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BIS(*tert*-BUTYLSULFONYL)ACETYLENE: A HIGHLY REACTIVE DIENOPHILE

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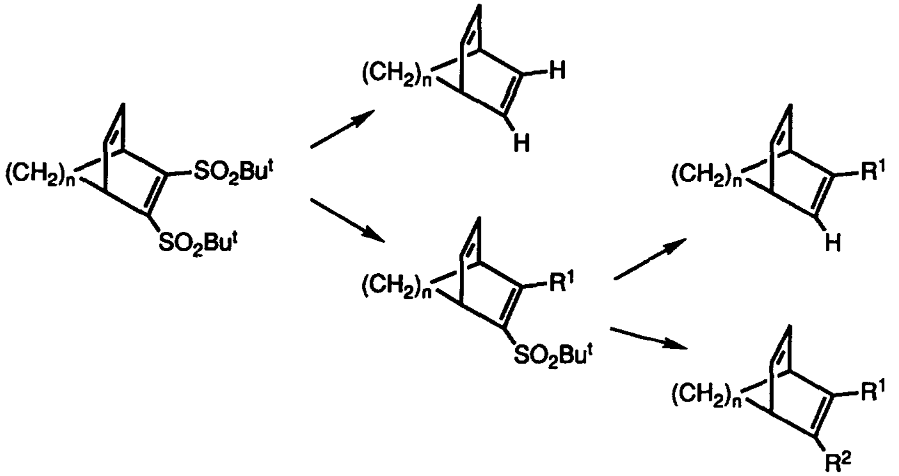
Summary: *Bis(tert-butylsulfonyl)acetylene, prepared in quantitative yield by m-CPBA oxidation of bis(tert butylthio)acetylene, reacts with a variety of 1,3-dienes under very mild conditions to afford the corresponding Diels-Alder adducts in high yield.*

The use of the sulfonyl group in the activation of alkenes and alkynes towards 4+2 cycloadditions is a well established methodology[1]. At variance with other commonly used activating groups, the sulfonyl moiety can be easily removed from the resulting Diels-Alder adducts by a variety of methods including reduction[2], oxidation[3] and alkylation[4].

As a consequence of the forementioned facts, different alkenyl[5] and alkynyl[2c,6] sulfones have been proposed as synthetic equivalents of alkenes and alkynes which are not prone to undergo Diels-Alder reactions.

However, no acetylenic bis-sulfone has been up to now employed as a dienophile, despite of the enormous potential of the resulting adducts. Thus, it appears that proper combinations of alkylation and/or reduction performed on these adducts should allow the establishment of synthetic equivalences between acetylenic bis-sulfones and acetylene, 1-alkynes and internal alkynes, as depicted in the following scheme.



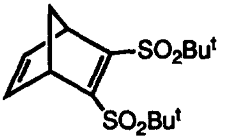
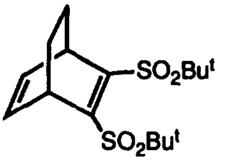
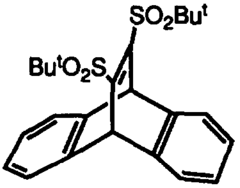
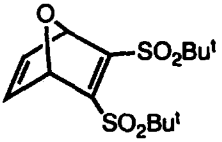
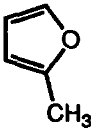
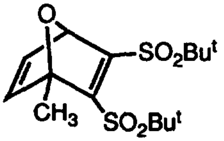
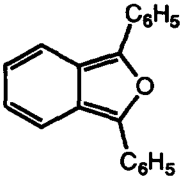
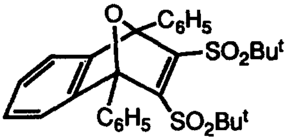
Bis(*tert*-butylsulfonyl)acetylene (1), the only acetylenic bis-sulfone described so far[8], was available in low yield by oxidation with perbenzoic acid of bis(*tert*-butylthio)acetylene (2c), a compound whose preparation from trichloroethylene was reported to take place also in low yield.

As a preliminary step, we have developed a new synthesis of acetylene dithioethers characterized by broad applicability and high yield[9]. We have subsequently studied the oxidation with m-chloroperoxybenzoic acid of bis(ptolylthio)acetylene (**2a**), bis(isopropylthio)acetylene (**2b**) and bis(*tert*-butylthio)acetylene (**2c**) in chloroform solution. Whereas in the first two cases complex reaction mixtures are obtained, and significant addition of m-chlorobenzoic acid to the carbon-carbon triple bond takes place, bis(*tert*-butylsulfonyl)acetylene **1** can be easily obtained in essentially quantitative yield[10].

$$\underset{\mathbf{2c}}{Bu^tS{-}C{\equiv}C{-}SBu^t} \xrightarrow[CHCl_3]{m\text{-}CPBA} \underset{\mathbf{1}}{Bu^tSO_2{-}C{\equiv}C{-}SO_2Bu^t} \quad 98\%$$

The Diels-Alder reaction of **1** with a variety of 1,3-dienes has been studied. The results obtained with a family of cyclic dienes are summarized in Table I[11].

Table I: Diels-Alder Reactions of Bis(tert-butylsulfonyl)acetylene

Diene	Adduct		Conditions	Yield [%]
		**3a**	CH_2Cl_2, r.t., 24h	92
		**3b**	C_6H_6, reflux, 3h Toluene, r.t., 2h	65 34
Anthracene		**3c**	Toluene, reflux, 20h	68
		**3d**	Toluene, r.t., 2h	89
		**3e**	Toluene, r.t., 3h	71
		**3f**	CH_2Cl_2, 5°C, 240h	53

As it can be readily seen, most of the dienes in Table I react with 1 at room temperature without the need of catalysis, thus indicating a very high dienophilic reactivity for this species. In fact, only ethyl (phenylsulfonyl)propiolate[6f] exhibits a similar reactivity among the known acetylenic sulfones.

It is worth noting that the higher temperature reactions of 1 with cyclohexadiene and anthracene were performed under "forbidden" conditions, i.e., at temperatures where 1 is no longer stable[12]. Reaction times in these experiments were not optimized.

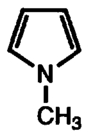
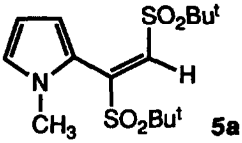
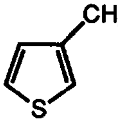
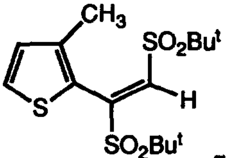
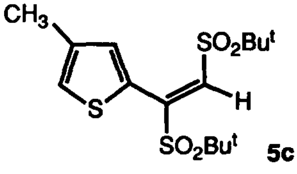
The reaction of 1 with diphenylisobenzofuran turns out to be readily reversible. Thus, when the adduct 3f is heated under reflux in toluene solution for a few minutes, a complete decomposition into 1 and diphenylisobenzofuran takes place.

The cycloaddition of 1 with other 1,3-dienes was also attempted. With isoprene and 2,3-dimethyl-1,3-butadiene, a fast reaction took place at room temperature, but a complex reaction mixture was formed. The process can be complicated in these cases by the isomerization and aromatization of the adducts. On the other hand, ene reactions could also compete here with the normal cycloadditions[13].

Quite unexpectedly[6a-b,6j] 1 did not react with tetracyclone. Much probably, the origin of this behaviour lies in the important steric demand of the *tert*-butylsulfonyl and phenyl substituents, that could either hinder the approach of the reactants required for the reaction to proceed, or destabilize the adduct relative to the reactants.

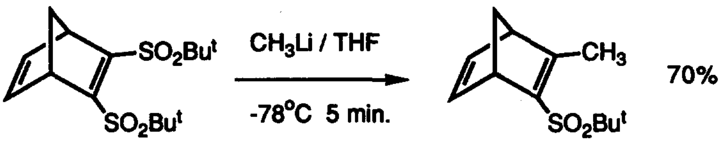
Finally, the cycloaddition of 1 with poor dienes, such as N-methylpyrrole and 3-methylthiophene was attempted. The reaction took place rather easily, but the products correspond to the Michael type addition of the heterocycle on the triple bond of 1, as shown in Table II.

Table II : Michael-type Additions on Bis(tert-butylsulfonyl)acetylene

Addend	Adduct	Conditions	Yield [%]
	 **5a**	C_6H_6 , r.t. , 5h	56
	 **5b**	Toluene, 90°C, 20h	38
	 **5c**	**5b / 5c** : 82 / 18	

The results recorded with N-methylpyrrole, which are not completely unexpected[14], contrast however with those reported for the reaction of N-methoxycarbonylpyrrole with ethynyl p-tolyl sulfone[15]. On the other hand, we found no precedent of the Michael type addition of thiophenes to acetylenic dienophiles.

The Diels-Alder adducts 3 can be submitted to the known chemistry of vinyl sulfones, thus allowing the establishment of synthetic equivalences between 1 and different kinds of alkynes. In this context, it is worth noting that 3a reacts with methyl lithium at low temperature to afford in a clean way the monosubstitution product 6.



3a **6**

Since both the reductive desulfonylation[6h] and the cross-coupling with Grignard reagents[4] of closely related vinyl sulfones have been reported, the synthetic potential of the adducts **3** appears to be very broad. Work along these lines is in progress in our laboratories and will be reported on due course.

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10. **Experimental procedure:** To a solution of **2c** (3.44g, 17mmol) in chloroform (50mL), 100% m-chloroperbenzoic ac (14.65g, 85mmol) in chloroform (200mL) was added at 0°C. After stirring for 48h at r.t., the precipitate was filtered off, the solution was washed with 10% $Na_2S_2O_3$(2x100 mL) and 10% $KHCO_3$ (2x100 mL), dried over Na_2SO_4 and evaporated to afford 4.45g (98% yield) of 1.
11. Correct elemental analyses and spectral data consistent with the given structures were obtained for all reported compounds.
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