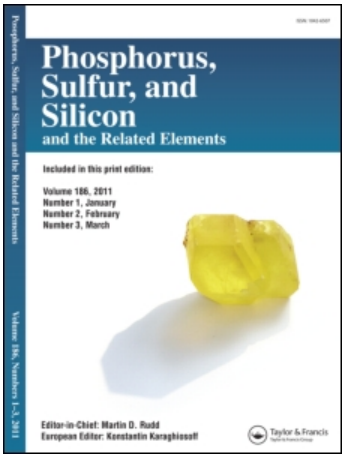

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article De Lucchi, Ottorino and Marchioro, Gaetano(1985) 'SYNTHESIS AND DIELS—ALDER REACTIONS OF 2,3-BIS(BENZENETHIO)-1,3-BUTADIENE', Phosphorus, Sulfur, and Silicon and the Related Elements, 24: 3, 305 — 309
To link to this Article: DOI: 10.1080/03086648508074242
URL: http://dx.doi.org/10.1080/03086648508074242

Phosphorus and Sulfur, 1985, Vol. 24, pp. 305–309
0308-664X/85/2403–0305/$10.00/0

SYNTHESIS AND DIELS–ALDER REACTIONS OF 2,3-BIS(BENZENETHIO)-1,3-BUTADIENE

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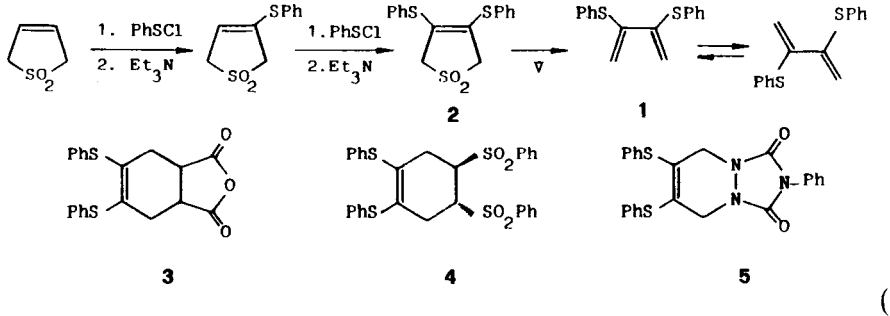
(*Received January 24, 1985*)

Two different routes to the preparation of 2,3-bis(benzenethio)-1,3-butadiene (**1**) are reported. Diene **1** is shown to react with maleic anhydride, (*E*)-1,2-bis(benzenesulfonyl)ethyene and 4-phenyl-1,2,4-triazoline-3,5-dione to give the respective Diels–Alder adducts. The adduct to (*E*)-1,2-bis(benzenesulfonyl)ethylene (**4**) has been reductively desulfonylated to the bisthioether **7** which was subsequently oxidized to the corresponding bissulfone **8**, providing an entry to bis(benzenthio) and bis(benzenesulfonyl) activated molecules.

Sulfur substituted 1,3-dienes have recently received much attention, either because of the activation imparted by the sulfide function or because of the synthetic potentiality of the derived adducts.[1] In connection with the recently reported utilization of bis(benzenesulfonyl) activated ethylenes in cycloaddition reactions[2] we synthesized 2,3-bis(benzenethio)-1,3-butadiene (**1**) as it was expected to be an activated diene and the Diels-Alder adducts, once oxidized, could have also served as activated dienophiles for the synthesis of polycyclic molecules.[3]

Two approaches to the synthesis of **1** have been undertaken. A first route entails retrocheleotropic loss of sulfur dioxide from precursor **2** that can be obtained via sequential addition of benzenesulfenyl chloride followed by hydrochloric acid elimination. Although **2** (though tolyl instead of phenyl) has already been prepared by Stirling *et al.*,[4] at the best of our knowledge it has never been thermolyzed to **1** nor has it been directly subjected to the reaction with dienophiles. Indeed on heating a toluene solution of **2** in the presence of an equimolar amount of maleic anhydride, adduct **3** is formed in 96% isolated yield. Similarly adduct **4** is obtained in 95% yield when (*E*)-1,2-bis(benzenesulfonyl)ethylene is used as dienophile.

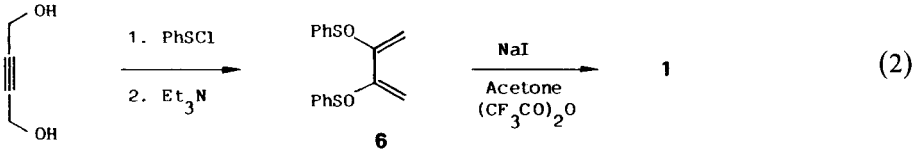


(1)

*Author to whom all correspondence should be addressed.

When heated in the absence of dienophiles, diene **1** can be isolated in very high yield, but it is rather unstable so that its isolation is in most cases inconvenient.

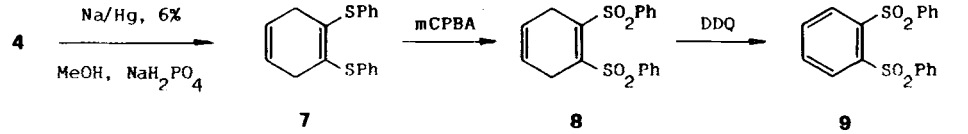
A more ready route to **1** is shown in Eq. (2). Here again, while the preparation of the mixture of meso and racemic sulfoxides **6** was already known,[4,5] no reduction to the corresponding sulfide **1** has, at the best of our knowledge, been reported. This procedure to **1** is more advantageous as it can be easily scaled up to multigram quantities and it requires inexpensive reagents.



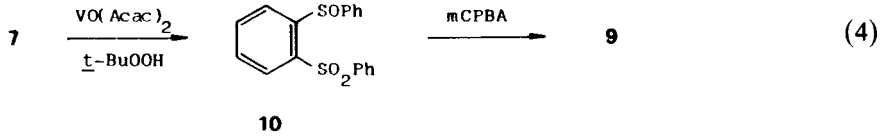
(2)

The dienophilic reactivity of **1** is not however as expected. Beside maleic anhydride and (*E*)-1,2-bis(benzenesulfonyl)ethylene, 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) reacts with **1**, but less activated dienophiles as (*Z*)-1,2-bis(benzenesulfonyl)ethylene, cyclohexenone, etc. failed to react under analogue reaction conditions. In the case of carbonyl activated dienophiles, Lewis acid catalysis proved also little rewarding as extensive decomposition of the diene occurs.

Adduct **3** was reductively desulfonylated with sodium amalgam in buffered methanol[2] to the bissulfide **7**, that on *m*-chloroperbenzoic acid oxidation gave **8** in 80% overall yield. With the use of *t*-butyl hydroperoxide in the presence of $VO(Acac)_2$ as catalyst the oxidation of **7** takes another course and *o*-benzensulfinyl-benzenesulfonylbenzene **10** is obtained in 88% yield (Eq. (4)). Further oxidation of **10** with *m*-chloroperbenzoic acid expectedly delivers **9** in virtually quantitative yield. The latter aromatic compound has also been obtained in quantitative yield from **8** upon treatment with dichlorodicyanoquinone (DDQ) as expressed in Eq. (3).



(3)



(4)

This alternative synthesis of **9** is amenable to the introduction of different functionalities for the obtainment of differently substituted bis aromatic sulfones.[6] These molecules are actively investigated either for their peculiar behavior on reduction[7] or for the synthesis of sulfone derivatives.[8]

From another point of view, this route represents a ready access to doubly thiosubstituted and hence highly nucleophilic, electron rich olefins that on simple oxidation become doubly benzenesulfonyl substituted, hence strongly electrophilic alkenes. These latter compounds can be subjected to numerous nucleophilic substitutions.[8]

Although activated by two benzenesulfonyl groups, olefin **8** proved to be a very poor dienophile, as most of the more conventional dienes did not react with it under a number of reaction conditions. This unreactivity has so far precluded a convenient access to a variety of functionalized polycyclic molecules. We do not have at this time a satisfactory explanation for the lack of dienophilic reactivity of cyclic bisbenzenesulfonyl activated alkenes, however we feel that steric factors should play a major role rather than the likely modest electronic effects attributable to the double alkyl substitution at the double bond. We are currently investigating in more detail this concept.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H-NMR spectra were recorded on a Bruker WP 200 or a Varian EM 360 A. Microanalysis were performed by Mr. G. Biasioli of Prof. E. Celon "Laboratorio di Microanalisi" staff.

3,4-Bis(benzenethio)-2,5-dihydrothiophene-1,1-dioxide (**2**). 3,4-Bis(benzenethio)-2,5-dihydrothiophenene-1,1-dioxide (**2**) was prepared as reported for the analogue tolyl derivative[4] in 83% yield from 3-(benzenethio)-2,5-dihydrothiophene-1,1-dioxide,[9] mp 85°C (EtOH). ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm): 3.75 (4 H, s), 7.30–7.53 (10 H, m). $C_{16}H_{14}O_2S_3$: Calcd.: C, 57.46, H, 4.22. Found: C, 57.67; H, 4.20.

Reaction of **2** *with maleic anhydride. Preparation of* **3**. 3,4-Bis(benzenethio)-2,5-dihydrothiophenene-1,1-dioxide (**2**) (3.35 g, 10 mmol), maleic anhydride (1 g, 10 mmol) and few crystals of hydroquinone are heated to reflux in ca. 40 ml of toluene for 8 h. The white crystals that form on cooling, are filtered and recrystallized from ethanol to afford 3.53 g (96% yield) of adduct **3**; mp 195°C. ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm): 2.50 (2 H, d, J = 15.9 Hz), 2.69 (2 H, d, J = 15.9 Hz), 3.33 (2 H, m), 7.38 (10 H, m). $C_{20}H_{16}O_3S_2$: Calcd.: C, 65.19; H, 4.37. Found: C, 65.27; H, 4.35.

Reaction of **2** *with (E)-1,2-bis(benzenesulfonyl)ethylene. Preparation of* **4**. 3,4-Bis(benzenethio)-2,5-dihydrothiophene-1,1-dioxide (**2**) (6.69 g, 20 mmol), (*E*)-1,2-bis(benzenesulfonyl)ethylene (6.17 g, 20 mmol) and few crystals of hydroquinone are refluxed in 50 ml of toluene overnight. On cooling a white solid is formed that is filtered and recrystallized from ethanol to give 11.0 g (95% yield) of adduct **4**; mp 162°C. ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm): 2.57 (2 H, d, J = 19.5 Hz), 2.84 (2 H, dd, J = 6.4 Hz and 19.5 Hz), 4.00 (2 H, d, J = 6.4 Hz), 7.12–7.63 (20 H, m). $C_{30}H_{26}O_4S_4$: Calcd.: C, 62.26; H, 4.53. Found: C, 62.23; H, 4.45.

Thermolysis of **2**. *Preparation of* **1**. A sample of 60 mg of **2** in 0.5 ml of toluene d_8, placed into a screw capped NMR tube, is heated at 110°C and its conversion to **1** via elimination of SO_2 is monitored by NMR. After ca. 1 h the resonances of the sulfone **2** are barely visible and clean formation of **1** is observed. This solution has been used without further purification for subsequent reactions. Isolation of **1** is inconvenient as evaporation of the solvent and further work-up frequently results in loss of material and polymerization, thus precluding the sample to be perfectly purified. ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm): 5.30 (2 H, bs), 5.95 (2 H, bs) 7.20–7.40 (10 H, m); (C_7D_8, TMS) δ (ppm): 5.24 (2 H, bs); 5.98 (2 H, bs), 7.18–7.45 (10 H, m).

Reaction of **1** *with PTAD. Preparation of* **5**. A solution of **1** containing ca. 251 mg (0.92 mmol) of diene as obtained from the thermolysis of **2** is added of 160 mg (0.92 mmol) of freshly sublimed PTAD. As soon as the brick red color of the PTAD has faded the solvent is evaporated at the rotoevaporator and the residue is crystallized from ethanol: 394 mg (96% yield); mp 121°C. ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm): 4.13 (4 H, s), 7.33–7.53 (15 H, m). $C_{24}H_{19}N_3O_2S_2$: Calcd.: C, 64.70; H, 4.30; N, 9.43. Found: C, 64.46; H, 4.30; N, 9.40.

Reduction of **6**. *Preparation of* **1**. A sample of 0.40 g (1.32 mmol) of bissulfoxide **6** is dissolved in 20 ml of dry acetone into a 100 ml round-bottomed flask containing some solid potassium carbonate and cooled at 0°C. Trifluoroacetic anhydride (0.44 ml, 3.18 mmol) and sodium iodide (0.95 g, 6.30 mmol) are added in one portion, stirred for few minutes and quenched with water and thiosulfate.[10] After extraction with dichloromethane and standard work-up, a yellow oil is obtained that is purified by rapid chromatography on silica gel: 0.31 g (87% yield).

Bisdesulfonylation of **4**. *Preparation of 1,2-bis(benzenethio)-1,4-cyclohexadiene* (**7**). To a solution of cycloadduct **4** (9.64 g, 16.66 mmol) in 150 ml of anhydrous methanol, containing 8 g of sodium phosphate monobasic monohydrate, 18 g (46.8 mg atoms of Na) of 6% sodium amalgam is added. After 20 h at room temperature, water (ca. 40 ml) is added and the mixture extracted with dichloromethane (3 × 40 ml). The organic phase is washed with water, dried over anhydrous sodium sulfate and evaporated to dryness to a slightly colored oil; 4.62 g (94% yields). ^{1}H-NMR ($CDCl_3$ TMS) δ (ppm): 2.81 (4 H, d, J = 1.2 Hz), 5.56 (2 H, t, J = 1.2 Hz), 7.20–7.44 (10 H, m). $C_{18}H_{16}S_2$: Calcd.: C, 72.93; H, 5.44. Found: C, 71.92; H, 5.38.

m-Chloroperbenzoic acid oxidation of **7**. *Preparation of 1,2-bis(benzenesulfonyl)-1,4-cyclohexadiene* (**8**). To a solution of 0.51 g (1.72 mmol) of bissulfide **7** in ca. 10 ml of dichloromethane and containing few crystals of potassium carbonate is added at 0°C and with vigorous stirring 2.96 g (7.00 mmol) of 85–90% *m*-chloroperbenzoic acid in ca. 20 ml of dichloromethane. After the dropwise addition has been completed, the cooling bath is removed and the mixture is kept stirring at room temperature 5 h. The resulting white suspension is filtered and the precipitated *m*-chlorobenzoic acid washed with little dichloromethane. The resulting solution is washed thoroughly with brine, aqueous sodium sulfite (saturated solution) and water, dried over anhydrous sodium sulfate and evaporated. The residue is chromatographed on silica gel (radial chromatography) with eluant dichloromethane to afford a colorless oil that was crystallized from ethanol; 0.52 g (86% yield), mp 134°C (EtOH). ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm): 3.36 (4 H, s), 5.70 (2 H, s), 7.44–8.23 (10 H, m). $C_{18}H_{16}O_4S_2$: Calcd.: C, 59.98; H, 4.47. Found: C. 59.97; H, 4.32.

Dichlorodicyanoquinone (*DDQ*) *oxidation of* **8**. *Preparation of o-bis(benzenesulfonyl)benzene* (**9**). A sample of **8** (50 mg, 0.14 mmol) was dissolved in 0.5 ml of deuterochloroform and small aliquots of DDQ were added. The reaction was monitored by TLC and 200 MHz ^{1}H-NMR spectra up to completion. The solution was chromatographed though 0.5 mm thick layer plate, eluting with dichloromethane to obtain **9** in virtually quantitative yields. Confirmation of the structure is based on comparison of R_f (silica gel, dichloromethane), ^{1}H-NMR and melting point with those obtained from an authentic sample.[6]

VO(Acac)$_2$ Catalyzed oxidation of **7**. To a solution of bissulfide **7** (3.91 g, 13.2 mmol) and $VO(Acac)_2$ (0.35 g, 1.3 mmol) in 70 ml of dichloroethane are added dropwise, under argon, 5.95 g (66.0 mmol) of *t*-butyl hydroperoxide in 10 ml of dichloroethane. After 24 h, aqueous sodium sulfite is poured into the reaction mixture and the solution is washed with 5% hydrochloric acid and water up to neutrality. The solution is dried over anhydrous sodium sulfate and rotoevaporated to dryness. The residue is crystallized from ethanol; 4.18 g (88% yield), mp 150°C (EtOH). ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm): 7.20–8.17 (complex m, 14 H). $C_{18}H_{14}O_3S_2$: Calcd.: C, 63.14, H, 4.12. Found: C, 62.99; H, 4.18.

A sample of this material oxidized with *m*-CPBA in dichloromethane under standard conditions (see before) gives **9** as confirmed by comparison of its spectral data with those obtained from an authentic sample.

ACKNOWLEDGMENT

Grateful thanks are due to Prof. G. Modena.

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