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A New Route to 1,3-Dithioles from Mesoionic 2-Piperidino-5-Aryl-1,3-Dithiolium-4-Thiolates. Synthesis of 2(1,3-Dithiolan-2-Ylidene)-1,3-Dithioles and Tetrathiafulvalenes Using these New Dithioles.

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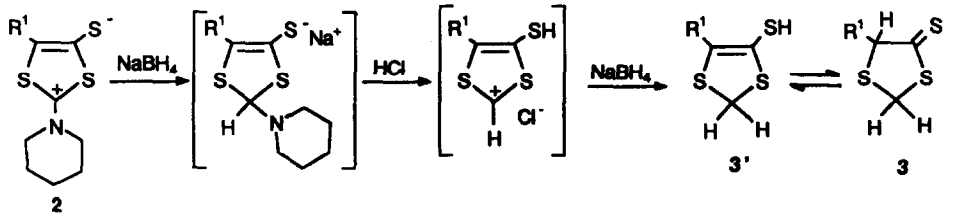
Abstract: An original synthesis of 1,3-dithioles prepared from mesoionic 2-piperidino-5-aryl-1,3-dithiolium-4-thiolates is described. The reaction of the carbanion derived from 1,3-dithiole with carbon disulfide followed by alkylation to yield 2(1,3-dithiolan-2-ylidene)-1,3-dithiole is also reported. This synthesis of dithioles led to substituted tetrathiafulvalenes not accessible by our usual procedure.

The 1,3-dithiole ring is of special interest in synthetic chemistry for organic materials due to its reactivity. The sulfur atoms exercise a stabilizing effect on neighboring positive as well as negative charges, an extremely useful feature for organic synthetic purposes. Indeed 1,3-dithiolium cations [1] and 1,3-dithiole anions [2] have been prepared starting from 1,3-dithiole compounds. The reactivity of 1,3-dithiolium salts have been widely studied and used in the synthesis of tetrathiafulvalenes and dithiafulvenes derivatives.[3] Surprisingly the formation of the 1,3-dithiole anion has been poorly investigated. We wish to describe here an original access to the 5-aryl-4-alkylthio-1,3-dithiole **1** starting from mesoionic 2-piperidino-5-aryl-1,3-dithiolium-4-thiolates **2** via the unsubstituted key intermediate **3**. We report a successful metallation of the dithiole **1** and its reaction with carbon disulfide in an attempt to generate the dianion to yield the dithiafulvene **6**. We also present some new tetrathiafulvalenes **9** substituted by acceptors starting from dithioles **1**.

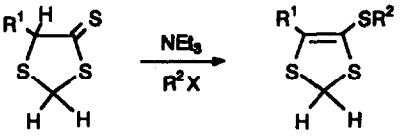
The synthetic methods described in the litterature for the synthesis of 1,3-dithioles **1** are essentially based on the reduction of 1,3-dithiolium salts either by the cycloheptatriene,[4] sodium borohydride,[5] or lithium aluminium hydride.[1] During the course of our studies on the mesoionic derivative **2** [6] we observed that when **2** was treated by an excess of sodium borohydride and carried out by an acidic hydrolysis we obtained **3**. We propose the mechanism below to account for this reduction (Scheme 1). The first step could be the reduction at the 2 position of the mesoionic dithiole, then during the acidic hydrolysis protonation and elimination of piperidine. As we are in presence of a large excess of sodium borohydride a second reduction would occur to yield the dithiole **3'**.[7]



2 3' 3

Scheme 1

Actually we obtained the thioxo form 3 rather than the thiol form 3', the equilibrium led towards the more stable tautomer. In each case NMR spectra confirmed the thioxo structure, ^1H NMR spectra show that the proton at the C 5 position appears at δ 5.2 ppm ,and ^{13}C NMR present a C=S at about δ 220 ppm. The alkylation of 3 has been done in basic medium to afford 1 [8] in good yields as presented in the table 1 (Scheme 2).



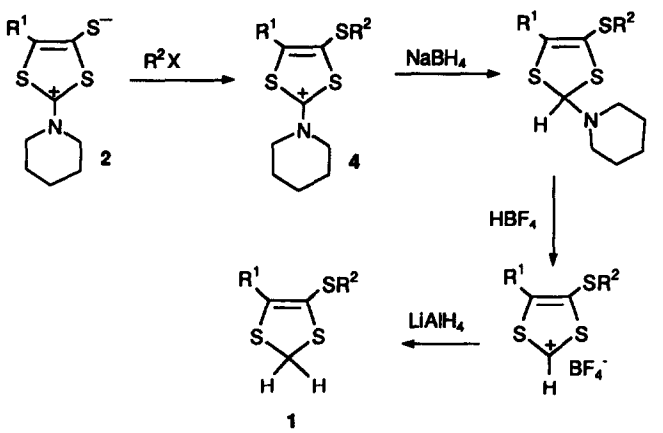
3 1

Scheme 2

Table 1

R^1	4-thioxo 1,3-dithiola-	Dithioles 1 (yield%)	
	nes 3 (yield %)	$R^2 = CH_3$	$R^2 = 3,5\text{-}(NO_2)_2C_6H_3CH_2$
$pMeC_6H_4$	93	96	76
$pClC_6H_4$	88	97	75
$pCO_2HC_6H_4$	90	95	

Compounds of type 1 have been earlier synthetized from mesoionic derivatives 2 in a multi-step process as shown in Scheme 3.[9] Compared to this route we have developed a simple, short, improved high yields procedure for the preparation of dithioles 1.[10] According to this new procedure we also synthetized dithioles 1 substituted by acceptor groups which were not obtained by the multi step process (Scheme 3) as the reduction of amino cation 4 yielded a mixture of products.

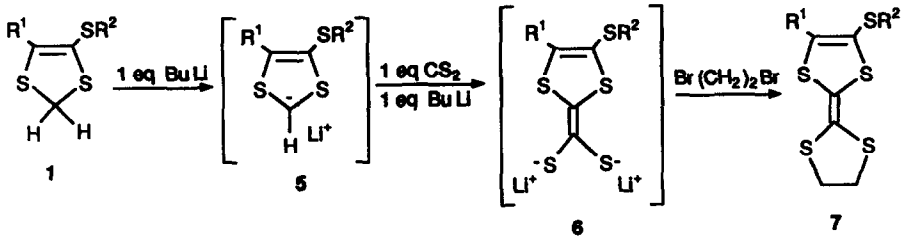


2 4 1

Scheme 3

As we are interested in the synthesis of new electron donors, we investigated the preparation of dianions of type 6 starting from dithioles 1. Nucleophilic addition of 1,3-dithiolane anion to carbon disulfide followed by a double alkylation has been described[11] but it seemed that on 1,3-dithioles the same type of reaction was not

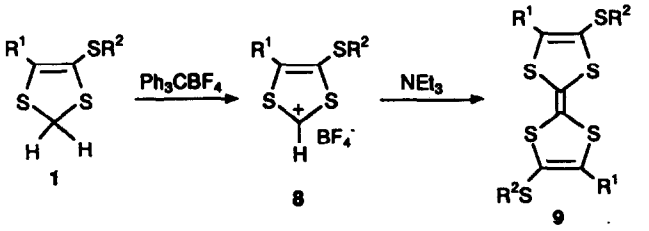
successful so far.[12] Starting from **1** we generated the carbanion **5** with 1 equiv of BuLi then we treated **5** by 1 equiv of CS_2 and another equiv of BuLi. Dianion **6** was trapped by 1,2-dibromo ethane to yield the tetrathiaethylene derivatives **7**.[13](Scheme 4)



Scheme 4

The dianion **6** is an interesting intermediate and opens the way to the access of some new donors as unsymmetrical tetrathiafuvalenes or dithiafulvenes. We are studying the scope of this reaction and the use of **7** as a donor.

In order to create intramolecular charge transfer in aryl sustituted TTF we were also interested in the syntheses of TTF **9** substituted by two acceptor groups as R^2. Those compounds as pointed out by Becker et al[14] in a D-A-D systems could crystallize with separated stacks of donors and acceptors. However, some R^2 groups were reduced during the $NaBH_4$ reduction of **4** according to our usual procedure.[15] It was thus of interest to use dithiole **3** for the syntheses of TTF **9** as shown in Scheme 5.



Scheme 5

The tetrafluoborate **8**, obtained by the treatment of dithiole **1** with triphenyl carbenium tetrafluoroborate, was treated by triethylamine to afford **9** in good conditions.[16]

In conclusion the new method described here for the synthesis of dithioles appears to be highly competitive with the other methods reported in the litterature. The exploration of the dithioles **1** and **3** in a variety of applications in the field of organic materials is currently in progress.

References and Notes

1. Takamizawa, A.; Hirai, K. Chem. Pharm. Bull. **1969**, 17, 1931-1936.
2. Ncube, S.; Pelter, A.; Smith, K.; Blatcher, P.; Warren, S. Tetrahedron Lett. **1978**, 2345-2348.
3. Lozac'h, N.; Stavaux, M., 1,3-Dithiolium Ion. In Advances in Heterocyclic Chemistry ; Katritzky, A.R.; Boulton, A.J., Ed. ; Academic Press : New York, 1980, vol. 27, pp. 199-239.

4. Hirai, K. Tetrahedron. **1971**, 27, 4003- 4011.

5. Nakayama, J.; Fujiwara, K.; Hoshino, M. Bull. Chem. Soc. Jp. **1976**, 49, 3567-3573.

6. Souizi, A.; Robert, A. Synthesis. **1982**, 1059-1061; Bssaibis, M.; Souizi, A.; Robert, A. J. Chem. Soc., Chem. Commun. Under press.

7. A typical experimental procedure for **3**: A stirred suspension of **2** (3 mmol) in EtOH (50 ml) was cooled to 0°C and $NaBH_4$ (500 mg, 13.2 mmol) was added . After 45 min, diluted HCl was slowly added and the reaction mixture was stirred for an additionnal 10 min and extracted with Et_2O (2 x 60 ml). The combined organic phase was washed, dried (Na_2SO_4) and evaporated to give the 4-thioxo-1,3-dithiolane **3** as an oil. All the compounds **3** prepared showed physical and spectral data in accordance to their expected structure. As an example we give a full description of compound **3** (R^1=$pCO_2HC_6H_4$). ^1H NMR ($CDCl_3$, TMS, 300 MHz) 4.45 (AB,2H); 5.31 (s, 1H); 7.85(m,4H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) 36.92; 71.13; 127.36; 128.74; 130.58; 143.22; 170.12; 220.2. HRMS calc. for $C_{10}H_8O_2S_3$ 255.968 found 255.967.

8. Preparation of dithiole **1**: To a solution of **3** (2 mmol) in CH_2Cl_2 (20 ml) was added Et_3N (0.5 ml) and 2.5 mmol of CH_3I. The reaction mixture was refluxed for 2 hours. After cooling the organic phase was washed with water (3 x 10ml) dried (Na_2SO_4) and concentrated to yield a light yellow oil. As an example we give a full description of compound **1** (R^1 = $pMeC_6H_4$). ^1H NMR ($CDCl_3$, TMS, 300 MHz) 2.28 (s, 3H); 2.3 (s,3H); 4.3 (s, 2H) 7.25 (m,4H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) 19.8; 21.3; 33.3; 120.8; 128.82; 129.64; 129.95; 132.82; 138.59. HRMS calc for $C_{11}H_{12}S_3$ 240.010 found 240.010.

9. The synthesis of dithiole **1** multi-step process was carried out in analogy with the litterature. For 2-amino-1,3-dithioles see Souizi, A.; Robert, A. Tetrahedron. **1984**, 40, 1817-1822. For dithiolium salts see reference (5). For dithiole **1** see reference (1).

10. This procedure is well suited when R^1 is an aryl group, however lower yields are observed when R^1 is aliphatic.

11. Baird, D.M.; Bereman, R. D. J. Org. Chem. **1981**, 46, 458-459.

12. Moradpour, A.; Bittner, S. Tetrahedron Lett. **1987**, 28, 3805-3808.

13. A typical experimental procedure for **7**: BuLi (1 ml, 1.6 M in Hexane) was added to a solution of dithiole **1** (1.5 mmol)in dry THF (15 ml) at -78°C under nitrogen. This solution was stirred for 1.5 h at -30°C and CS_2 was added (0.1 ml, 1.7 mmol). Immediately an additionnal 1ml of BuLi was added. After 20 min 1,2-dibromoethane (1.5 mmol) was added. The reaction mixture was allowed to warm at room temperature and stirring was continued for an additionnal 12 hours. The THF was removed, the reaction mixture was extracted with CH_2Cl_2 (2x 20 ml) and washed with water. The organic phase was dried (Na_2SO_4) evaporated and the residu purified by chromatography on silica gel with CH_2Cl_2/ Petroleum ether (4:1) as eluent. As an example we give a description of compound **1** (R^1 = $pMeC_6H_4$, R^2= CH_3).yield 21%. ^1H NMR ($CDCl_3$, TMS, 300 MHz) 2.3 (s, 3H); 2.32 (s,3H); 3.42 (m, 4H) 7.25 (m,4H). HRMS calc for $C_{14}H_{14}S_5$ 341.9699 found 341.970.

14. Becker, J. Y.; Bernstein, J.; Bittner, S.; Shaik, S.S. Synth. Met. **1988**, 27, B197-B204.

15. Le Paillard, M. P.; Robert, A. Bull. Soc. Chim. France. **1992**, 129, 205-208.

16. Preparation of tetrathiafulvalene **9**: Triphenyl carbenium tetrafluoroborate (2 mmol) in 10 ml of CH_3CN was added dropwise to a solution of dithiole **1** 2 mmol at 0°C. The reaction mixture was stirred for 1 hour at 0°C and anhydrous ether (20 ml) was added. The cation **8** was filtered and washed with dry ether. Compound **8** was used in the following reaction without further purification. To the cation **8** dissolved in 10 ml of dry CH_3CN was added NEt_3. The reaction mixture was stirred at room temperature for 30 min and extracted with CH_2Cl_2(2x30 ml). The organic phase was washed with water, dried over Na_2SO_4.The solution was concentrated and **9** was precipitated by addition of ether and recrystallised from CH_3CN.As an example we give a description of compound **9** (R^1 = $pMeC_6H_4$, R^2= $3,5\text{-}(NO_2)_2C_6H_4CH_2$).mp 188°C. ^1H NMR ($CDCl_3$, TMS, 300 MHz) 2.3 (s, 6H); 4,01 (s,4H); 7,26 (m, 8H) 8,22 (d,4H) 8,80 (t,2H). Anal calc for $C_{34}H_{24}N_4O_8S_6$ C 50.47; H 2.99; S 23.78; N 6.92 found.C 50.52; H 2.69; S 23.56; N 6.83.

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