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FORMATION AND ISOMERIZATION OF 3H,6H-2,5-BISARYL-1,2-THIAZOLINO[5,4-d]1,2-THIAZOLINE-3,6-DITHIONES - DERIVATIVES OF A NEW HETEROCYCLIC SYSTEM

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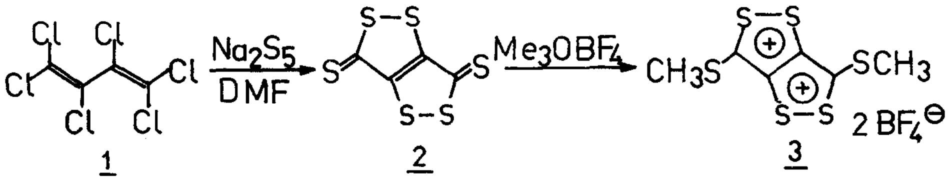
Abstract - The reaction of 3H,6H-1,2-dithiolo[4,3-c]1,2-dithiole-3,6-dithione (2) and of its alkylation product 3 with anilines 8 gives, depending on the conditions of the reaction, 3H,6H-3-arylimino-1,2-dithiolo[4,3-c]1,2-dithiole-6-thiones 9, 3H,6H-2,5-bisaryl-1,2-thiazolino[5,4-d]1,2-thiazoline-3,6-dithiones 10, and 3H,6H-3,6-bisarylimino-1,2-dithiolo[4,3-c]1,2-dithioles 11. The compounds 10 can be converted into the isomeric 11 and vice versa.

3H,6H-1,2-Dithiolo[4,3-c]1,2-dithiole-3,6-dithione (2) is an attractive starting material for synthesizing other heterocycles and dyes. It can be obtained easily by thiolating perchlorobutadiene (1) with sodium pentasulfide.[1] In this paper we report on the reaction of 2 and of its alkylation product 3 with primary aromatic amines.



It is known that 1,2-dithiole-3-thiones 4 (or the salts 5) react with primary amines to yield apart from open-chained derivatives of thioacrylic acid, 1,2-dithiole-3-imines 6 and 1,2-thiazoline-3-thiones 7.

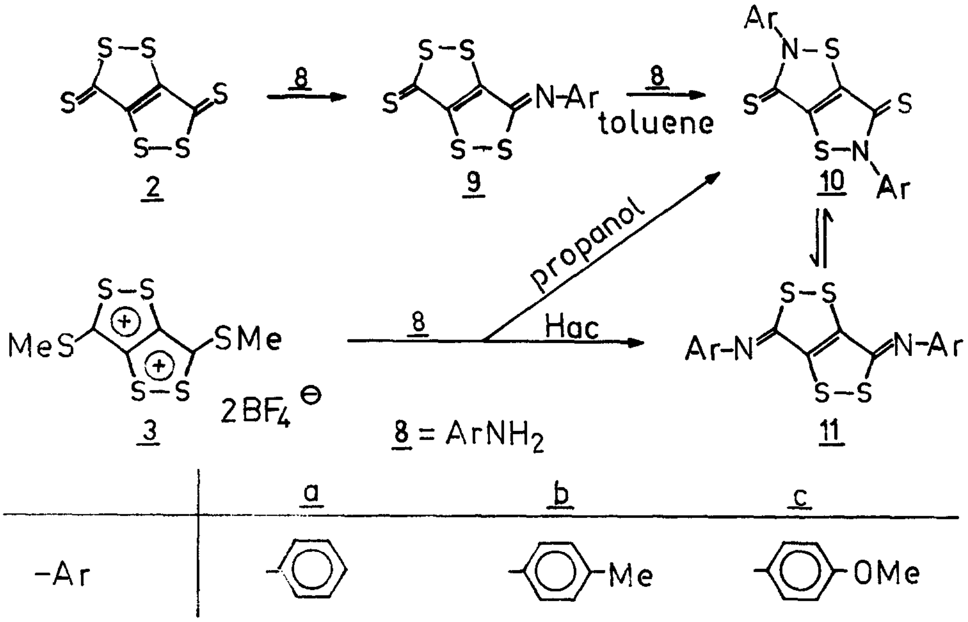
Comp.	4	5
X	S	$\overset{\oplus}{S}$Alkyl

	a	b	c
R	Alkyl	Aryl	Acyl

With aliphatic amines the thiazolines 7 are preferably formed, whereas with primary aromatic amines dithiole-imines 6 and on no account the thiazolines 7 are obtained.[2-5] The thiazolines 7a are able to undergo a reversible rearrangement to the dithiole-imines 6a[6-8] (for the isomerization of open-chained thioamides to thioimidoesters and vice versa see[9]). The conversion of the arylimino-dithioles 6b to the N-aryl-thiazoline-thiones 7b has failed until now.

The dithiolo-dithiole 2 reacts in non polar solvents like toluene with aniline and its donor-substituted derivatives 8 [10] via the isolable, orange coloured 3H,6H-3-arylimino-1,2-dithiolo[4,3-c]1,2-dithiole-6-thiones 9 to give the purple 3H,6H-2,5-bisaryl-1,2-thiazolino[5,4-d]1,2-thiazoline-3,6-dithiones 10. The compounds 10 are the first 3H,6H-1,2-thiazolino[5,4-d]1,2-thiazolines as well as the first N-aryl-substituted 3H-1,2-thiazoline-3-thiones 7b. As a by-product, the yellow 3H,6H-3,6-bisarylimino-1,2-dithiolo[4,3-c]1,2-dithioles 11 are obtained.

In propanol the dithiolium salt 3 reacts with the anilines 8 to form preferably the thiazolines 10, the monoimines 9 being formed in small amounts only (detection by TLC). In acetic acid not the thiazolines 10, but the isomeric bisimines 11 are obtained.



On more detailed investigations we observed an equilibrium between the compounds 10 and 11. The position of the equilibrium depends on the nature of the solvent. In acidic solvents like acetic acid it is completely located on the side of the more basic imines 11. [11] In the presence of soft electrophiles like iodine, tetracyanoquinodimethane, chloranil, or mercury(II)-acetate the equilibrium is displaced to the side of the imines 11 too. [12] We assume that the rearrangement occurs due to electrophilic attack on the thione group, followed by nucleophilic cleavage of the S-N-bond. [13] In accordance with that the isomerization rate of 10a to 11a in acetic acid in the presence of iodide is about ten times higher than without iodide ions. In non-polar solvents like methylene chloride, dichloroethane, or toluene, in the presence of a high concentration of soft nucleophiles like iodide, rhodanide, or thiourea and only a small amount of a protonic acid like hydrochloric acid or trifluoroacetic acid the position of equilibrium is more on the side of the thiazolines 10. [14] Under conditions where the slightly soluble thiazolines 10 are removed from the equilibrium by precipitation the conversion of the dithioles 11 to the isomeric 10 has been achieved on a preparative scale.

The rearrangement of 11 to 10 by heating, as described for the alkyliminodithioles 6a [7], failed. For the monoimines 9 an equilibrium between the dithiole-imines and the isomeric thiazoline-thiones, using the analogous conditions as for the isomerization of 11 to 10, could not be observed.

The structure elucidation of the new heterocyclic compounds is based upon the results of infrared spectroscopy and mass spectrometry. In their IR spectra the bisimines 11 give broad bands of C=N-valence vibrations (1540 cm^{-1}) but none of the C=S-bond. On the other hand, in the IR spectra of the thiazoline-thiones 10 and of the monoimines 9 intensive bands of C=S-valence vibrations are observed (1125, 1020 cm^{-1}). The N-C=S-structural element in the thiazoline thiones 10 is characterized by three typical bands in the regions of 1540-1520, 1445-1440, and 1125-1120 cm^{-1}.[15]

The mass spectra of the compounds 9, 10, and 11 are rather similar to each other. The main difference between the dithioles 9 and 11, and the thiazolines 10 is that only the compounds 9 and 11 give intensive peaks of ions, formed by twofold S_2 fragmentation from the molecular ions. These ions represent the carbon skeleton with the exocyclic heteroatoms of the compound analyzed (9: $[S{=}C{=}C{=}C{=}N{-}Ar]^{+\cdot}$; 11: $[Ar{-}N{=}C{=}C{=}C{=}N{-}Ar]^{+\cdot}$).

The thiazoline-thiones 10 do not show a fragmentation of S_2 from the molecular ions.

EXPERIMENTAL

The analytical data of the synthesized compounds 9, 10, and 11 are summarized in table 1.

3H,6H-1,2-Dithiolo[4,3-c]1,2-dithiole-3,6-dithione (2) - The dithiolo-dithiole 2 was prepared as recommended by Richter, Fanghänel.[1]

3H,6H-3,6-Bismethylthio-1,2-dithiolo[4,3-c]1,2-dithiolium tetrafluoroborate (3) 240 mg of the dithiolo-dithiole 2 (1mmol) and 1.5 g of trimethyloxonium tetrafluoroborate[16] were stirred at 90 °C for 6 h in 20 ml of 1,2-dichloroethane. After cooling 20 ml of dried ether were added dropwise. The orange coloured precipitate was filtered off, reprecipitated from acetonitrile with ether and dried in vacuo to give 409 mg of the dithiolium salt 3 (92 %), mp.157-160 °C (decomp.), IR (KBr) 3000, 2920, 2910 (CH), 1430, 1275 (dithiolium), 1150-950 (tetrafluoroborate) cm^{-1}; λ (CH_3CN) 228, 262, 311, 392, 504 nm. Calcd. for $C_6H_6S_6B_2F_8$ (mol wt 444.1): C, 16.23; H, 1.36;S, 43.32 %.
Found C, 16.01; H, 1.42;S, 43.9 %.

3H,6H-2,5-Bisaryl-1,2-thiazolino[5,4-d]1,2-thiazoline-3,6-dithiones 10, 3H,6H-3-arylimino-1,2-dithiolo[4,3-c]1,2-dithiole-6-thiones 9, and 3H,6H-3,6-bisarylimino-1,2-dithiolo[4,3-c]1,2-dithioles 11 from the dithiolo-dithiole 2 (General procedure) - 5mmol of the dithiolo-dithiole 2 and 0.1 mol of the aniline 8 in 50 ml of toluene were refluxed with stirring for 3 to 12 h. After cooling 20 ml of methanol were added. The dark purple precipitate of 10 was filtered off and recrystallized from toluene. The filtrate was concentrated in vacuo and chromatographed on silica gel using toluene as eluting solvent, wich afforded the orange coloured monoimines 9 and the yellow bisimines 11. If only 10 mmol of the anilines 8 were used, the monoimines 9 were the main product of the reaction.

Ratio 2:8	Compound	Yield (%) 9	 10	 11
1:20	a	3	70	14
	b	6	72	15
	c	6	70	15
1:10	a	55	14	9
	b	70	12	5
	c	70	10	7

3H,6H-2,5-Bisaryl-1,2-thiazolino[5,4-d]1,2-thiazoline-3,6-dithiones 10 from the dithiolium salt 3 (General procedure) - 2mmol of the dithiolium salt 3 and 15 mmol of the anilines 8 in 30 ml of propanol were refluxed with stirring for 20 to 30 minutes (until no more methylmercaptane was formed). After cooling the dark purple crystals were filtered off and recrystallized from toluene.

Compound	10a	10b	10c
Yield (%)	91	81	85

3H,6H-3,6-Bisarylimino-1,2-dithiolo[4,3-c]1,2-dithioles 11 from the dithiolium salt 3 (General procedure) - 2mmol of the dithiolium salt 3 and 15 mmol of the aniline 8 in 20 ml of acetic acid were refluxed with stirring for 30 minutes. After cooling 10 ml of ether were added. The yellow precipitate was filtered off and recrystallized from propanol.

Compound	11a	11b	11c
Yield (%)	92	80	85

3H,6H-2,5-Bisphenyl-1,2-thiazolino[5,4-d]1,2-thiazoline-3,6-dithione (10a) from the dithiolo-dithiole-monoimine 9a - 1mmol of the monoimine 9a and 10mmol of aniline 8a in 10 ml of toluene were refluxed with stirring for 90 minutes. After cooling 10 ml of methanol were added. The precipitate was filtered off and recrystallized from toluene to yield 93 % of the thiazoline-thione 10a.

3H,6H-3,6-Bisarylimino-1,2-dithiolo[4,3-c]1,2-dithioles 11 from the thiazoline-thiones 10

a) with mercury(II)-acetate (General procedure) - 5 mmol of the thiazoline 10 and 10 mg of mercury(II)-acetate ($3 \cdot 10^{-5}$ mol) in 100 ml of acetic acid were stirred at room temperature for 20 to 30 minutes, until all of the thiazoline 10 was consumed. After adding 50 ml of water the yellow precipitate was filtered off and recrystallized from propanol.

Compound	11a	11b	11c
Yield (%)	96	95	96

b) with chloranil (General procedure) - 5 mmol of the thiazoline 10 and 120 mg of chloranil (0.49 mmol) in 300 ml of toluene were stirred at 70°C. The reaction course was followed up by TLC. After cooling the reaction mixture was concentrated in vacuo to about 5 ml. After adding 5 ml of methanol the yellow precipitate was filtered off and recrystallized from propanol.

Compound	11a[17]	11b	11c
Reaction time (h)	10	10	1
Yield (%)	94	94	95

3H,6H-2,5-Bisaryl-1,2-thiazolino[5,4-d]1,2-thiazoline-3,6-dithiones 10 from the dithiole-imines 11 (General procedure) - 5 mmol of the bisimine 11 and 15 mmol of tetrabutylammonium iodide were dissolved in 75 ml of 1,2-dichloroethane. 0.2 ml of trifluoroacetic acid were added ($2.6 \cdot 10^{-6}$ mol) and the mixture was cooled with ice water. After adding 10 ml of dried ether the precipitate was separated by centrifugation, washed three times with 20 ml of ether and dried in vacuo. The thiazolines 10 were purified by recrystallization from toluene.

Compound	10a	10b	10c
Yield (%)	80	83	77

Table 1 - Analytical data of the compounds 9, 10 and 11

Compd.	Mp.	Formula (%)	Found (%) Calcd. (%)				IR$^{b)}$ cm^{-1}	VIS$^{c)}$ nm(logε)
			C	H	N	S		
9a	132-135	$C_{10}H_5S_5N$	40.04	2.01	4.19	54.07	1543	513(3.52)
			40.1	1.68	4.68	53.54	1020	486(3.78)
								464(3.79)
9b	203	$C_{11}H_7S_5N$	41.86	2.42	4.25	51.38	1535	513(3.97)
			42.14	2.25	4.47	51.14	1020	477(4.07)
9c	178-180	$C_{11}H_7OS_5N$	40.13	2.5	3.92	48.86	1535	508(4.09)
			40.1	2.14	4.25	48.66	1025	485(4.10)
10a	214-216$^{a)}$	$C_{16}H_{10}S_4N_2$	53.34	3.08	7.36	36.1	1535	532(3.98)
			53.6	2.81	7.81	35.77	1440	
							1125	
10b	194-195$^{a)}$	$C_{18}H_{14}S_4N_2$	55.64	3.78	6.97	33.41	1525	536(3.78)
			55.92	3.65	7.25	33.18	1445	
							1125	
10c	218-221$^{a)}$	$C_{18}H_{14}O_2S_4N_2$	51.29	3.52	6.3	31.02	1535	551(4.08)
			51.65	3.37	6.69	30.64	1445	
							1125	
11a	203-205	$C_{16}H_{10}S_4N_2$	53.41	3.05	7.42	36.08	1545	415(4.09)
			53.6	2.81	7.81	35.77		
11b	202-203	$C_{18}H_{14}S_4N_2$	55.61	3.83	6.96	33.4	1540	421(4.09)
			55.92	3.65	7.29	33.18		
11c	220-222	$C_{18}H_{14}O_2S_4N_2$	51.32	3.58	6.28	30.93	1540	434(4.22)
			51.65	3.37	6.69	30.64		

a) decomposition; b) in KBr; c) 9, 10 from $CHCl_3$ solution, 11 from CH_3CN solution

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11 Contrary to the thiazoline-thiones 10 the imines 9 and 11 may be protonated by dichloroacetic acid.
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17 Because of the very small reaction rate, 1.23 g of chloranil (5 mmol) were used.