

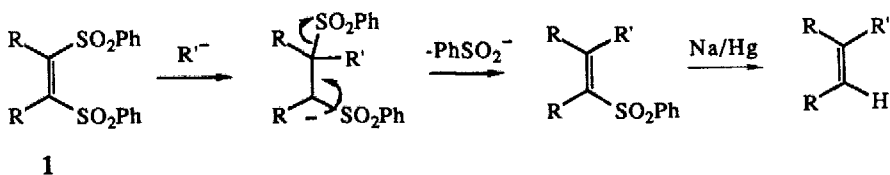
**1,2-BIS(PHENYLSULFONYL)ALKENES AS VERSATILE GROUPS IN  
ORGANIC SYNTHESIS: THE PREPARATION OF ALKYL- AND ARYL-SUBSTITUTED  
NORBORNADIENES VIA THE DIELS-ALDER CYCLOADDITION - GRIGNARD REACTION  
- DESULFONYLATION SEQUENCE**

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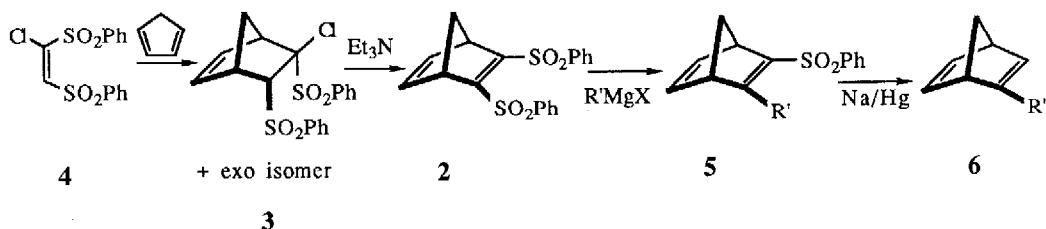
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**Summary:** A synthetic methodology for the preparation of the formal Diels-Alder cycloadducts of alkyl- and aryl-substituted acetylenes which exemplifies the utility of bis(phenylsulfonyl)alkenes **1** in organic synthesis is presented. The procedure entails [4+2]-cycloaddition of (*E*)-1,2-bis(phenylsulfonyl)-1-chloroethylene (**4**), Grignard reaction and desulfonylation; each step occurs in high yield.

The chemistry of unsaturated phenyl sulfones is receiving increasing attention because of the versatility in their transformations and the efficient activation by the sulfonyl group.<sup>1</sup> In addition must be mentioned the ready availability of numerous derivatives and the intrinsic simplicity of technical operations derived from the usually high crystallinity of the products. The development of such chemistry might consider the use of doubly phenylsulfonyl substituted alkenes of type **1** as versatile precursors to substituted olefins. The sequence shown offers an expedient route to the preparation of difficultly accessible or hitherto unknown olefins.



1,2-Diphenylsulfonyl-substituted alkenes **1** are very little represented in the chemical literature although they can be prepared *via* addition-elimination to suitably substituted vinyl sulfones,<sup>2</sup> Michael addition to acetylenic sulfones,<sup>3</sup> thioarylation of  $\beta$ -phenylthioketones,<sup>4</sup> and appropriate modifications of the procedures derived therefrom. Following our interest in cycloaddition reactions, we report here on the reactions applied to substrate **2**. The sequence ultimately leads to alkyl- and aryl-substituted norbornadienes **6** which may be of interest in solar energy storage because they should be amenable to photochemical cyclization to quadricyclanes in a process similar to that extensively studied for the parent molecule.<sup>5,6</sup>



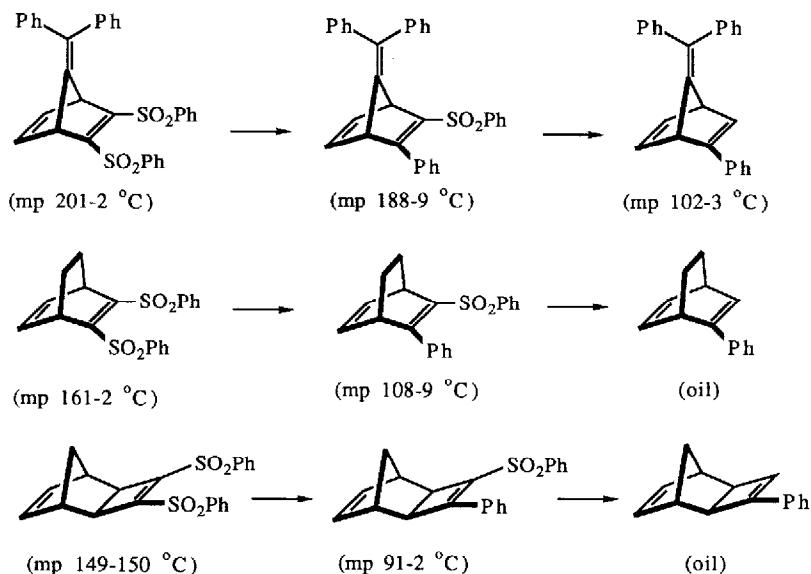
R' = Me	82%	Ref.12
= n-Pr	78%	94%
= Ph	87%	95%
= 1-Napht	70%	Ref.15

Dienophile **4** is readily available from cheap starting materials by the method of Montanari.<sup>7</sup> Cycloaddition to cyclopentadiene in a sealed vessel affords a 4:1 mixture of the cycloadducts which is readily dehydrochlorinated by triethylamine to the bis(phenylsulfonyl)derivative **2** in 89% overall yield.<sup>8</sup> Such a substituted norbornadiene represents the formal addition product of the hitherto unknown bis(phenylsulfonyl)acetylene and hence dienophile **4** may be viewed as an equivalent of this synthetically appealing acetylene.<sup>9</sup>

Reaction of norbornadiene **2** with Grignard reagents affords high yields of substituted adducts **5**.<sup>2,10</sup> The reaction works well both for aliphatic and aromatic derivatives as exemplified by the preparation of the methyl, *n*-propyl, phenyl and naphthyl systems.<sup>11</sup>

Compounds **5** can be subjected to the rich chemistry of vinyl sulfones.<sup>1</sup> A case of interest here is their desulfonation<sup>14</sup> to alkyl and aryl-substituted alkenes as exemplified by the preparation of the 2-substituted norbornadienes **6**.<sup>15,16</sup> These dienes cannot be prepared *via* the direct cycloaddition because of the unreactivity of the unactivated acetylene towards cyclopentadiene. In this context (*E*)-1,2-bis(phenylsulfonyl)-1-chloroethylene constitutes a synthetic equivalent for substituted acetylenes as dienophiles in Diels-Alder reactions.<sup>17</sup>

It is worth mentioning that the dienophilic reactivity of **4** is not limited to cyclopentadiene and hence the utility of the present methodology has been expanded to other polycycles such as those illustrated below.



The isomeric (*E*)-1,2-bis(phenylsulfonyl)-1-chloroethylene is even more reactive as dienophile than the (*Z*)-isomer; but, as observed previously,<sup>18</sup> the adducts could not be readily dehydrochlorinated.

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9. Attempts to prepare bis(phenylsulfonyl)acetylene via Diels-Alder retrocyclization of **2** have been so far unsuccessful.
10. To the best of our knowledge, addition-elimination reactions to 1,2-bis(phenylsulfonyl)alkenes have been so far reported for the parent system (Meek, J.S.; Fowler, J. S. *J. Org. Chem.* 1968, **33**, 985) and *ortho*-bis(phenylsulfonyl)benzene (Koebrich, G. *Chem. Ber.* 1959, **92**, 2981).
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