds has been reported. Whether, or not high pressure or the latest activation techniques described in the preceding section would be beneficial to the reactions remains to be determined. The cyclobutene **17** was used in another type of cycloaddition as a building block for the synthesis of dihydrodiazepines (Eq. 20).[51]



(20)

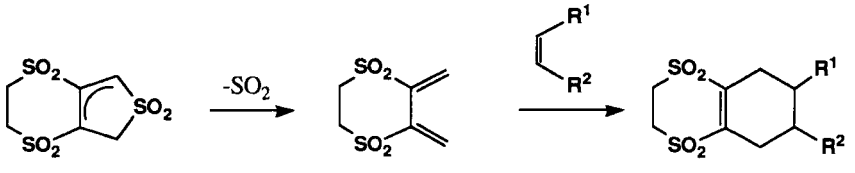
The reagent **18** is a potential precursor of 1,2-*bis*(arylsulfonyl)alkenes *via* cycloaddition with dienophiles and oxidation as shown in Eq. 21. Our expectation that this reagent could serve as an iterative building block for cyclohexenylation did not materialize.[54]



(21)

18

The related molecule shown in Eq. 22 also proved to be reactive towards a number of dienophiles.[55]

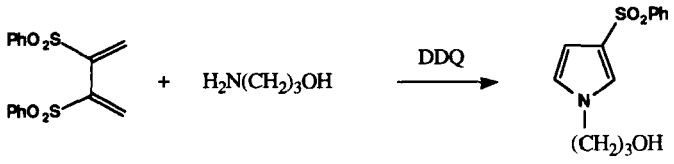


(22)

R^1 = COMe, CO_2Me, OEt, Ph R^2 = H

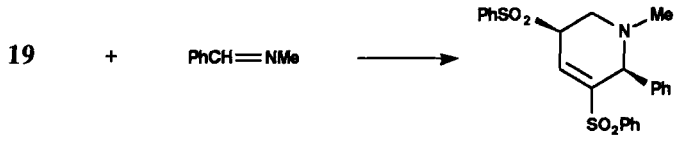
R^1-R^2 = 

Incidentally, diene **19** reacts with amines,[56] imines,[57] oximes[58] to give the products illustrated in Eqs. 23-25.

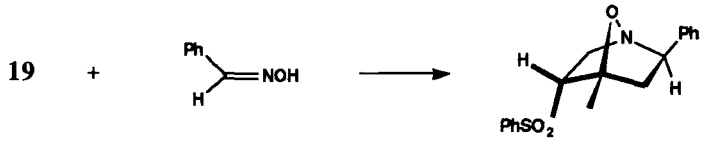


(23)

19



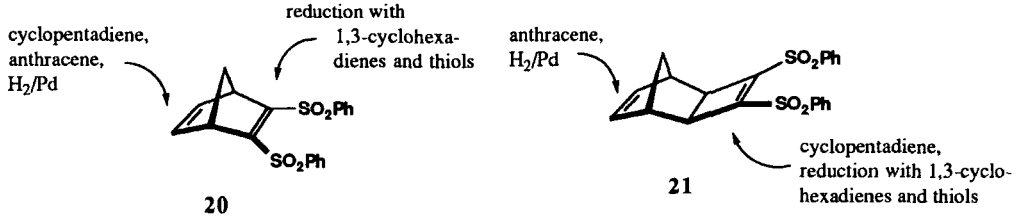
(24)



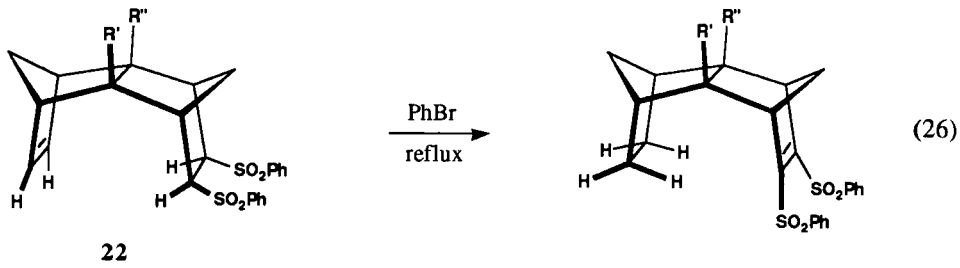
(25)

In our own experience, the 1,2-*bis*(arylsulfonyl)alkene, even incorporated into the usually very reactive norbornene skeleton[59] as in **20**, did not react with dienophiles preventing a simple way to obtain norbornatriene and similar molecules. Indeed, **20** reacts with cyclopentadiene with the unsubstituted double bond (Scheme 2). Only a few reagents add to the electrophilic olefin. Grignard reagents and thiols are examples.[60] For comparative purposes it is worth noting that the reactivity of the related molecule **21**, containing a 1,2-*bis*(arylsulfonyl)alkene is quite similar except for the reaction with cyclopentadiene.

Scheme 2



Molecules of type **22** show the intramolecular hydrogen migration shown in Eq. 26. The rate of migration depends on the distance between the two reactive sites which was modified varying the substituents at the central C(4)-C(9) bond.[61]



(26)

22

R', R" = H R'-R"= *i*-Pr-N
R'-R" = -O- R'-R" = CH_2

c. Disubstituted Benzodithiin Derivatives

To alleviate the poor reactivity problem of 1,2-*bis*(arylsulfonyl)alkenes, we initiated an investigation which sought to take advantage of the higher reactivity of benzodithiin derivatives of type **11** over the 1,2-*bis*(arylsulfonyl) derivatives. Indeed, it was reasoned that the olefin was too shielded by the two arylsulfones to allow reaction even with standard dienes. The geometry of the benzodithiin was better suited (at least from one side of the double bond) for further cycloaddition reactions.

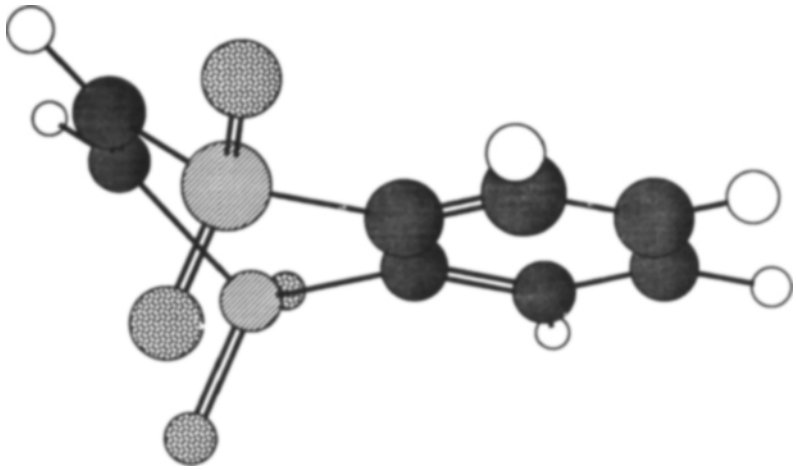
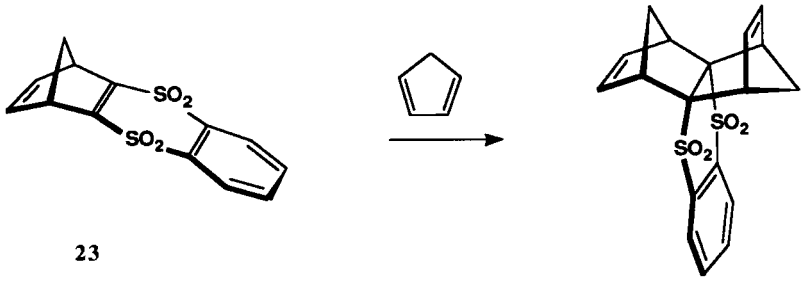


Fig. 3. Chem 3D Drawing of Benzodithiin.

Preliminary experiments suggest that the expectation is correct. The norbornadiene **23** (Eq. 27), in contrast to norbornadiene **20** (Eq. 28) reacts at the activated double bond; based on this observation, we are now evaluating the synthetic potential of these reagents .[37]



23

(27)

On this basis, we are confident that benzodithiin sulfones will widen the horizon to 1,2-*bis*(arylsulfonyl) chemistry.

20

(28)

Note added in Proof. After our review was submitted, an efficient procedure for the reductive desulfonylation of phenyl sulfones by samarium(II)iodide-hexamethylphosphoric triamide was reported.[62]

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