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Intramolecular Diels Alder Adducts from 1,2-Dithiolium Salts and Metal Cyclopentadienides

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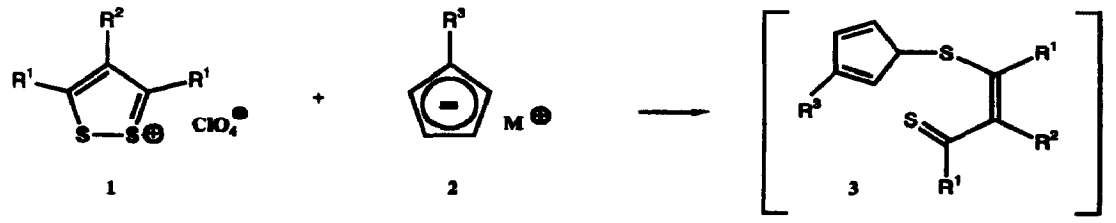
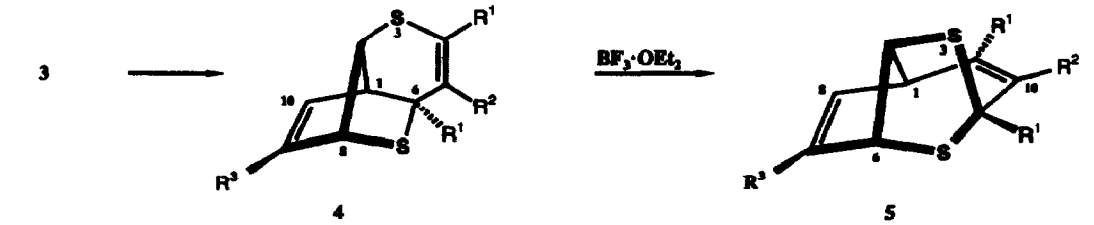
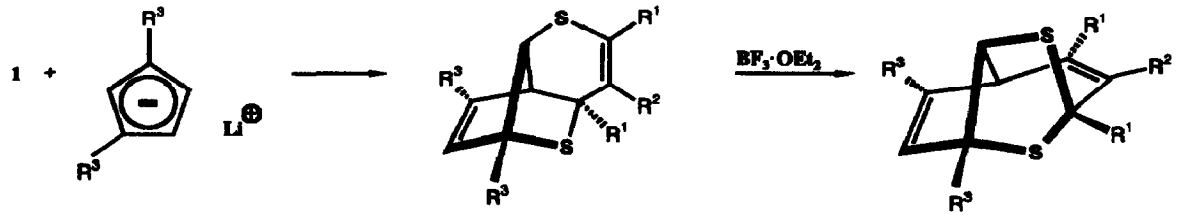
Abstract: Reactions of 3,5-diaryl-1,2-dithiolium salts **1** with alkali cyclopentadienides **2** lead to a scission of the S,S-bond followed by an intramolecular Diels Alder addition to yield the tricyclic products **4**.These rearrange readily to the more stable isomers **5**.

1,2-Dithiolium salts such as **1** react readily with nucleophiles. Depending on the nature of the nucleophile and the substitutents R at the 1,2-dithiolium cation different reaction pathways have been observed. These may lead to ring opening by fission of the S,S-bond, to an attack at C-3/C-5 or to a deprotonation of aliphatic side chains. Numerous examples are cited in review articles[1]. Carbon nucleophiles - with the exception of acidic methylene compounds - have hardly been used. Only the condensation of 3-alkylthio-1,2-dithiolium salts with highly substituted metal cyclopentadienides such as tetraphenyl[2] or pentakis(methylthio) cyclopentadienides[3] has been reported leading to the formation of 2,3-dithiafulvalenes.

We studied the reactions of 3,5-diaryl-1,2-dithiolium perchlorates **1** (R^1 = aryl)[4] with alkali salts of cyclopentadiene **2** (R^3 = H), tert-butyl cyclopentadiene **2** (R^3 = t-Bu) and di-tert-butyl cyclopentadiene **6** (R^3 = t-Bu). The results were rather unexpected. The first step is most probably a clear cut scission of the S,S-bond in **1** by the carbon nucleophile **2** or **6**, leading to the intermediate **3**. The short life time of **3** does not allow 1.5 H shifts to occur that would give rise to more stable isomers. Instead an intramolecular Diels Alder reaction of the cyclopentadiene ring with the thiocarbonyl group takes place immediately yielding the tricyclic compound **4**. At room temperature, **4** only has limited stability and rearranges to the isomeric structure **5** by a 1.3 shift of the S(7)-C(6)-bond. This process can be accelerated by small amounts of Lewis acids such as boron trifluoride diethyl ether at -40°C; higher temperatures favour side reactions[5].







	R^1	R^2	R^3	m.p.[°C]	yield [%]		m.p.[°C]	yield[%]
4a	C_6H_5	H	H	113	40	**5a**	130	51
4b	C_6H_5	Me	H	137	24	**5b**	148	57
4c	4-$MeOC_6H_4$	H	H	-	-	**5c**	108	23
4d	C_6H_5	H	t-Bu	142	42	**5d**	115	75
4e	C_6H_5	Me	t-Bu	148	64	**5e**	163	77
4f	4-$MeOC_6H_4$	H	t-Bu	129	57	**5f**	139	50
7a	C_6H_5	H	t-Bu	130	58	**8a**	175	74
7b	C_6H_5	Me	t-Bu	156	60	**8b**	187	79
7c	4-$MeOC_6H_4$	H	t-Bu	138	46	**8c**	185	45

The ^1H NMR pattern of **4** and **5** is quite different for the hydrogen atoms at the tricyclic skeleton. In **4**, the chemical shift of the aliphatic hydrogens 1-H, 2-H and 8-H is about 3.1 ppm, 3.3 ppm and 4.5 ppm, whereas the corresponding hydrogens in **5** show signals at 4.0 ppm, 4.9 ppm and 5.0 ppm. The olefinic hydrogen atoms originating from the cyclopentadiene ring are observed at 5.8 ppm and 6.5 ppm in **4**, and at 6.0 ppm and 6.2 ppm[6] in **5**. The proposed structures **4** and **5** have been confirmed by X-ray analyses of **4e** and **5e** as shown in fig. 1 and fig. 2.

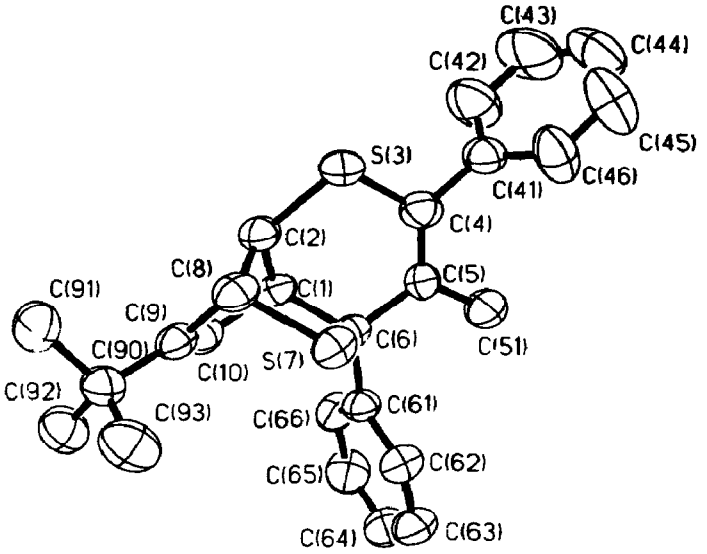


FIG. 1: ORTEP plot of 4e

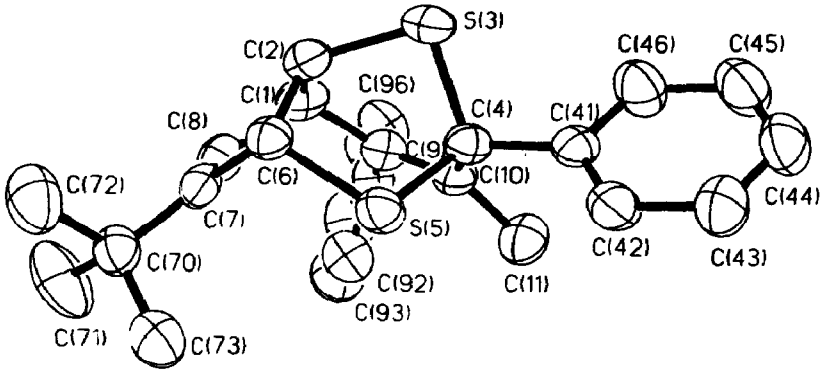


FIG. 2: ORTEP plot of 5e

In the cycloadducts **7a-c**, obtained with lithium di-tert-butyl cyclopendienide **6** (R^1 = t-Bu, M = Li), the tert-butyl groups are found at C-8 and C-10. This means that the Diels Alder reaction is more rapid for that transition state in which the thiocarbonyl sulfur is getting bonded to a cyclopentadiene carbon bearing a tert-butyl group.

The primary cycloadducts **4** and **7** are stabilized by an increasing number of tert-butyl groups in the cyclopentene moiety. On the other hand, electron donating groups in R^1 (e.g. 4-$MeOC_6H_4$) destabilize **4** and **7**; thus the reaction of **1c** with **2** (R^3=H) directly gave **5c**, and ^1H NMR signals of **4c** could not be detected even in the crude product. In general, isolation of pure **4** requires some experience since chromatographical purification of **4** accelerates the

rearrangement to **5** and to by-products. Best results were obtained by simple crystallization experiments. Therefore the yields reported for pure **4** do not reflect the nearly quantitative result of ring opening and cycloaddition.

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3. Gompper, R.; Guggenberger, R. *Tetrahedron* **1986**, 835-848.
4. These compounds were obtained from 1,3-diketones or chalcones with P_4S_{10} following mainly Veber, M.; Jallabert, C.; Strzelecka, H. *Synth. Commun.* **1987**, *17*, 693-701.
5. General procedure to obtain **4** and **5**: To a stirred solution of the metal cyclopentadienide **2** (1.1 mmol) in dry THF (40 ml) under nitrogen at -78°C the solid 1,3-dithiolium salt **1** (1 mmol) is added in one portion. The reaction mixture is allowed to warm up to room temperature and is then extracted with diethyl ether (50 ml)/ water (150 ml). The organic layer is evaporated in vacuo and the oily residue treated with a few ml of an organic solvent (e.g. acetone, methanol) to induce crystallization of **4**.
To a stirred solution of pure **4** (100 mg) in $CHCl_3$ (20 ml) under nitrogen at -40°C is added $BF_3{\cdot}OEt_2$ (2 drops). The reaction mixture is allowed to warm up to room temperature and after standing for 2 h is extracted several times with water. The organic layer is evaporated in vacuo and the residue treated as described above.
6. The complete NMR data for **4a** and **5a** are:
4a: ^{1}H NMR ($CDCl_3$): δ(ppm) = 3.18 (m, 1H, 1-H); 3.24 (m, 1H, 2-H); 4.47 (m, 1H, 8-H); 5.77 (m, 1H, 9-H); 6.47 (s, 1H, 5-H); 6.49 (m, 1H, 10-H); 7.2-7.6 (m, 10H, Ph-H). - ^{13}C NMR ($CDCl_3$): δ(ppm) = 53.9 (C-1); 58.9 (C-2); 63.6 (C-6); 65.0 (C-8); 128.0 (C-5); 132.2 (C-9); 137.0 (C-4); 138.6 (C-10); 126.1, 126.8, 128.10, 128.13, 128.20 (Ph-C, bearing H); 137.0, 143.3 (Ph-C, quart.).
5a: ^{1}H NMR ($CDCl_3$): δ(ppm) = 4.04 (m, 1H, 1-H); 4.92 (m, 1H, 2-H); 4.98 (m, 1H, 6-H); 6.05 (m, 1H, 7-H); 6.16 (m, 1H, 8-H); 6.91 (s, 1H, 10-H); 7.20-7.42 (m, 8H, Ph-H); 7.72-7.75 (m, 2H, Ph-H). - ^{13}C NMR ($CDCl_3$): δ(ppm) = 48.8 (C-1); 59.6 (C-6); 64.6 (C-2); 70.3 (C-4); 134.0 (C-7); 134.3 (C-8); 136.3 (C-10); 139.1 (C-9); 125.5, 126.7, 127.5, 128.1, 128.4, 128.6 (Ph-C, bearing H); 135.8, 140.2 (Ph-C, quart.).

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