Monatshefte für Chemie 122, 71 – 75 (1991)

Monatshefte für Chemie
Chemical Monthly

Addition Compounds of Nucleophiles and 3-Ethylthio-6-oxo-6*H*-1,2-dithiolo[4,3-c]1,2-dithiolium Tetrafluoroborate. Synthesis of 3 *H*,6 *H*-1,2-Dithiolo[4,3-c]1,2-dithiole-3-one-6-thione

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Summary. A smooth method of synthesizing 3*H*, 6*H*-1,2-dithiolo[4,3-c]1,2-dithiole-3,6-dithione (**3**), and also its partial desulfuration to yield 3*H*, 6*H*-1,2-dithiolo[4,3-c]1,2-dithiole-3-one-6-thione (**4**) is presented. The ethylation product **5** of the monothione **4** reacts with various nucleophilic reagents to form remarkably stable adducts. The adducts of **5** with methanol, *tert*-butyl mercaptan, and with aniline could be isolated and characterized by their ^{1}H-NMR spectra.

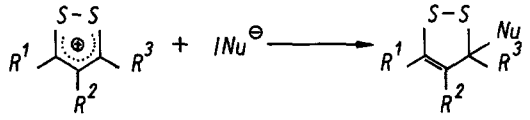
Keywords. 3*H*, 6*H*-1,2-Dithiolo[4,3-c]1,2-dithiole-3,6-dithione, synthesis and partial desulfuration of; 3*H*,6*H*-1,2-Dithiolo[4,3-c]1,2-dithiole-3-one-6-thione, synthesis and alkylation of; 3-Ethylthio-6-oxo-6*H*-1,2-dithiolo[4,3-c]1,2-dithiolium tetrafluoroborate, synthesis and formation of adducts with nucleophiles of.

Anlagerungsverbindungen von Nukleophilen an 3-Ethylthio-6-oxo-6*H*-1,2-dithiolo[4,3-c]1,2-dithiolium-tetrafluoroborat. Synthese von 3*H*,6*H*-1,2-Dithiolo[4,3-c]1,2-dithiol-3-on-6-thion

Zusammenfassung. Eine glatte Synthese für 3*H*,6*H*-1,2-Dithiolo[4,3-c]1,2-dithiol-3,6-dithion (**3**) und für dessen partielle Entschwefelung zu 3*H*,6*H*-1,2-Dithiolo[4,3-c]1,2-dithiol-3-on-6-thion (**4**) wird angegeben. Das Ethylierungsprodukt **5** des Monothions **4** reagiert mit unterschiedlichen Nukleophilen zu bemerkenswert stabilen Addukten. Die Addukte mit Methanol, *tert.*-Butylmercaptan und mit Anilin wurden isoliert und durch ihr ^{1}H-NMR-Spektrum charakterisiert.

Introduction

Since the reactive 1,2-dithiolium salts **1** are easily available, they are valuable intermediates for further syntheses [1–5]. In most cases the reactions of 1,2-dithiolium compounds follow an addition-elimination mechanism, whereby the primary reaction step consists in the attack of the nucleophile at position 3 or 5 of the heterocycle. Thereby a non-aromatic five-membered ring adduct is obtained. If one of the substituents R^1 or R^3 is hydrogene, with tertiary amines an intermediate formation of a carbene is postulated [6]).



1 2 **Scheme 1**

The adducts **2** may react in different ways. Besides the elimination of the substituents R^3 and the cleavage of the C(3)-S bond, also the S-S bond can be cleaved by the action of nucleophilic or reducing agents [4]. Acceptors in the ring should inhibit the two first mentioned decomposition reactions of the dithiole **2**. Indeed, up to now, it was only possible to isolate adducts **2** in a few cases, and in each case the heterocycle **2** was substituted by at least one phenyl group [7, 8][1].

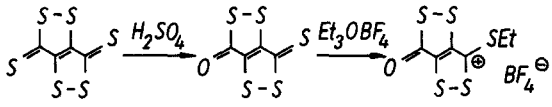
Results and Discussion

Synthesis of 3 H,6 H-1,2-Dithiolo[4,3-c]1,2-dithiole-3,6-dithione **3** *and of 3 H,6 H-1,2-dithiolo[4,3-c]1,2-dithiole-3-one-6-thione* **4**

For **3** an improved synthesis is presented (see Exp. Part). In comparison to the previous synthetic method [10], the reproducibility of the yield could be increased significantly. Besides that an acceptable method for the partial desulfuration of the dithione **3** with sulfuric acid to the monothione **4** was found. We attempted this in the usual way with mercuric acetate, but without success (see [9]). The intermediate formed (monothione **4**) reacts fast by desulfuration of the second thiono group to form 3*H*,6*H*-1,2-dithiolo[4,3-c]1,2-dithiole-3,6-dione **9**. Therefore it is difficult to isolate the monothione **4**, and the yield is only about 2%. The new synthesis allows the formation of **4** with a yield of about 30%. The initial reaction step for sulfuric acid is the protonation of one thiono group in **3**. This can be observed by a strong bathochromic shift (about 50 nm) of the longest absorption band in relation to the solution of **3** in acetonitrile (**3**: $\lambda_{max}(CH_3CN) = 524$ nm, $\lambda_{max}(H_2SO_4) = 572$ nm, see also [11]). If the acidic solution is diluted with water, the dithione **3** is recovered unchanged. At higher temperatures one thiono group changes oxidatively into a carbonyl group. Too long a reaction period leads to the destruction of the dithiolo-dithiole system.

Derivation of **4**

The monothione **4** is alkylated at the thiono group by triethyloxonium tetrafluoroborate to the dithiolium salt **5** (see [9]). The vigorous reaction conditions which are necessary for the alkylation of **4** illustrate the efficient acceptor substitution of the 1,2-dithiole-3-thione by the condensed 1,2-dithiole-3-one ring (see Exp. Part).



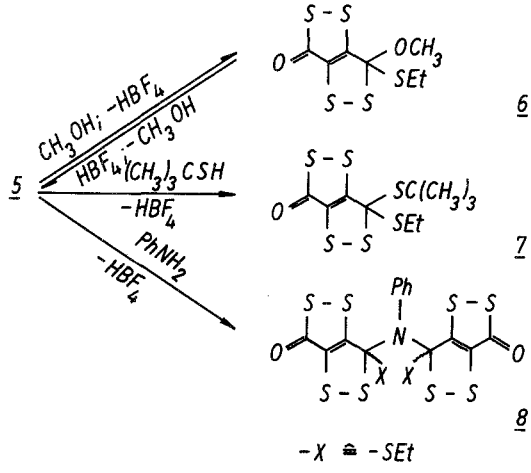
3 4 5 **Scheme 2**

[1] For the 1,3-dithiolium system many stable additives with various nucleophiles have been isolated and characterized [4]

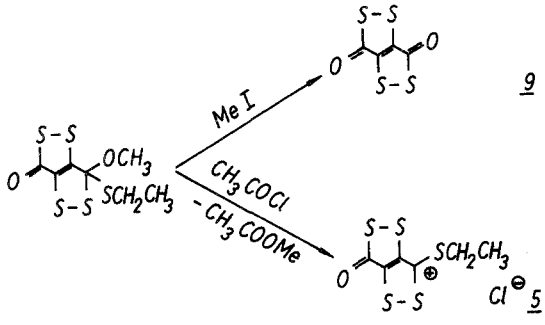
When **5** is dissolved in methanol, a strong acidic solution is obtained in which no dithiolium salt **5** can be detected (UV/VIS; TLC). Removing the solvent, the starting compound **5** is recovered quantitatively. When the acid is neutralized by sodium hydrogen carbonate, the adduct **6** can be isolated as a yellow oily substance. The compounds **7** and **8** are obtained analogously with *tert*-butyl mercaptan and aniline, respectively.

The adducts **6–8** are characterized by their ^{1}H-NMR spectra (the results are summarized in Table 1). In **8** both N−H protons of the starting aniline are substituted (absence of an N−H signal in the NMR spectrum; intensity distribution of the signals in this spectrum; absence of an N−H vibration band in the related infrared spectrum).

With the "soft" electrophilic methyl iodide, **6** is mainly S-alkylated and further reaction leads to **9** (see also related reactions of 1,3-dithiolium compounds [12]). In comparison the "harder" reagent acetyl chloride attacks the "harder" O-atom and the dithiolium salt **5** is obtained as the chloride.



Scheme 3



Scheme 4

Table 1. ^{1}H-NMR data of the adducts **6–8** (90 MHz Bruker HX 90; $DCDl_3$, *HMDS*; chemical shifts in ppm)

Compd.	S−−−CH_2−−−−−CH_3		−−Nu	
6	q, 2.93, 2H	t, 1.33, 3H	s, 3.58, 3H	(OCH_3)
7	q, 3.44, 2H	t, 1.46, 3H	s, 1.37, 9H	(S-*tert*-butyl)
8	q, 3.25, 4H	t, 1.40, 6H	m, 7.26–6.8, 5H	(N-phenyl)

Experimental Part

3 H,6 H-1,2-Dithiolo[4,3-c]1,2-dithiole-3,6-dithione (**3**)

27.5 g (0.25 mol) sodium disulfide (synthesized from the elements in liquid ammonia) and 24.1 g (0.75 mol) sulfur are dissolved with stirring and warming to about 50 °C in 700 ml *DMF* and 50 ml water. With vigorous stirring 21.8 g (84 mmol) perchlorobutadiene are added at once. The temperature increases to about 70 °C. After a period of 30 min the reaction mixture is poured onto ice, which had been treated with 100 ml hydrochloric acid. The precipitate is filtered off and washed several times with methanol and then with acetone. After drying the precipitate the excess sulfur is eliminated by extraction with carbon disulfide (4 portions of 200 ml). Finally the dithione **3** is separated by extracting the residue with anisole at the boiling temperature of the solvent. The dithione **3** in this solution crystallizes as deep purple needles on cooling. The yield is 4.1 g (22.5%). M.p. 253 °C (dec.; Ref. [9] 253 °C).

3 H,6 H-1,2-Dithiolo[4,3-c]1,2-dithiole-3-one-6-thione (**4**)

2 g (8.33 mmol) dithione **3** are added to 400 ml of concentrated sulfuric acid. The reaction mixture is heated with stirring to 100 °C. When a sample of this solution, diluted with water, no longer shows a red colour (about 20 – 30 min), the mixture is poured onto ice. The precipitate is filtered off, washed with water until it reaches *pH* 7 and then dried. The monothione **4** is separated by extraction of the precipitate with boiling tetrachloromethane. This solution is chromatographed on silica gel using tetrachloromethane as eluting agent. The yield is 540 mg (28.9%). M.p. 153 °C (Ref. [9] 153 °C).

6 H-3-Ethylthio-6-oxo-1,2-dithiolo[4,3-c]1,2-dithiolium Tetrafluoroborate (**5**)

1 g (4.46 mmol) monothione **4** and 1.5 g (7.9 mmol) triethyloxonium tetrafluoroborate are stirred in 30 ml 1,2-dichloroethane at 70 °C, until all of **4** has reacted (about 4 h; TLC). After cooling, 300 ml ether are added, and the precipitate is separated, washed several times with dried ether, and dried in vacuo. A further purification is possible by reprecipitation with ether from a concentrated solution in acetonitrile. The salt **5** then crystallizes as orange coloured plates. The yield is 1.36 g (90%). M.p. 135–138 °C (dec.). $C_6H_5BF_4OS_5$ (340.2). Calc. C 21.18, H 1.48, S 47.12; found C 21.30, H 1.62, S 46.83. IR (KBr) 2950–2870, CH; 1635, C=O; 1100–1000 cm^{-1}, BF_4^-. UV/VIS (CH_3CN) 465 (3.85), 393 (3.85), 299 (3.86), 260 (3.82), 229 (4.00), 212 nm ($lg\varepsilon = 3.92$).

Adduct Formation of **5** *with Nucleophiles*

a) With methanol to 6 H-3-methoxy-3-ethylthio-1,2-dithiolo [4,3-c]1,2-dithiole (**6**). 100 mg (0.29 mmol) dithiolium salt **5** are dissolved in 3 ml absolute methanol. After addition of sodium hydrogencarbonate the mixture is stirred for 10 min at room temperature. The sediment is separated and the excess methanol is removed in vacuo from the filtrate. The obtained yellow oil is characterized by its ^{1}H-NMR spectrum (see Table 1). The yield is 83 mg (quantitatively). $C_7H_8O_2S_5$ (284.45). Calc. C 29.56, H 2.83; found C 29.30, H 3.12. VIS ($CHCl_3$) $\lambda_{max} = 360$ nm.

b) With tert-butyl mercaptan to 6H-3-ethylthio-3-tert-butylthio-1,2-dithiolo[4,3-c]1,2-dithiole (**7**). 100 mg (0.29 mmol) dithiolium salt **5** are dissolved in 3 ml acetonitrile. Then 0.4 ml (3.5 mmol) of *tert*-butyl mercaptan and sodium hydrogen carbonate are added by stirring. After 15 min the sediment is separated and the excess mercaptan and acetonitrile are removed in vacuo from the filtrate to yield 100 mg of **7** as a yellow oil (quantitatively). $C_{10}H_{14}OS_6$ (342.6). Calc. C 35.06, H 4.12; found C 35.38, H 4.36. VIS ($CHCl_3$) $\lambda_{max} = 360$ nm.

c) With aniline to N,N-Di(6H-3-ethylthio-1,2-dithiolo[4,3-c]1,2-dithiole-3-yl)-aniline (**8**). 100 mg (0.29 mmol) dithiolium salt **5** are dissolved in 3 ml acetonitrile. 0.5 ml aniline (5.4 mmol) in 1 ml acetonitrile are added by stirring. Immediately a yellow to light brown coloured oily product separates

off. This is isolated, washed with a minimum of acetonitrile and dried in vacuo. The yield is 80 mg (92%). $C_{18}H_{15}NO_2S_{10}$ (597.95). Calc. C 36.15, H 2.53, N 2.34; found C 36.03, H 2.83, N 2.25. VIS ($CHCl_3$) $\lambda_{max} = 354$ nm.

Reaction of 6 H-3-Methoxy-3-ethylthio-1,2-dithiolo[4,3-c]1,2-dithiole (**6**) *with Methyl Iodide*

150 mg (0.53 mmol) adduct **6** and 5 ml methyl iodide are stored in a closed flask for three weeks at room temperature. The reaction mixture is chromatographed on silica gel using toluene as the eluting agent. The yield of the dione **9** is 62 mg (65%). M.p. 220–222 °C (identical to a sample, which was synthesized in accordance with [9]). IR (KBr) 1 660, 1 643 cm^{-1} (C=O).

Reaction of **6** *with Acetyl Chloride*

150 mg (0.53 mmol) adduct **6** are dissolved in 10 ml 1,2-dichloroethane at room temperature. 0.5 ml (7 mmol) acetyl chloride are added by vigorous stirring. After 30 min the precipitate is separated by a centrifuge, washed twice with dried ether and dried in vacuo. The yield is 125 mg (81.6%) of orange coloured plates. M.p. 144–145 °C (no depression of the melting point with a sample obtained by an anion exchange of **5** with tetrabutylammonium chloride).

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Received May 18, 1990. Accepted June 25, 1990