REACTION OF METAL CYCLOPENTADIENIDES WITH 1,3-BIS(METHYLTHIO)-1,2-DITHIOLIUM SALTS

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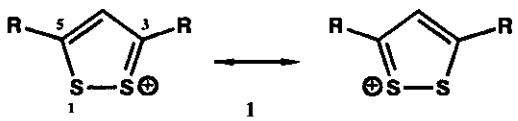
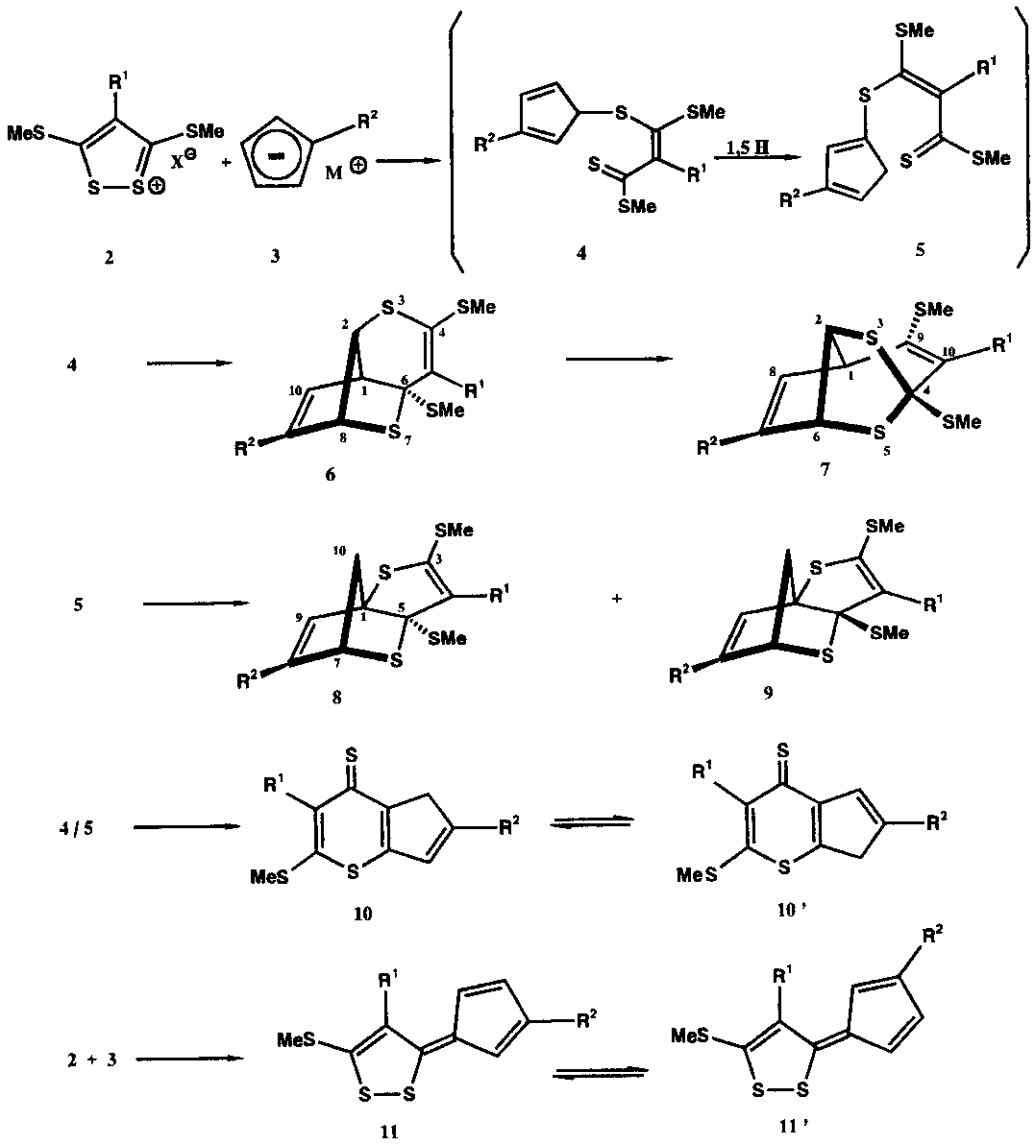
This paper is dedicated to Professor Dr. Dr. h.c. R. Huisgen on the occasion of his 75th birthday

Abstract - Thallium and lithium cyclopentadienides (**3**) cleave the S,S-bond of 1,2-dithiolium salts (**2**) giving rise to intramolecular Diels-Alder adducts such as **6**, **7**, **8**, and **9** or to intramolecular condensation products such as **10**. Substitution of a methylthio group in **2** leads to the 2,3-dithiafulvalenes (**11**).

Nucleophiles attack 1,2-dithiolium cations (**1**) at C-3/C-5, at the S,S-bond or at the aliphatic side chain R (abstraction of an α-proton). These reactions have been studied extensively.[1] Almost nothing is known about chemical transformations of **1** with metal cyclopentadienides, only some highly substituted 2,3-dithiafulvalenes were isolated from the reaction of 3-alkylthio-1,2-dithiolium salts and sodium tetraphenylcyclopentadienide[2] or sodium pentakis(methylthio)cyclopentadienide.[3]



We investigated reactions of 3,5-bis(methylthio)-1,2-dithiolium salts (**2**) with the metal salts (**3**) of unsubstituted or monoalkyl substituted cyclopentadienes. A variety of products were obtained, mainly formed by a nucleophilic scission of the S,S-bond. The primary intermediate



	R^1	R^2	mp[°C]	yield [%]
6a	*p*-Tol	*t*-Bu	—	50
7a	*p*-Tol	*t*-Bu	126-127	50
7b	*p*-Tol	H	155-158	70
7c	H	H	105	96
7d	H	*t*-Bu	105	28
7e	Et	H	oil	5

	R^1	R^2	mp[°C]	yield [%]
8a	H	H	83	29
9a	H	H	—	
10a	*p*-Tol	H	185	25
10b	Et	H	87-90	38
11a	Et	H	88-91	30
11b	Et	*t*-Bu	98-100	34

should have the supposed structure (**4**) and might rearrange to **5** by a 1,5 H shift. **4** could also follow an intramolecular (4+2) cycloaddition pathway giving rise to the Diels-Alder product (**6**). According to our experience, **6** is comparatively unstable at room temperature and rearranges to **7** by a 1,3 shift of the S(7)-C(6) bond This process is obviously favored by the methylthio group at C-6 Reactions of **3** with 3,5-diaryl-1,2-dithiolium salts led to more stable Diels-Alder products (**6**) X-Ray analyses of these examples unequivocally established structures (**6** and **7**).[4]

Interception of **6** as the primary Diels-Alder product was only observed in the reaction of **2** (R^1=*p*-Tol, X=I) with thallium *tert* -butylcyclopentadienide (**3**) (R^2=*t*-Bu) in boiling THF (3 h). Isolated **6a,** slightly red crystals, rearranged quantitatively to **7a** on standing in a $CHCl_3$ solution at room temperature for a few days. The ^{1}H-nmr data for the skeleton protons in **6** and **7** are rather characteristic and quite different [5] The reaction of **2** (R^1=*p*-Tol, X=I) with thallium cyclopentadienide (**3**) (R^2=H) in THF at room temperature also gave rise to a primary product with structure (**6**) according to the ^{1}H-nmr data of the crude material. It rearranged, however, completely to **7b** during chromatographic purification on silica gel

In the condensation of the 3-unsubstituted 1,2-dithiolium iodide (**2**) (R^1=H, X=I) with metal cyclopentadienides (**3**) no stable or partially stable Diels-Alder adducts (**6**) were observed With thallium cyclopentadienide (**3**) (R^2=H) in THF at room temperature a nearly quantitative yield of **7c** was obtained. With lithium cyclopentadienide (**3**) (R^2=H) in THF at -78 °C (4 h) neither **6** nor **7** could be detected; instead, a mixture of the two isomers (**8a**) and (**9a**) was isolated and separated by hplc This result is probably due to an intramolecular Diels-Alder reaction of intermediate (**5**), leading to endo isomer (**8a**) and exo isomer (**9a**). The rearrangement of **4** to the thermodynamically more stable **5** *via* a deprotonation/reprotonation process[6] catalyzed by basic lithium cyclopentadienide is faster than a 1,5-sigmatropic hydrogen shift in the presence of nonbasic thallium cyclopentadienide. Under the same conditions, **2** (R^1=H, X=I) and lithium *tert* -butyl cyclopentadienide (**3**) (R^2=*t*-Bu) gave a mixture of **7d**, **8b** (R^2=*t*-Bu) and **9b** (R^2=*t*-Bu) from which only **7d** could be isolated in pure state. The most characteristic structural element in the ^{1}H-nmr spectra of **8a** and **9b** are the methylene protons at C-10 with a chemical shift of about 2 ppm and a geminal coupling

constant of ^2J=9 Hz. In the *endo* isomer (**8a**) the 5-SCH_3 is diamagnetically shifted to δ = 2.15 ppm due to shielding by the 8,9-double bond.

Condensation of 3-ethyl-1,2-dithiolium tetrafluoroborate (**2**) (R^1=Et, X=BF_4) and thallium cyclopentadienide (**3**) (R^2=H) at 0 °C in THF led to a mixture of products consisting mainly of **7e** and the 2,3-dithiafulvalene (**11a**).[7] Therefore, nucleophilic attack had occurred not only at the S,S-bond of **3** but also at C-3. With thallium *tert* -butylcyclopentadienide (**3**) (R^2=*t*-Bu) no tricyclic product (**6**) or (**7**) was detected at all; only **11b** could be isolated as dark red crystals, showing in solution both possible isomers (**11b**) (minor) and (**11b'**) (major). More strongly nucleophilic lithium cyclopentadienide (**3**) (R^2=H) once again cleaved the S,S-bond of 3-ethyl-1,2-dithiolium tetrafluoroborate (**2**) (R^1=Et, X=BF_4) leading to the rearranged intermediate (**5**), which cyclized to yield the thiopyran-4-thione(**10b**). A similar behaviour was observed with lithium cyclopentadiende (**3**) (R^2=H) and 3-*p*-tolyl-1,2-dithiolium iodide (**2**) (R^1=*p*-Tol, X=I) giving rise to **10a**. In solution a tautomeric equilibrium **10** ⇌ **10'** is observed.

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5. **6a** (CD_2Cl_2): δ(ppm) = 5.89 (m, 1H, 10-H); 4.53 (m, 1H, 8-H); 3.24 (m, 1H, 1-H); 3.20 (m, 1H, 2-H); **7a** ($CDCl_3$): δ(ppm) = 5.82 (m, 1H, 8-H), 4.81 (m, 1H, 6-H); H); 4.65 (m, 1H, 2-H); 3.74 (m, 1H, 1-H).
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7. Due to the decomposition of **11a** on silica gel, a clear cut separation proved difficult. **11a** slowly precipitated as violet needles from a solution of the crude product in *n*-hexane at -78 °C, whereas **7e** was obtained as a slightly red oil by chromatography of the mother liquor on silica gel.

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