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Oxidative versus Vicarious Nucleophilic Substitution of Hydrogen in the Reaction of Dithiane Derivatives with Nitroarenes

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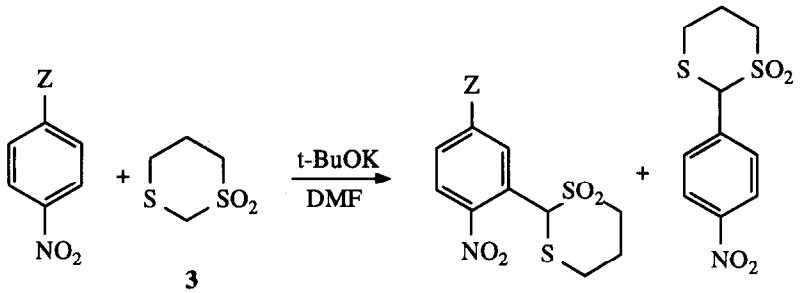
Abstract:, Carbanions of dithiane monosulfone and dithiane monosulfonium salt react with nitroarenes in different ways: oxidative and vicarious nucleophilic substitution of hydrogen correspondingly.

In our previous paper[1] we have reported that the ring opening vicarious nucleophilic substitution of hydrogen (VNS) in nitroarenes[2] with the carbanion of 1,3-benzodithiolane sulfoxide was hindered, probably due to the rigid structure of the five membered ring fused with the aromatic benzene ring. Thus it was of substantial interest to learn how more flexible six membered 1,3-dithiane ring system will behave in this reaction. Reactions of 1,3-dithiane carbanions with a variety of electrophiles have found wide applications in organic synthesis.[3] Contrary to that very little is known about reactions of such carbanions with nitroarenes. The addition of lithium dithiane to nitroarenes carried out in THF at low temperature results in the formation of the relatively stable σ^H-adducts which can be oxidized to dithioacetals of nitroarylaldehydes.[4] In the reaction of such carbanions with tricarbonyl-chromium π-complexes of arenes, which in many respects behave similarly to nitroarenes, relatively stable anionic σ^H-adducts are formed. Subsequent oxidation results in oxidative substitution of hydrogen with the dithiane moiety.[5]

In our hands the reaction of carbanion of 1,3-ditiane (**1**) (in the form of the potassium salt generated by treatment of **1** with t-BuOK) with nitrobenzene carried out at -5 to -30°C in DMF gave only tars. Taking into account the results of Kienzle[4a] and particularly those reported by Bartoli,[4b] one could suppose that the corresponding σ^H-adducts do not enter the ring opening ß-elimination, and uncontrolled processes including probably electron transfer dominate. Similar results we have observed in the reaction of corresponding monosulfoxide **2** with nitrobenzene, no definite products were obtained under the applied conditions.

On the other hand the reaction of the carbanion of more acidic dithiane-1,1-dioxide **3** with nitroarenes gave interesting results (Scheme 1). The reaction of **3** with nitrobenzene carried out in the presence of t-BuOK in DMF gave a mixture of 2- and 4-nitrophenyl derivatives of dithiane-1,1-dioxide **4a** and **5** which were obviously formed *via* an oxidation of the σ^H-adducts. The process is very sensitive to the conditions: temperature, concentration and amount of the base - in some experiments total yield of the oxidative nucleophilic substitution of hydrogen products amounted to 67%. Identical process was observed in the reaction of **3** with other nitroarenes: 4-chloro-, 4-trifluoromethyl- and even 4-fluoronitrobenzene!!.

Scheme 1



Z = H	**4a**	47%	**5**	20%
Cl	**4b**	68%	-	
F	**4c**	55%	**5**	6%
CF_3	**4d**	67%	-	

Whereas the oxidative nucleophilic substitution of hydrogen (ONSH) in 4-chloronitrobenzene with some carbanions[6] and other nucleophiles[7] was already observed, the observation that this process dominates in the reaction of a nucleophile with 4-fluoronitrobenzene (FNB), which is known to enter S_NAr of the halogen very readily,[8] is unexpected and unprecedented. In our early papers we have shown that the nucleophilic addition of carbanions to FNB proceeds faster at the position 2- giving σ^H adduct than at the position 4- giving σ^F-adduct, however it appears that these rates do not differ substantially. The process can be directed toward replacement of the hydrogen provided there is a rapid reaction in which further conversion of the σ^H-adduct can occur.[9] This is the case of the reaction with α-halocarbanions carried out in the presence of an excess of base, in which rapid ß-elimination of hydrogen chloride from the σ^H-adduct can occure resulting in formation of the VNS product.[10] When a base is in insufficient concentration the rate of the elimination is decreased and the, conventional S_NAr of fluoride becomes the main process. Since oxidation of the σ^H-adducts is usually not a fast reaction,[9,11] oxidative nucleophilic replacement of hydrogen in 4-fluoronitrobenzene was never observed, unless there was a special stabilization of the σ^H-adducts which prevent equilibration and extended their life span as for example *via* the formation of *O*-silyl derivatives,[12] or the addition of the Grignard reagents.[13] Taking into account relatively high yield of the ONSH products with carbanion of **3** even in FNB, the oxidation in this instance should be rather a surprizingly efficient process. Thus, there is an important question concerning identity of the oxidizing agent: it could be the atmospheric oxygen or the nitroarene itself. Detailed analysis of the reaction of FNB with **3** carried out in DMF has not provided unambiguous answer - the results of the reaction were not much different when it was carried out in the deoxygenated system (a few vacuum - argon cycles) or under pure oxygen. Variation of the temperature (-15°-40°C) affected total yield of the products of ONSH and S_NAr reactions (amount of tars formed) but not their ratio. Similar observations were made for the reaction of **3** with nitrobenzene and 4-chloronitrobenzene - the results were not meaningfully affected by the presence or absence of oxygen. Contrary to that, the course of the reaction of **3** with 4-trifluoromethyl nitrobenzene was strongly affected by the presence of oxygen, which assured good yield of the ONSH product **3d**, whereas under the deoxygenated conditions formation of tars dominated. We were unable to rationalize the differences in the behaviour of these nitroarenes. It should be stressed that we could not find any reduction products of the nitroarenes (azo- or azoxycompounds or anilines) in the reaction mixture

when it was carried out in the deoxygenated systems. The observation that in the reaction of carbanion of **3** with 4-fluoronitrobenzene carried out apparently without external oxidizing agents nucleophilic replacement of hydrogen dominates is really remarkable.

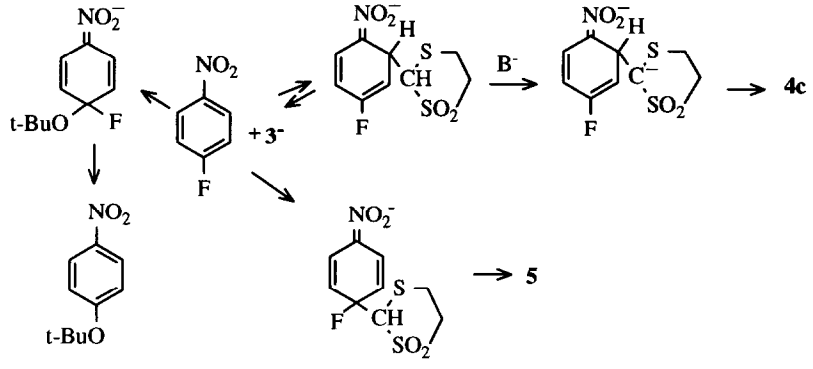
Such surprizing course of the reaction of **3** with FNB promted us to make some additional studies of this problem. From the results given in table 1, picture of the reaction shown on scheme 2 emerged.

Table 1. Reactions of FNB with **3** under various conditions

Ratio to FNB		Solv.	O_2	Yield of %[a]		FNB
3	t-BuOK			**4c**	**5**	recov.
1	5	DMF	+	55	6	-
1	5	DMF	-	29	3	22
2	1	DMF	+	18	5	28
1	5	NH_3	-	26	4	10
1	5	NH_3	+	66	4	-
2	1	NH_3	-	8	5	22
2	1	NH_3	+	9	8	31
1	2	DMSO[c]	-	11	39	
1.1	1	DMSO[c]	-	traces	66	

a.Calculated according to the actual stoichiometry b. t-butyl p-nitrophenyl ether was also formed, yield 33% c.Reverse addition order, temp. +45°C

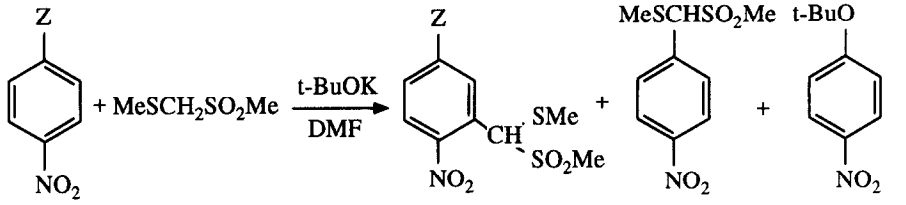
Scheme 2



The addition of 3^- to FNB at position 2- to form the σ^H-adduct is the fastest process in the system. This adduct is subsequently rapidly oxidized to **4c**. The high rate of the oxidation process and the absence of defined products of the reduction of FNB which could eventually act as an oxidant, implies that this transformations proceed under action of the atmospheric oxygen. Being aware that removal of traces of oxygen in simple vacuum - argon cycles could be insufficient we have used conditions which should assure more

complete deoxygenation in a chemical way, namely liquid ammonia solvent with traces of dissolved sodium so the pale blue colouration persists. Under such conditions we have observed that ONSH is depressed, but still takes place to a substantial extend, the main product was *t*-butyl 4-nitrophenyl ether resulting from S_NAr of the halogen with *t*-BuOK which is used in a great excess. On the other hand, when under the same conditions the reaction mixture was saturated with oxygen, **4c** was formed in a good yield. Thus undoubtedly the σ^H-adduct is oxidized with oxygen, nevertheless one cannot exclude that also the nitroarene acts as the oxidant. Although we could not find in the reaction mixture the azoxy and azo compounds and have shown that they are stable under the reaction conditions, in all experiments tars are formed in substantial quantities presumably via transformations of the nitroaromatic radical anions. The results indicate that for the oxidation to proceed an excess of base in the reaction mixture should be present. It appears therefore that depronation of the σ^H-adduct takes place and actually the dianion is the oxidized species. Similar supposition was formulated for the ONSH in nitroarenes with OH^- anion. The results show also that the addition of $\mathbf{3}^-$ to FNB proceeds much faster at the position 2- than 4-. This regularity has been already observed for many other carbanions. It can be also concluded that *t*-BuO^- adds at the position 4- occupied with fluoro substituent faster than $\mathbf{3}^-$ does. No estimation can be however made concerning relation of the rates of addition of $\mathbf{3}^-$ and *t*-BuO^- at position 2- of FNB as well as to compare the rates of the addition of *t*-BuO^- at positions 4- and 2- because the σ^H adduct of *t*-BuO^- cannot be readily converted into a product. Taking into account that attempts of the VNS hydroxylation of FNB with cumyl hydroperoxide anion resulted in S_NAr of the halogen[14] one can suppose that the O-anions add to the nitroaromatic ring in positions bearing fluorine with the rate higher or comparable to that in positions bearing hydrogen. The rate of S_NAr of the halogen in 4-FNB with $\mathbf{3}^-$ in liquid ammonia is rather low so even under conditions disfavouring ONSH it proceeds to a small extend. The S_NAr becomes the main process when the reaction is carried out in DMSO at +45°C provided low base concentration is maintained throughout the reaction, otherwise ONSH become the competing process.

Scheme 3



Z = Cl	**6**	**6b**	66%	-		
F		**6c**	20%	**7**	3%	38%
F [a]	**6**	**6c**	traces	**7**	37%	traces

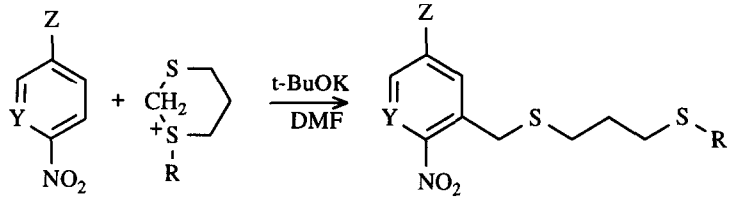
[a] In DMSO, reverse addition order, temp +45°C

In order to clarify whether absence of the eliminative conversion of the σ^H-adducts of the carbanion of **3** to nitroarenes leading to the VNS products is connected with the cyclic structure of **3**, which could impose limited steric flexibility, thus hindering the ring opening ß-elimination, an open chain analogue of **3** - methyl methylthiomethyl sulfone **6** was prepared and tested in the reaction with some nitroarenes (scheme 3).

With *p*-chloronitrobenzene again ONSH proceeded exclusively giving **6b** in a good yield. The reaction

with FNB was somewhat more complicated. Again ONSH with the carbanion dominated over S_NAr, with the carbanion, however yields of the corresponding products **6c** and **7a** were low 20% and 3%, and the main product was t-butyl 4-nitrophenyl ether, resulting from the S_NAr of F with *t*-butoxide anion. Only when the reaction was carried out at higher temp. in DMSO S_NAr of F was dominating. These results indicate clearly that the factors responsible for the difficulties in the eliminative conversion of the σ^H-adducts, hence the oxidative transformations dominate over the VNS process, are not connected with the cyclic structure of the carbanions. Taking into account our early observations that phenyl phenylthiomethyl sulfone and the corresponding sulfoxide[1] and other carbanions containing PhS substituent enter the VNS reaction with a variety of nitroarenes we can conclude that PhS, - PhSO and $PhSO_2$ substituents act as efficient leaving groups in the VNS reaction,[2] whereas alkyl-S and alkyl-SO_2 substituents are not readily eliminated from the corresponding σ-adducts, perhaps because of lower acidity of the corresponding aliphatic thioles and sulfinic acids. It should be noted however that some S-methyl thioglycolonitrile derivatives enter the VNS reaction *via* the ß-elimination of the MeS group.[15]

Scheme 4



Y, Z = CH, H R = Me, **8**
CH, Cl Et, **9**
CH, F
N , MeO

8a 35%
8b 55%
8c 40%
8d 60% **9d** 55%

Another series of experiments directed toward the ring opening VNS was carried out with sulfonium salts **8** and **9** prepared in the reaction of dithiane **1** with methyl and ethyl iodides. These compounds are relatively strong CH acids and can be easily deprotonated to the corresponding ylides. Interestingly we could not find any examples of reactions of such cyclic ylides in the literature. The reaction of these ylides with nitrobenzene and some other nitroarenes proceeded *via* the ring opening ß-elimination process in the initially formed σ^H-adducts to give the expected products of the VNS reaction. It is interesting to note that in the reaction with nitrobenzene the substitution occurs only in the *ortho* position. Apparently an electrostatic attraction between the positively charged sulfur atom and the negatively charged oxygen atoms of the nitro group is responsible for this orientation.

Thus the VNS reaction proceeding *via* the 6-membered ring opening occurs satisfactorily, it was therefore of interest to clarify the situation with 5-membered ring, because our early observations indicated some difficulties in this respect.[1] The sulfonium salt produced in the reaction of 1,3-dithiolane with methyl iodide did not react with p-chloronitrobenzene in the presence of *t*-BuOK in DMF, similarly no products of the reaction with the of 1,3-dithiolane-1,1-dioxide were found under these conditions. Apparently the eliminative decomposition of the five-membered carbanion precursors under the action of a strong base proceeds faster than the carbanions formation or the carbanions decompose before the eventual reaction with

the nitroarene.[16]

Results of the reactions of carbanions of **3**, **4** and **6** with nitroarenes indicate that there are no difficulties in the ring opening VNS reaction when both the leaving and the carbanion stabilizing groups are parts of the 6-membered ring provided the leaving group exhibit high activity in the ß-elimination process. It should be also noted that the ß-elimination of MeS or alkyl-S moieties from the σ^H-adducts of the corresponding carbanions of $RSCH_2SO_2R$ does not proceeded readily, contrary to the cases of MeSRCHCN (R = NEt_2 or RO).

Experimental

Melting points are uncorrected. The ^1H NMR spectra were measured on Varian Gemini Spectrometer at 200 MHz, in $CDCl_3$ unless otherwise stated using TMS as an internal standard. The mass spectra were obtained on AMD-604 (Intercta GmbH), silica gel (230-400 mesh, Merck) was used for column chromatography, starting materials were commercial or prepared according to the described procedures: 1,3-dithianemonoxide (**2**),[17] 1,3-dithiane-1,1-dioxide (**3**),[18] methyl methylthiomethyl sulfone (**6**),[19] 1,3-dithiane mono-methyl and ethyl iodides (**8**,**9**).[20]

The Reactions of the Carbanions of 3 and 6 with Nitroarenes, General Procedures

1. In DMF without oxygen.

To a solution of potassium t-butoxide (0,561 g, 5 mmole) in dry DMF (6 ml) which was deoxygenated via evacuation-argon cycle (4 times) and cooled to -35°C a solution of the nitroarene (1 mmole) the sulfone **3** (0.152 g, 1 mmole) was added dropwise within 3 min. The reaction was carried out for 20 min and the mixture was poured into water (60 ml) containing hydrochloride acid (2 ml). The product was extracted with ethyl acetate (3 x 20 ml), the extract washed, dried and the solvent evaporated. The residue was chromatographed using a mixture hexane-ethylacetate as the eluent.

2. In DMF with oxygen.

Exactly as in procedure 1, oxygen was used instead of argone for saturation of the reaction mixture

3. In liquid ammonia, without oxygen.

To a solution of potassium t-butoxide (0.561 g, 5 mmole) in liquid ammonia (~ 6 ml) a small piece of sodium was added to obtain persistent pale blue colour. Then a solution of the nitroarene (1 mmole) and **3** (0.152 g, 1 mmole) in DMF 1.5 ml was added dropwise within 3 min. After 20 min the solution was cooled and cold, deoxygenated 10% aqueous NH_4Cl (20 ml) was added. The mixture was extracted with ethyl acetate and treated as in procedure 1.

4. In liquid ammonia with oxygen.

Through a solution of potassium t-butoxide (0.561 g, 5 mmole) in liquid ammonia (6 ml) a slow stream of oxygen was bubled and a solution of the nitroarene (1 mmole) and **3** (0.152 g, 1 mmole) in DMF (1.5 ml) was added dropwise within 3 min. After 20 min the mixture was poured into ice (60 g) acidified with hydrochloric acid (2 ml) and treated as in procedure 1.

5. Reactions of 3 with p-fluoronitrobenzene under various conditions:

In liquid ammonia without excess of t-BuOK. To a boiling solution of p-fluoronitrobenzene (0.141 g, 1 mmole) in liquid ammonia (6 ml) a solution of **3** (0.305 g, 2 mmole) and t-BuOK (0.112 g, 1 mmole) in DMF (1.5 ml) was added dropwise. The reaction was carried out for 3 h under argone and the mixture treated according to procedure 3.

In DMSO, reverted addition order. To a solution of p-fluoronitrobenzene (0.141 g, 1 mmole) in dry DMSO (6 ml) at 45°C under argone a solution of **3** (0.152 g, 1 mmole) and t-BuOK (0.225 g, 2 mmole) in DMSO (2 ml) was slowly added dropwise during 20 min. The mixture is poured into water (60 ml) containing hydrochloric acid (2 ml) and treated as in procedure 1.
As above but a solution of **3** (0.167 g, 1.1 mmole) and t-BuOK (0.112 g, 1 mmole) in DMSO (2 ml) was used.

*The reaction of sulfonium ylides from generated from **8** and **9** 1,3-dithianemonosalts*
To a deoxygenated solution of *t*-BuOK (0.367 g, 3 mmole) in DMF (9 ml) cooled to -30°C a solution of **8** or **9** (1 mmole) and a nitroarene (1 mmole) in DMF (3 ml) was added during 5 min. The reaction was carried out for 20 min and the mixture poured into water (100 ml) containing hydrochloric acid (2 ml). Further treatment as in procedure 1.

Properties and spectral data of compounds obtained
2-(2-Nitrophenyl)-1,3-dithiane-1,1-dioxide (**4a**) Mp 191-193°C (AcOEt/hexane); ^{1}H NMR: 2.48-2.92 (m,3H), 3.04-3.41 (m,3H), 6.37 (s,1H), 7.50-7.73 (m,2H), 7.95 (dd,J=12.8,1.6,1H), 8.00 (dd,J=13.0,1.7,1H). Anal.calcd for $C_{10}H_{11}NO_4S_2$: C, 43.94; H, 4.06; N, 5.12%; found: C, 43.89; H, 3.93; N, 5.18%.
2-(4-Nitrophemyl)-1,3-dithiane-1,1-dioxide, (**5**) Mp. 225-227°C (AcOEt/hexane); ^{1}H NMR: 2.52-2.96 (m,3H), 3.0-3.49 (m,3H), 5.25 (s,1H), 8.27, 7.74 (AA^1XX^1,4H) Anal.calcd for $C_{10}H_{11}NO_4S_2$: C, 43.94; H, 4.06; N, 5.12%; found: C, 43.73; H, 3.86; N, 4.93%.

2-(2-Nitro-5-chlorophenyl)-1,3-dithiane-1,1-dioxide (**4b**), Mp. 217-218°C (AcOEt) ^{1}H NMR: 2.53-2.97 (m,3H); 3.08-3.47 (m,3H), 6.42 (s,1H), 7.55 (dd,J=8.8,2.3),1H), 7.95 (d,J=2.3,1H), 8.79 (d,J=8.8,1H). Anal.cald for $C_{10}H_{10}ClNO_4S_2$: C, 39.02; H, 3.28; N, 4.55%; found: C, 39.11; H, 3.11; N, 4.48%.

2-(2-Nitro-5-fluorophenyl)1,3-dithiane-1,1-dioxide (**4c**), Mp. 161-163°C (AcOEt) ^{1}H NMR: 2.52-2.96 (m,3H), 3.08-3.46 (m,3H), 6.47 (d,J=1,1H), 7.33-7.37 (m,1H), 7.71 (dd,J=9.0,2.8,1H), 8.13 (dd,J=5.1,1H). Anal.calcd for $C_{10}H_{10}FNO_4S_2$: C, 41.33; H, 3.46; N, 4.81; found: C, 41.29, H, 3.35; N, 4.62%.

2-(2-Nitro-5-trifluoromethylphenyl)-1,3-dithiane-1,1-dioxide (**4d**) Mp 207-209°C (AcOEt); ^{1}H NMR: 2.54-2.99 (m,3H), 3.09-3.47 (m, 3H), 6.33 (s,1H), 7.82-7.90 (m,1H), 8.13 (d,J=8.5,1H),8.22 (d,J=1.9,1H). Anal.calcd for $C_{11}H_{10}F_3NO_4S$: C, 38.71; H, 2.95; N, 4.10%; found: C, 38.64; H. 2.77; N, 4.00%.

α-Methylthio-2-nitro-5-chlorobenzyl methyl sulfone (**6b**), Mp. 132-134°C (AcOEt-Hexane); ^{1}H NMR: 2.45 (s,3H), 3.04 (s,3H), 6.08 (s,1H), 7.54 (dd, J=8.8,2.3,1H), 7.93 (d,J=2.3, 1H), 8.01 (d,J=8.8,1H). Anal. calcd for $C_9H_{10}ClNO_4S_2$: C, 36.55; H, 3.41; N, 4.74%; found: C, 36,61; H, 3.37; N, 4.70%.

α-Methylthio-2-nitro-5-fluorobenzyl methyl sulfone (**6c**), Mp. 115-117°C (AcOEt-Hexan); ^{1}H NMR: 2.45 (s,3H), 3.04 (s,3H), 6.14 (s,1H), 7.25 (ddd,J=11.9,6.8,2.8,1H), 7.67 (dd,J=9.2,2.8,1H), 8.12 (dd,J=9.1,5.1,1H). Anal. calcd for $C_9H_{10}FNO_4S_2$: C, 38.70; H, 3.61; N, 5.02%; found: C, 38.91; H, 3.64; N, 5.09%.

α-Methylthio-4-nitrobenzyl methyl sulfone (**7**), Mp. 171-173°C (AcOEt -Ethanol); ^{1}H NMR: 2.45 (s,3H), 2.95 (s,3H), 4.89 (s,1H), 7.70, 8.28 (AA'XX',2H). Anal. calcd for $C_9H_{11}NO_4S_2$: C, 41.36; H, 4.24; N,5.36%; found: C,41.32; H,4.31; N, 5.31%.
1-(2-Nitrophenyl)-2,6-dithiaheptane (**8a**), Oil, ^{1}H NMR 1.75-1.90 (m,2H), 2.07 (s,3H), 2.54 (t,J=7.1,2H), 2.56 (t,J=7.2,2H), 4.07 (s,2H), 7.35-7.63 (m,3H), 7.97 (dd,J=8.0,1.3,1H). Anal.calcd for $C_{11}H_{15}NO_2S_2$: C, 51.33; H, 5.88; N, 5.44%; found: C, 51.19; H, 5.92; N, 5.23%.

1-(2-Nitro-5-chlorophenyl)-2-6-dithiaheptane (**8b**), Oil, ^{1}H NMR: 1.75-1.95 (m,2H), 2.08 (s,3H), 2.56 (t,J=7.0,2H), 2.58 (t,J=7.2,2H), 4.04 (s,2H), 7.39 (dd,J=8.7,2.4,1H), 7.51 (d,J=2.4,1H), 7.95 (d,J=8.7,1H). Anal.calcd for $C_{11}H_{14}ClNO_2S_2$: C, 45.27; H, 4.84; N, 4.80%; found: C, 45.14; H, 4.59; N, 5.07%.

1-(2-Nitro-5-fluorophenyl)-2,6-dithiaheptane (**8c**), Oil, ^{1}H NMR: 1.70-1.90 (m,2H), 2.07 (s,3H), 2.55 (t,J=7.0,2H), 2.58 (t,J=7.1,1H), 4.06 (s,2H), 7.03-7.15 (m,1H), 7.24 (dd,J=8.7,2.7,1H), 8.05 (dd,J=9.0,5.1,1H). Anal.calcd for $C_{11}H_{14}FNO_2S_2$: C, 47.98; H, 5.12; N, 5.09%; found: C, 47.95; H, 5.26; N, 4.96%.

1-[2-(3-nitro-6-methoxy)pyridyl]-2,6-dithiaheptane (**8d**), Oil, ^{1}H NMR: 1.80-2.00 (m,2H), 2.08 (s,3H, 2.57 (t,J=7.2,2H), 2.72 (t,J=7.2,2H), 4.04 (s,3H), 4.19 (s,2H), 6.47 (d,J=9.0,1H), 8.32 (d,J=9.0,1H). Anal. calcd for $C_{11}H_{16},N_2O_9S_2$: C, 45.81; H, 5.59; N, 9.72%; found C, 45.75; H, 5.63; N, 9.65%.

1-[2-(3-nitro-6-mehtoxy)pyridyl]-2,6-dithiaoctane (**9d**), Oil, ^{1}H NMR: 1.24 (t,J=7.4,3H), 1.80-2.00 (m,2H), 2.52 (q,J=7.4,2H), 2.60 (t,J=7.2,2H),2.72 (t,J=7.2,2H), 4.04 (s,3H), 4.18 (s,2H), 6.74 (d,J=9.0,1H), 8.33 (d,J=9.0,1H). Anal. calcd for $C_{12}H_{18}N_2O_3S_2$: C, 47.66; H, 6.00, N, 9.27%; found: C, 47.52; N, 6.15; N, 9.28%.

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