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Catalytic sulfuration of dienes with metallocene polysulfides

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Abstract

Elemental sulfur reacts with conjugated 1,3-dienes to give cyclic di-and tetrasulfides. The yield is significantly improved in the presence of catalytic amounts of organometallic polysulfides. The nature of this effect is discussed. © 1998 Elsevier Science Ltd. All rights reserved.

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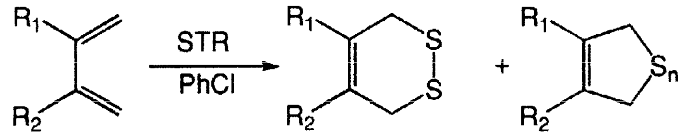
The strong interest in new, selective methods of sulfur transfer to dienes, to form dithiins **1** has resulted in the development of a number of new synthetic methodologies [1-3]. The procedures were designed to make sulfur transferable in form of diatomic units (likely in the singlet state) to dienes, in a Diels–Alder fashion parallel to the chemistry of singlet oxygen. In the initial approach, $R_3GeSSSGeR_3$ was used; an extrusion of S_2 is induced by dibromotriphenylphosphine (PPh_3Br_2) [4]. Later, we mimicked the Steliou approach using some common metallocene polysulfides bearing metals from group IV, although with modest success [5]. A thermal extrusion from inorganic compounds with S_2 persulfido ligands was also tried but no S_2 transfer was observed [6]. The concept of catalytic sulfuration with organometallic compounds is not new. Non-selective sulfuration of the dienes with a palladium catalyst was reported [7], and it has been known for a long time that zinc dithiocarbamate improves the process of rubber vulcanization [8]. However, there has been no successful application of this method to the synthesis of dithiins.

In a search for new and more selective sulfur transfer reagents (STR) we have again employed metallocene polysulfides Cp_2MS_X, (M = Mo [9], W [10], Ti [11], Zr [12], X= 4, 5). Here we report on the results obtained using this approach.



3 **1** **2**

Scheme 1

a) R_1, R_2 = Me; b) R_1, R_2 = Ph; c) R_1 = H, R_2 = $Me_2C{=}CH(CH_2)_2$; n = 3, 4

STR = Cp_2MoS_4 (**4**), Cp_2WS_4 (**6**), Cp_2TiS_5,(**7**) Cp_2ZrS_5 (**8**), S_8,

S_8 + catalyst (0.1 eq. of **4**, **6**, **7** or **8**)

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Encouraged by our former success in the sulfuration of dienes using elemental sulfur without any specific activator in an exclusively thermal process [13], we applied the same method with Cp_2MS_x compounds. We expected that the sulfur transfer might occur more selectively and under milder conditions than the S_8/diene approach. Initially, we chose molybdocene tetrasulfide Cp_2MoS_4 (4) as a potential source of sulfur. A product of this sulfur extrusion, molybdocene disulfide (5), is stable enough to assure that this proposed transformation was reasonable: Cp_2MoS_4 (4) $\longrightarrow$ Cp_2MoS_2 (5) + S_2 [14].

Contrary to the results obtained with elemental sulfur [13], the use of polar solvents like DMSO or DMF did not result in efficient sulfur transfer. In DMSO, 4 decomposed quite rapidly, transferring sulfur to the diene in low yield; in DMF, the reaction was very slow. Chlorobenzene turned out to be more effective; decomposition of the STR was inhibited and the yield of di- and tetrasulfide increased.

We examined the reaction in more detail with the relatively electron-rich tungstenocene tetrasulfide (6), as well as with zirconocene (7) and titanocene (8) pentasulfides which do not have a HOMO electron pair. The comparative kinetic studies were carried out in boiling chlorobenzene; the 2,3-diphenylbutadiene and metallocene polysulfides were used in a 1:2 ratio. The progress of reactions was measured by ^1H NMR with 1,3,5-tri-*t*-butylbenzene added as an internal standard; the results are shown in Figure 1.

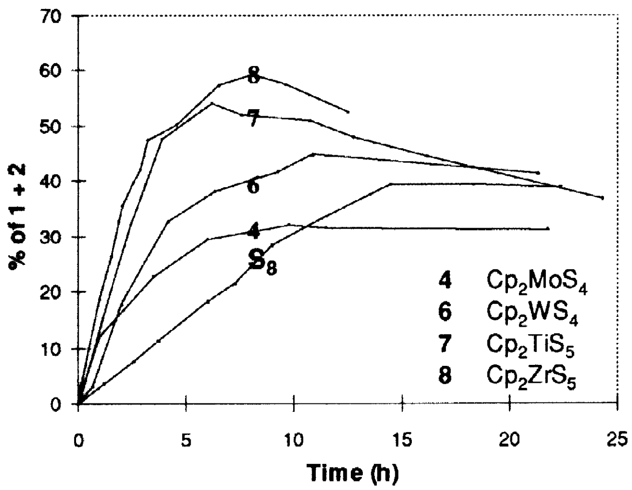


Fig. 1. The combined yields **1+2** for different Cp_2MS_X

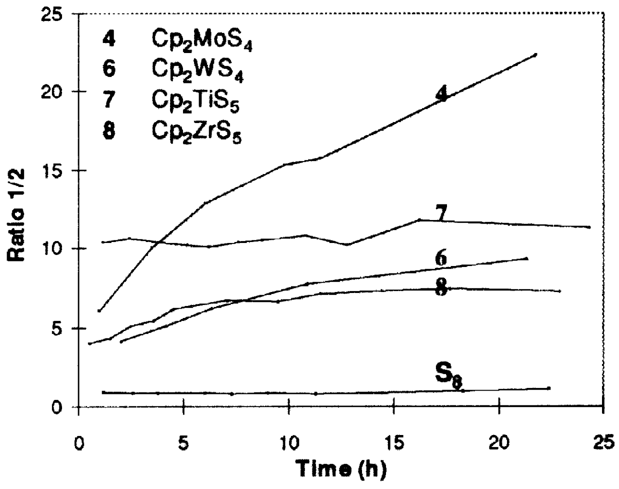


Fig. 2. Ratios of **1/2** for different Cp_2MS_X.

The use of electron-deficient pentasulfides (7, 8) resulted in 50-60% sulfur-transfer, and in case of molybdocene and tungstenocene tetrasulfides (4, 6) the yields were comparable with the ones obtained in a control reaction with elemental sulfur, *i.e.* 30-45% (Fig. 1). The efficiency of organometallic polysulfides used alone appears to be a function of their stability which is controlled by electronic properties of the metal centers (the initial sulfuration rates for 4 and 6 were 3-4 times higher and for 7 and 8 they were 6-7 times higher when compared with S_8 alone). Additionally, 7 and 8 resulted in 1.5 - 2 times higher yield when compared with 4 and 6).

The evolving **1/2** ratios (Fig. 2) probably depend on the equilibrium between the corresponding Cp_2MS_X and its decomposition products. The increasing ratios were observed when metallocene polysulfides from group IV were used. They are more stable and can deliver only limited amounts of sulfur. When 7 and 8 are used, the **1/2** ratios do not change much with time, while the combined yields of products **1** + **2** diminished (likely as a result of an irreversible addition to the STR or to material from its decomposition). This process is absent in the control experiments with elemental sulfur only. The flat line observed there reflects the ratio of products formed initially as elemental sulfur does not equilibrate significantly with either **1** or **2** under the reaction conditions [13]. To block side reactions of **1** and **2**, a two-fold excess of elemental sulfur (S_8) was added to the reaction mixture. It was expected that sulfur could regenerate the reacted STRs (Scheme 2). In fact, it was observed that yields of both trapped products increased significantly (Fig. 3) compared with the yield using only **4** - **8** (30 - 60%; Fig. 1). Even when 0.1 eq. of organometallic polysulfides was employed, a combined yield of *ca.* 60% of trapped di- and tetrasulfide resulted; this was 5-30% higher than with 1 equivalent of Cp_2MS_x alone. Further increasing the Cp_2MS_x /diene ratio by a factor of 3 produces only a modest (*ca.* 5%) improvement. Apart from increasing the yields, the presence of sulfur in excess makes the catalytic activity of all metallocene polysulfides very similar (only **8** is slightly different). This seems to be again the result of their resulfurization. It is interesting that **1** + **2** yields decline after reaching the maximum (*ca.* 75-80%) even in the presence of S_8 .

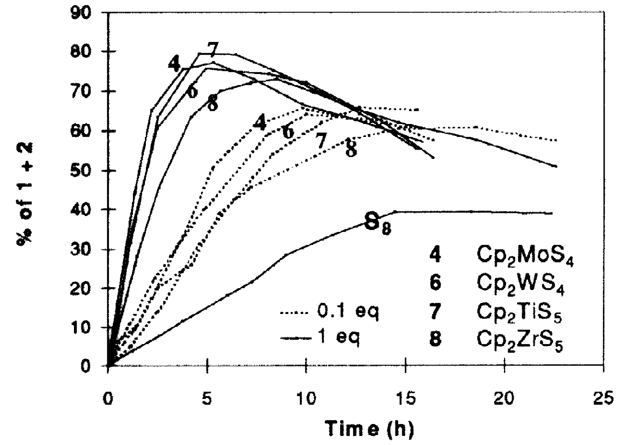


Fig. 3. Yields of **1**+**2** with varying Cp_2MS_x and S_8

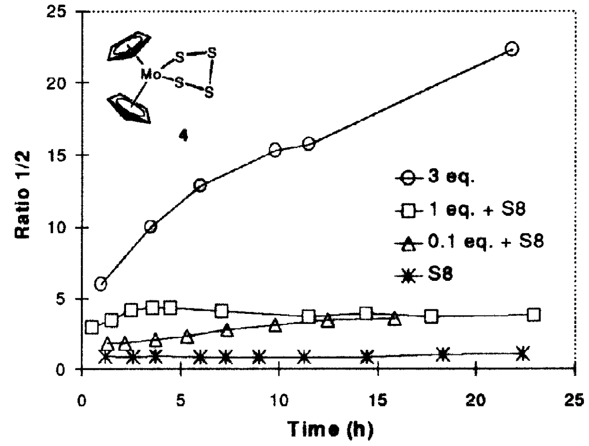
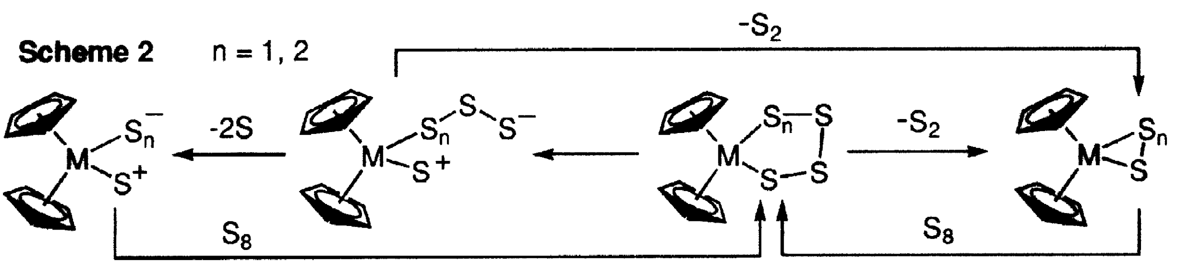


Fig. 4. Ratios of **1**/**2** with varying Cp_2MoS_4 and S_8

The effect sulfur addition on **1**/**2** ratios was also interesting (Fig. 4). It is immediately seen that the **1**/**2** ratio parallels the one obtained for elemental sulfur alone. The tetrasulfide **2**, once formed, is not further desulfurized. The ratio of **1**/**2** using 3 equivalents of **4** is shown for comparison (see Fig. 2 also).

Scheme 2



It is obvious that the addition of organometallic polysulfides results in a significant improvement in the formation of **1** and **2**. The nature of this influence is not fully clear but appears to involve resulfurization of Cp_2MS_{n-2} formed, leading to effective sulfur transfer. The mechanism of the sulfur transfer can involve discrete sulfur units or some ionic species [13]. This former path is especially plausible when **4** is used (both Cp_2MoS_2 and Cp_2MoS_4 are observed in the reaction mixture). However, not all observations fit this pattern (especially in the case of **6**; no Cp_2WS_2 was present in the reaction mixture although its presence as an intermediate can not be excluded) leaving the left part of Scheme 2 as a possible alternative.

The procedure used in kinetic studies (involving 0.1 equivalent of Cp_2MoS_4) was optimized. The choice of **4** as a catalyst resulted from its enhanced stability (up to 70% of **4** can be recovered after the reaction), clean formation of products and lack of problems in the workup. The results are given in the Table. Desulfurization with PPh_3 can be employed to convert tetrasulfides to the disulfides [13].

Table. Isolated Yields of Disulfides **1** in the Sulfuration of **3**; the **1**/**2** ratio was determined by NMR

Disulfides	**1a**	**1b**	**1c**
%; Time (h)	64, 5	79, 7	58, 4
(**1**/**2** ratio)	3.3/1	3.5/1	2.7/1

A typical procedure is as follows: 1 mmol of diene, 0.1 mmol of Cp_2MoS_4 and 2 mmols (512 mg) of S_8 are added to 5 mL of PhCl (in case of volatile dienes, 0.25 mL of hexanes is added to the reaction mixture). The mixture is refluxed for 4-7 h, cooled, poured into 20 mL of MeOH and filtered. The filtrate is treated with 1.8 mmol of Ph_3P (the amount of Ph_3P varies as a function of isolated sulfur), warmed to boiling and left at room temperature for about 1 h. Next, an excess of S_8 (0.2 mmol), dissolved in a small amount of CS_2 is added (to ensure complete conversion of Ph_3P to $Ph_3P{=}S$) and the solution stirred for additional 10 min. After the solvent is removed, the residue was washed 5 times with hexanes to ensure recovery of disulfide. The solvent is removed and the residue (dissolved in CS_2) purified by the chromatography (silica gel; hexanes). The disulfide is obtained in 58-79% isolated yield.

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