

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

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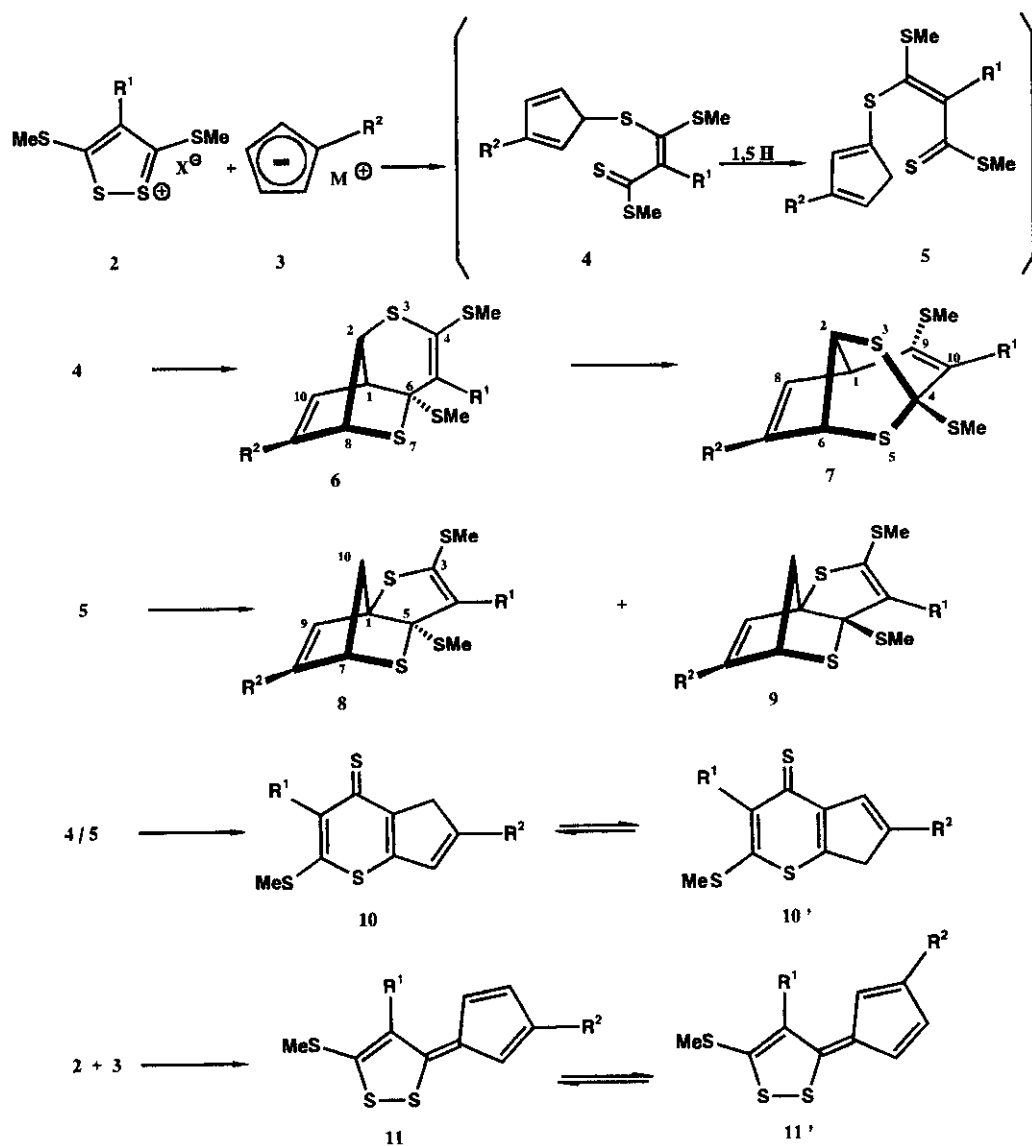
This paper is dedicated to Professor Dr. Dr. h.c. R. Huisgen on the occasion of his 75th birthday

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 tetraphenylcyclopentadienide² 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	<i>p</i> -Tol	<i>t</i> -Bu	—	50
7a	<i>p</i> -Tol	<i>t</i> -Bu	126-127	50
7b	<i>p</i> -Tol	H	155-158	70
7c	H	H	105	96
7d	H	<i>t</i> -Bu	105	28
7e	Et	H	oil	5

	R ¹	R ²	mp[°C]	yield [%]
8a	H	H	83	} 29
9a	H	H	—	
10a	<i>p</i> -Tol	H	185	25
10b	Et	H	87-90	38
11a	Et	H	88-91	30
11b	Et	<i>t</i> -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 ($R^1=p\text{-Tol}$, $X=I$) with thallium *tert*-butylcyclopentadienide (3) ($R^2=t\text{-Bu}$) 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 ^1H -nmr data for the skeleton protons in 6 and 7 are rather characteristic and quite different.⁵ The reaction of 2 ($R^1=p\text{-Tol}$, $X=I$) 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 ^1H -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 process⁶ 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) ($R^2=t\text{-Bu}$) gave a mixture of 7d, 8b ($R^2=t\text{-Bu}$) and 9b ($R^2=t\text{-Bu}$) from which only 7d could be isolated in pure state. The most characteristic structural element in the ^1H -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-SCH₃ is diamagnetically shifted to $\delta = 2.15$ 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 cyclopentadienide (**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 $10 \rightleftharpoons 10'$ is observed.

REFERENCES AND NOTES

1. Reviews: H. Prinzbach, E. Futterer, *Adv. Heterocycl. Chem.*, **1966**, 7, 39. N. Lozac'h, M. Stavaux, *Adv. Heterocycl. Chem.*, **1980**, 27, 151. C. T. Pedersen, *Adv. Heterocycl. Chem.*, **1982**, 31, 63. D. M. McKinnon in *Comprehensive Heterocyclic Chemistry* (A. R. Katritzky, C. W. Rees, Eds.), Vol. 6, p. 783, Pergamon Press, Oxford, 1984.
2. A. Lüttringhaus, E. Futterer, H. Prinzbach, *Tetrahedron Lett.*, **1963**, 1209.
3. R. Gompper, R. Guggenberger, *Tetrahedron*, **1986**, 42, 835.
4. K. Hartke, A. Kraska, W. Massa, M. Molinier, S. Wocadlo, *Tetrahedron Lett.*, **1994**, in press.
5. **6a** (CD₂Cl₂): 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** (CDCl₃): 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).
6. S. McLean, P. Haynes, *Tetrahedron*, **1965**, 21, 2329.
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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