

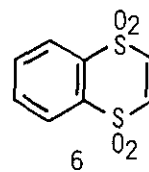
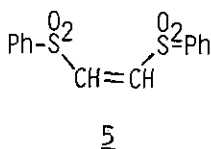
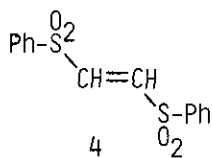
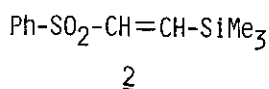
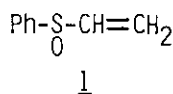
1,4-BENZODITHIIN 1,1,4,4-TETRAOXIDE AS DIENOPHILE

Juzo Nakayama,* Yoichi Nakamura, and Masamatsu Hoshino

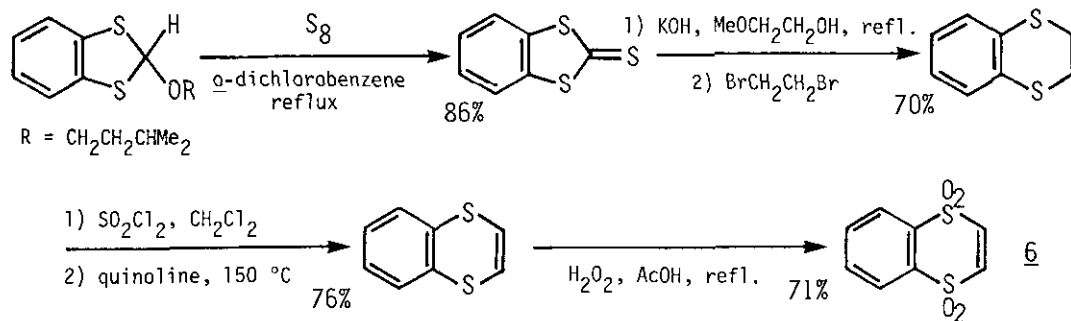
 Department of Chemistry, Faculty of Science, Saitama University,
 Urawa, Saitama 338, Japan

Abstract — 1,4-Benzodithiin 1,1,4,4-tetraoxide undergoes the Diels-Alder reaction with a series of dienes under mild conditions to provide the corresponding adducts in excellent yields. The adduct with anthracene is desulfonated to afford dibenzobarrelene, thus showing that the title compound functions as an acetylene equivalent.

A number of ethylene and acetylene equivalents have recently been developed to circumvent the drawbacks of the low reactivity of unadorned ethylene and acetylene as dienophilic reagents. Among them, of particular interest and synthetically important are the olefinic dienophiles that are activated by sulfur functionalities such as sulfoxides and sulfones. Paquette et al. developed acetylene equivalents (1)¹ and (2)² and an ethylene equivalent (3),^{3,4} while De Lucchi et al. reported that the doubly sulfonyl-activated (4)^{5,7} and (5)^{6,7} which have higher dienophilic reactivity serve as acetylene equivalents. Herein we report that the cyclic disulfone, 1,4-benzodithiin 1,1,4,4-tetraoxide (6),⁸ is a much stronger dienophile than any other reagents described above and functions as an acetylene equivalent.^{9,10}



Scheme 1



The known sulfone 6⁸ was most conveniently prepared from easily accessible 2-isopentyloxy-1,3-benzodithiolo¹¹ as the starting material (Scheme 1).

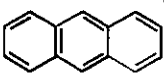
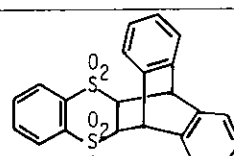
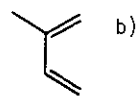
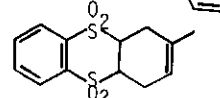
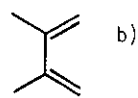
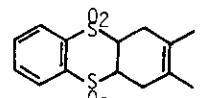

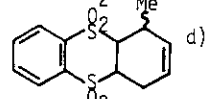

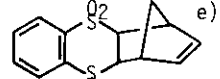

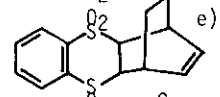

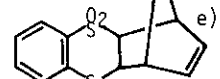

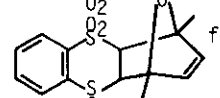
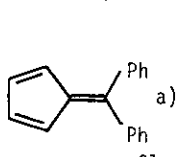
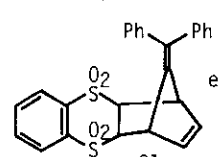
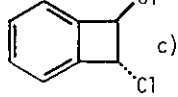
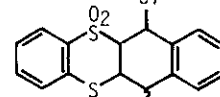
The cyclic sulfone 6 smoothly undergoes the Diels-Alder reaction with a series of dienes under mild conditions to provide the corresponding adducts nearly quantitatively. Tetraphenylcyclopentadienone exceptionally resists reaction with 6 probably because of the electron-deficient nature of the both reactants. The procedure of the reaction is very simple; a solution of 6 and a diene in an appropriate solvent was allowed to stand at ambient temperature or heated and the adducts were easily isolated by column chromatography on silica gel. The results are summarized in Table 1.

The sulfone 6 is a much stronger dienophile than compounds 1-5. Heating 6 and anthracene (1.1 equiv) in refluxing toluene for 4 h affords the Diels-Alder adduct in 93% yield (entry 1). The Diels-Alder reaction of anthracene with compounds 1-5 requires more forced conditions; the conditions employed for the reaction of anthracene with 1, 2 (trans), 3, 4, and 5 are 130 °C for 120 h,¹ 160 °C for 1 week,^{2,4} 155 °C for 100 h,^{3,4} 170 °C for 24 h,⁷ and 160 °C for 18 h,⁷ respectively. Similar comparison with other dienes leads to the same conclusion.

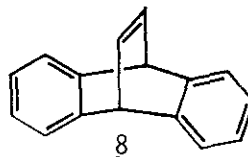
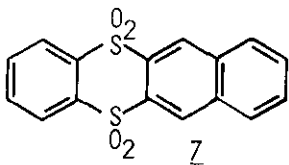
An equimolar mixture of anthracene, 6, and maleic anhydride in toluene was refluxed for 0.5 h. In that time, about 60% of anthracene was consumed and the adducts of anthracene with 6 and maleic anhydride were formed in nearly equal amounts, thus suggesting that the dienophilic reactivity of 6 toward anthracene is nearly equal to that of maleic anhydride.

When *trans*-1,2-dichloro-1,2-dihydrobenzocyclobutene was heated with 6 in refluxing *o*-dichlorobenzene, under the conditions of which the former undergoes the ring-opening reaction leading to the *o*-quinodimethane form, the reaction afforded

Table 1 Diels-Alder Reaction of 1,4-Benzodithiin 1,1,4,4-Tetraoxide with a Series of Dienes

entry	diene	adduct	conditions		
			(solvent, temperature, time)	yield (%)	mp of adduct (°C)
1			toluene reflux 4h	93	367-369 (dec.)
2			CH ₂ ClCH ₂ Cl 50 °C 10 h	98	158-159
3			CH ₂ Cl ₂ r.t. 25 h	99	183.5-184.5
4			CH ₂ ClCH ₂ Cl 50 °C 10 h	96	160 (dec.) ^{d)} 184-187
5			CH ₂ Cl ₂ r.t. 1 h	95	278-279 (dec.)
6			CH ₂ ClCH ₂ Cl 50 °C 10 h	95	301-309 (dec.)
7			CH ₂ Cl ₂ r.t. 20 h	98	212-221
8			CH ₂ Cl ₂ r.t. 20 h	98	214-221
9			CH ₂ Cl ₂ r.t. 20 h	99	261-262 (dec.)
10			<u>o</u> -dichloro- benzene reflux 6.5 h	83	230-234 (dec.) ^{g)} 345-348 (dec.)

a) 1.1 Equiv of dienes were used. b) These dienes were used in large excess (5-10 equiv).
 c) 2 Equiv of dienes were used. d) Two isomers were isolated by column chromatography in nearly equal amounts, one of which decomposes above 160 °C, and the other melts at 184-187 °C.
 e) Endo adducts were exclusively formed. f) Stereochemistry of these compounds is unknown.
 g) This compound melts at 230-234 °C with evolution of gas, solidifies, and remelts at 345-348 °C. The latter melting point corresponds to that of compound **7** which has mp of 348-353 °C. In one case, the dehydrochlorinated compound **7** was directly obtained in 87% yield under the applied conditions.



the Diels-Alder adduct in 83% yield (entry 10). Treatment of the adduct with triethylamine affords compound 7 quantitatively.

Finally the adduct of 6 with anthracene was desulfonated by 1.3% sodium amalgam in MeOH-THF (2:1) in the presence of sodium dihydrogen phosphate at room temperature. This resulted in the formation of dibenzobarrelene (8) in 66% yield,¹² thus suggesting that 6 functions as an acetylene equivalent.

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