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BIS(*TERT*-BUTYLSULFONYL)ACETYLENE AS A GENERAL SYNTHETIC EQUIVALENT OF ALKYNES IN DIELS-ALDER CHEMISTRY. II: REDUCTIVE AND ALKYLATIVE DESULFONYLATIONS OF BICYCLIC 1-ALKYL-2-(*TERT*-BUTYLSULFONYL)ETHENES

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Summary: *Both reductive and alkylative desulfonylations of bicyclic vinyl sulfones derived from Diels-Alder cycloadducts of bis(tert-butylsulfonyl)acetylene (1) are described. These transformations establish the synthetic equivalence of* **1** *with acetylene, 1-alkynes and internal alkynes in Diels-Alder chemistry.*

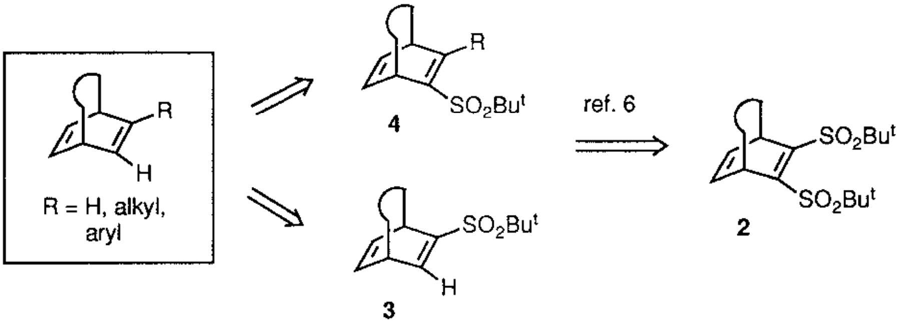
The poor dienophilicity of acetylene in cycloaddition reactions has been overcome from a synthetic point of view through the use of several synthetic equivalents.[1] There are however very few synthons for alkynes other than the parent acetylene,[2-5] and only two[3,5] of these allow the more or less direct introduction of a single alkyl substituent. In the preceding paper, we have shown that bis(*tert*-butylsulfonyl)acetylene **1**,[6] the only stable acetylenic bis-sulfone described so far, is an effective surrogate of 1-alkyl- and 1-aryl-2-(*tert*-butylsulfonyl)acetylenes in Diels-Alder reactions.[7] We show in this paper that **1** can also be considered as a synthetic equivalent of acetylene, 1-alkynes and internal alkynes in Diels-Alder cycloadditions.

$Bu^tSO_2-C\equiv C-SO_2Bu^t$

1

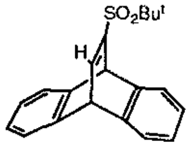
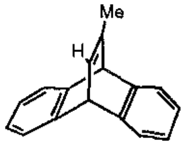
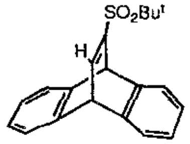
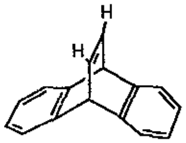
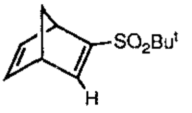
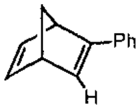
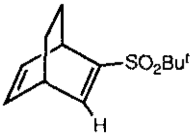
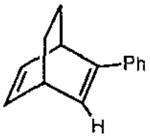
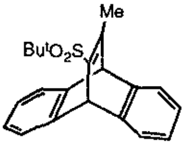
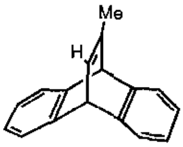
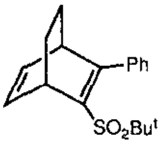
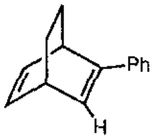
1. Synthetic Equivalence to Acetylene and 1-Alkynes.

The synthesis of monosubstituted bicyclic dienes from the bis-sulfones **2** could in principle be achieved either by alkylative desulfonylation of modified Diels-Alder adducts **3** or by reductive desulfonylation of monosulfones **4**.



In practice, both ways are feasible, as shown by the results summarized in Table I.

TABLE I

Entry	Monosulfone	Reaction conditions	Product	Yield
1	 **3a**	A (R=Me)	 **5**	45%
2	 **3a**	A (R=Et)	 **6**	67%
3	 **3b**	A (R=Ph)	 **7**	40%
4	 **3c**	A (R=Ph)	 **8**	68%
5	 **4am**	B	 **5**	31%
6	 **4cp**	A (R=Et)	 **8**	67%

Reaction conditions: A: RMgBr, 10% $Pd(acac)_2$, THF, reflux. B: Na/Hg, THF, MeOH, Na_2HPO_4.

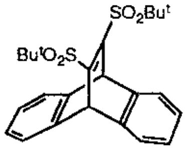
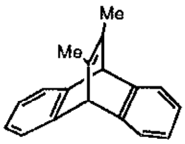
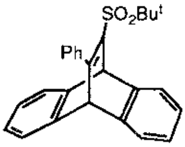
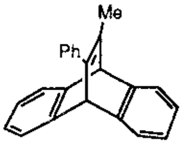
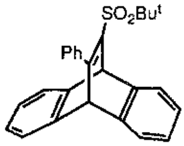
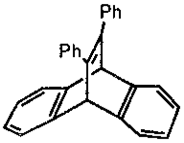
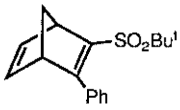
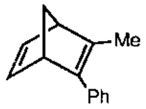
The alkylative desulfonylation of several *tert*-butyl vinyl sulfones by means of Grignard reagents in the presence of nickel and iron catalysts has been described by the group of Julia.[8] In our hands, however, much better results are obtained by using $Pd(acac)_2$ as the catalyst (see entries 1, 3 and 4 of Table I). This protocol allows the direct substitution of a *tert*-butylsulfonyl group by an aryl or alkyl moiety. It should be noted however that this strategy is not useful for the introduction of alkyl groups having β-hydrogens.[9]

Interestingly, the reaction of monosulfones **3** and **4** with ethylmagnesium bromide under Pd(II) catalysis constitutes in fact the method of choice for the reductive desulfonylation of these compounds (see entries 2 and 6 of Table I). It is worth noting that a variety of reductive desulfonylation procedures described in the literature for aryl vinyl sulfones (sodium dithionite,[10] sodium[4a,5,11] and aluminium[12] amalgams) are unsuccessful for our substrates and lead to double bond reduction. In a similar way, as stated in the preceding paper,[7] reduction with samarium diiodide does not proceed beyond the monosubstitution stage. A most revealing exception occurs in the case of the methyl substituted sulfone **4am** (entry 5 of Table I), which under treatment with sodium amalgam produces, albeit in low yield, the desired olefin **5**. These facts suggest that these sulfone reduction methods are initiated by electron transfer at the most unsaturated sulfone substituent, which is the vinyl group in the case of of *tert*-butyl sulfones, and the phenyl group in the case of aryl sulfones.[13] It is therefore clear that the unique efficiency of the Pd based reduction of *tert*-butyl vinyl sulfones relies on the mechanistic avoidance of electron transfer processes.

2. Synthetic Equivalence to Internal Alkynes.

The equivalence of bis(*tert*-butylsulfonyl)acetylene **1** to internal (both symmetrical and unsymmetrical) alkynes is evinced through the results shown in Table II.

TABLE II

Entry	Starting compound	Reaction conditions	Product	Yield
1	 **2a**	A	 **9**	82%
2	 **4ap**	A	 **10**	100%
3	 **4ap**	B	 **11**	100%
4	 **4bp**	A	 **12**	44%

Reaction conditions: A: MeMgBr, 10% Pd(acac)$_2$, THF, reflux. B: PhLi, THF, 0°C

As we have already said in the preceding paper,[7] the reaction of organolithium compounds with the vinylic bis-sulfones **2** does not proceed in general beyond the monosubstituted product. The only exception we have found is in the case of the phenyl substituted sulfone **4ap**, which upon further addition of phenyl lithium cleanly undergoes a second substitution (see entry 3 of Table II).[14] In addition to that, the synthesis of disubstituted bicyclic dienes can be achieved *via* Pd(II) catalyzed coupling of a Grignard reagent either with bis-sulfones **2** (for symmetrical products) or with monosulfones **4** (see entries 1, 2 and 4 of Table II).

In summary, we have presently shown how the Diels-Alder adducts of bis(*tert*-butylsulfonyl)acetylene **1** can be transformed into products in which one or both sulfone groups have been substituted by hydrogen, alkyl or aryl. Bis-sulfone **1** can be thus considered as the first general synthetic equivalent to acetylene, 1-alkynes or internal alkynes in Diels-Alder cycloadditions.

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13. In effect, the obtention of **5** from **4am** could be accounted for by fragmentation of an intermediate allyl anion (or *radical) arising from hydrogen loss of the vinyl radical anion of* **4am**.
14. Interestingly, the analogous reaction with alkyl lithiums either does not proceed at all or with very low yield. For some precedent, see: Eisch, J. J.; Behrooz, M.; Galle, J. E. *Tetrahedron Lett.* **1984**, *25*, 4851.

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