Pergamon

Tetrahedron, Vol. 52, No. 39, pp. 12677-12698, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00752-1

1,2-Dithiines and Precursors, XVI[1]: Synthesis, Structure, and Reactivity of Non-Anellated 1,2-Dithiines☆

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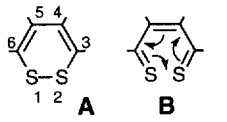
Abstract: Various monocyclic 1,2-dithiines **6a,b,d-t** were prepared via (*Z,Z*)-1,4-difunctionalized butadienes (**4-11,19,20**). A twisted cyclic structure **A** is unequivocally proved rather than of the ringopened valence isomer **B**. The reactivity of these 1,2-dithiines is described. Thermal as well as day-light induced sulfur extrusion is an important feature of their chemistry. The latter mode of sulfur extrusion depends to a significant extent on absorption in the visible region.

Introduction

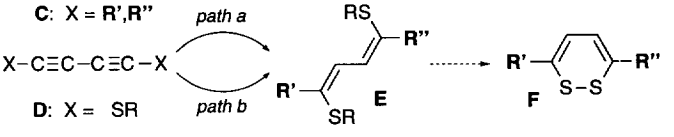
Concurrent with our initial synthetic work[1a-c] on the title compounds **A** (*Scheme 1*) various 3,6-di(polyynyl) substituted C_{13}-representatives were discovered as plant constituents.[4] As subsequently reported,[5] these compounds ("thiarubrines") show promising biological activities. In view of these properties, 1,2-dithiines are becoming important compounds with respect to their synthesis, structure elucidation and reactivity.[6] From the beginning of our programme, our studies have focused on some other outstanding aspects i.e. a) the controversy of a cyclic disulfide structure versus a ring-opened valence isomer **B** (as disclosed in the related 1,2-dithiete series)[6i,7], b) the presence of an unusual red colour, and c) the sulfur extrusion under mild conditions. The cyclic title system **A** represents formally an 8π-electron system, a butadiene-bridged disulfide, and a sulfur-expanded thiophene, respectively. Theoretical treatment of these molecules has also been well documented.[6g-j]



Scheme 1

Significant differences can exist both in the synthesis as well as the behaviour of non-anellated and anellated 1,2-dithiines. Thus we have carefully differentiated between both classes in our considerations. In general however, the synthesis of both types can be achieved from (*Z,Z*)-buta-1,3-dien-1,4-dithiols or their salts which suffer oxidation in the final step.[8]

The ***synthesis of non-anellated 1,2-dithiines*** starts from C_4-precursors, especially butadiynes (**C, D**) as illustrated in *Scheme 2*. S-Deblocking of the intermediates **E**, R = protective group, affords the above mentioned (*Z,Z*)-butadiene-1,4-dithiols **E** (R = H) leading finally to maximally (in 3- and 6-positions) disubstituted 1,2-dithiines **F**. Access to **E** is differentiated by the origin of the RS group. In our initial synthesis (path *a*),[1a-c] a two-fold nucleophilic thiol addition at **C** produces **E**.[9] The whole sequence represents formally the addition of hydrogen sulfide to a butadiyne in an appropriate protected form. This method has been modified recently by *M. Koreeda* and *W. Yang*[6b] and by *D. E. Bierer* et al.[6d] In the other alternative (path *b*), recently reported by *E. Block* et al.,[6c] the RS-group is already installed in the butadiyne precursor **D**, and the substituents R' and R'' are introduced subsequently by C,C-coupling via organotin functionalization. Both strategies complement each other.



Scheme 2

The ***synthesis of anellated 1,2-dithiines*** is based on the successive assembly of the (*Z,Z*)-1,4-dithiobuta-1,3-diene unit starting from appropriate functionalized *cyclic* precursors (cf. references[1h-o]).

In view of the latest developments in the area of 1,2-dithiines a detailed presentation of various results of our current work now seems appropriate.

Results and Discussion

1. Synthesis

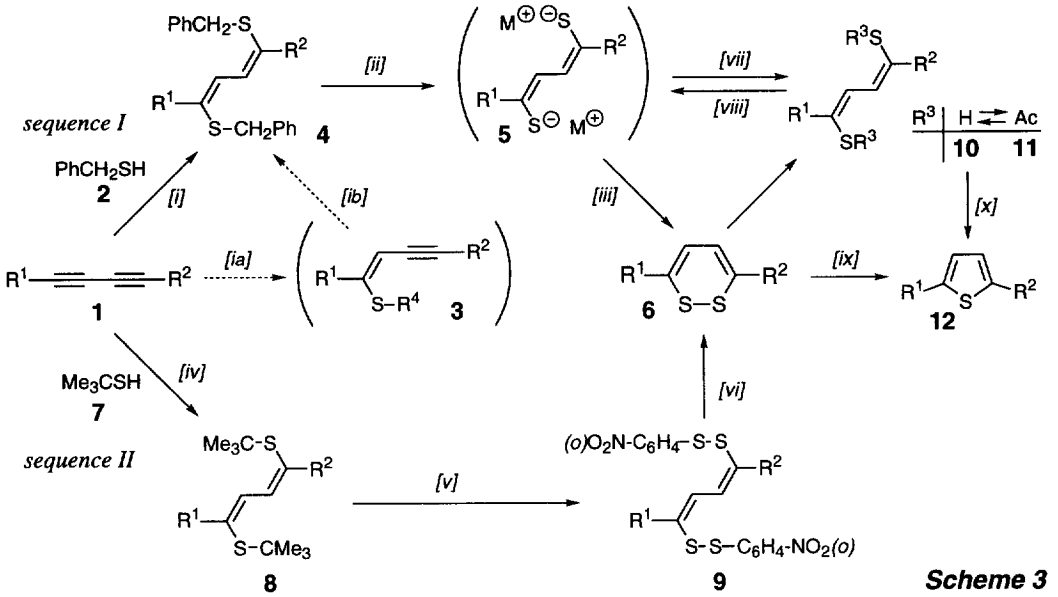
As outlined in *Scheme 3*, the synthesis can proceed via two sequences depending upon the choice of the S-protective group (i.e. according to R in Scheme 2, path a). Its potential is demonstrated by the listed 1,2-dithiines **6** (cf. our initial reports in ref.[1a,c,d]). These include the parent compound (**6a**) as well as alkyl (**6b,d-g**), aryl (**6h-s**) and hetaryl substituted 1,2-dithiines (**6t**). The products **6** form, at room temperature, mainly yellow to red crystals, with exception of the oily parent compound **6a** and the 3,6-di-*n*-butyl-1,2-dithiine (**6b**). The latter compound is *not* identical with a compound previously claimed to possess this structure and obtained by a different procedure.[10]

In ***sequence I*** the butadiynes **1** undergo a regio- and stereoselective nucleophilic bis-addition of benzylmercaptan (**2**) under basic conditions leading to the (*Z,Z*)-1,4-dithiobutadienes **4** (step *[i]*). If required the mono-adducts **3** can be isolated (steps *[ia]/[ib]*).[11] In the case of aryl substituents in **1** (**h-s**) the addition at the terminal α- and α'-positions of the butadiyne chain is strictly observed even although arylacetylenes normally undergo thiol addition at the β-position relative to the aryl group (cf. also example **15** in Scheme 4),[12] thus indicating the dominating influence of an adjacent triple bond compared with an aryl substituent. The reductive debenzylation of **4** was performed by means of sodium in liquid ammonia at -70°C (*step ii*). The resulting dithiolate salts **5** (M = Na) are immediately oxidized to the 1,2-dithiines **6**, either by potassium cyanoferrate(III), ferric chloride, iodine or even air (*step iii*).

The thiol-addition to **1**, the most crucial part of the whole sequence, is favoured by acceptor and disadvantaged by donor effects in the substituents R^1 and R^2. For example, the *t*-butyl-diyne **1c** yields only the mono-adduct **3c** in spite of an excess of **2**, whilst **1d** smoothly affords the bis-adduct **4d**. Various procedures are possible. Thus **4h** is obtainable from **1h** and **2** by reaction in EtOH/NaOH at elevated temperature (sometimes more profitable under in situ conditions using benzylisothiouronium chloride) in a yield of about 55%, in benzene/KOH/18-crown-6 at 20°C, in 68% yield, in diglyme/KOH with (58%) or KO-*t*-Bu[catalytic] at room temperature, in 61% yield, or in sulfolane/KOH or KO-*t*-Bu[catalytic] at 20°C, in 62% yield. In DMSO/KOH cyclization of the mono-adducts **2** takes place forming thiophene formation due to the addition of CH_2 of the benzyl group to the triple bond.[13a] In general the twofold thiol addition in dimethylformamide with catalytic amounts of KOH, initially proposed by *M. Koreeda* and *W. Yang*,[6a] seems to be the most suitable technique (as previously stated,[2a] NaOH in place of KOH is not as efficiently).

The debenzylation of **4** (step *[ii]*) by alkali metal in liquid ammonia is disadvantaged by substituents which can suffer additional reductive attack, such as halogen (e.g. **4i** → **6h**) and unsaturated groups (as in the synthesis of thiarubrines, cf. ref.[6b,c][13b]. A *selective* reductive debenzylation despite the presence of such substituents, however, is achievable with the aid of lithium 1-(N,N-dimethylamino)naphthalenide as described in ref.[6c]. An advantageous alternative consists of the use of S-protective groups other than CH_2Ph as demonstrated recently with $CH_2CH_2SiMe_3$ [6b] and CH_2CH_2CN [6d] (R in Scheme 2) which allow deprotection by fragmentation or β-elimination, respectively, in the subsequent step. Another non-reductive technique is described in the following.

In ***sequence II*** *t*-butylmercaptan (**7**) can be used as protected thiol supplier (cf. ref.[14]). After uncomplicated addition of **7** to **1**, the resulting (*Z,Z*)-1,4-di(*t*-butylthio)butadienes **8** are deprotected by reaction with (2-nitrophenyl)sulfenyl chloride affording the poorly soluble mixed bis-disulfides **9** (steps *iv*, *v*). From the latter the 1,2-dithiines **6** are smoothly produced by reduction with sodium borohydride and subsequent oxidation, or better by treatment with catalytic amounts of 2-mercaptoethanol, with facile removal of the co-formed bis(2-nitrophenyl) disulfide (step *vi*). Even attempts to recrystallize the **9**, e.g. from DMF, symmetrization to the 1,2-dithiines **6** takes place spontaneously and the colour of the solution becomes red. This method is especially useful in the aromatic series with good yields throughout (examplified by **6 h,j,l**).



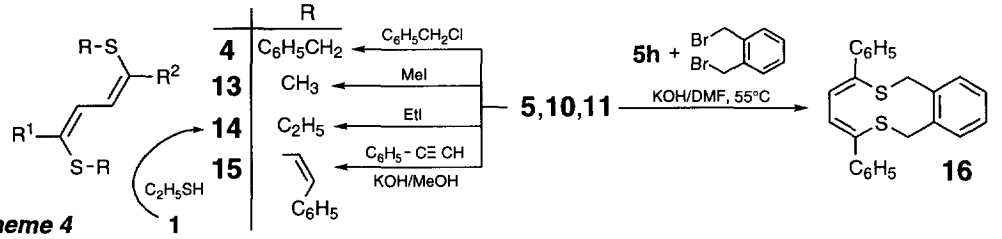
Scheme 3

1 3-6 8-12	R^1- -R^2	1 3-6 8-12	R^1- -R^2	1 3-6 8-12	R^1- -R^2
a	H- -H	h		o	
b	nC_4H_9- -nC_4H_9 [a]	i	Br- -Br [c]	p	
c		j	H_3C-	q	
d		k	H_3C- -CH_3	r	
e		l	H_3CO-	s	
f		m	H_3CO- -OCH_3	t	
g		n	nC_4H_9- -nC_4H_9		

[a] **6b**: oil, extreme tendency to S-extrusion. – [b] only formation of the mono-adduct **3c**. – [c] step *[ii]* leads to **5h/6h**.

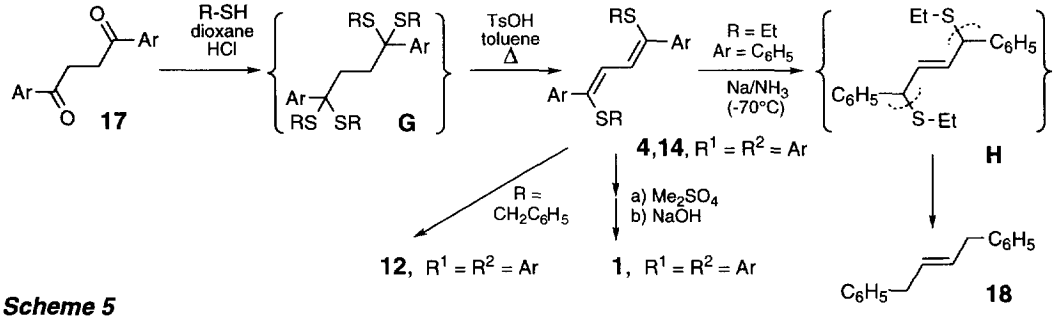
From **5** the S-acetylderivatives **11** are obtained (by treatment with acetic anhydride or acetyl chloride) and since these can readily be saponified back to the **5** (e.g. with methanolic KOH) they can therefore be used as storable sources for the latter compounds (steps *vii*, *viii*). Furthermore, careful acidification of **5** enables the liberation of the (*Z*,*Z*)-buta-1,3-diene-1,4-dithiols **10**[15] which can also be be prepared by reduction of the 1,2-dithiines **6** with sodium borohydride. The latter compounds can be transformed into the thiophenes **12** by heating thus illustrating an intermediate step within the classical Paal-Knorr synthesis of thiophenes from 1,4-diketones (step *x*). Thiophenes **12** also result from **6** by extrusion of sulfur (step *ix*, see also part 2). The favoured formation of **12** is likewise indicated in the mass spectroscopic fragmentation of **6** or **10** and even of the precursors **4** and **8** (base peaks).

The intermediates **5** undergo other characteristic substitution reactions at the thiolate group which can occasionally be performed by use of the equivalents **10** or **11**. As outlined in *Scheme 4* the reaction with benzyl chloride leads back to the precursors **4**, and with methyl iodide to the methylthio derivatives **13**. The analogous ethyl thioethers **14** are identical with those produced by the addition of ethylmercaptan to the diacetylenes **1**. Finally, vinylation of **5h** with phenylacetylene results in the formation of the (*Z*)-styryl sulfide **15h**. By contrast, alkylating ring closure reactions succeed only to rather limited extent. For example, the reaction of **5h** with o-di(bromomethyl)benzene gives the ten-membered cyclic thioether **16** in low yield with thiophene **12h** and 1,3-dihydro-benzo[c]thiophene (intrachain cyclization). Moreover, it should be emphasized that all attempts to obtain 1,4-dithiocines by ring closure reactions of **5a** or **5h** with both (*Z*)-1,2- and 1,1-dichloroethene failed.[16a]



Scheme 4

Various efforts to produce 1,2-dithiines **6** starting from 1,4-dicarbonyl compounds **17** instead of the diacetylenes **1**, as illustrated in *Scheme 5*, were disappointing.[16b] Thus, the acid-assisted reaction of aromatic 1,4-diketones with ethanethiol, indeed, affords the dimercaptals **G** and subsequently the 1,4-di(ethylthio)butadienes **14**.[1e] But in attempts for their reductive deprotection with the aid of sodium in liquid ammonia the Birch reduction competes successfully, e.g. from **14h** (Ar = C_6H_5) (*E*)-1,4-diphenylbutene (**18**) is formed, and ethylmercaptan is liberated during work-up. The intermediate **H** of the Birch reduction offers two new benzylthio subunits which subsequently suffer a reductive fission at the indicated positions.



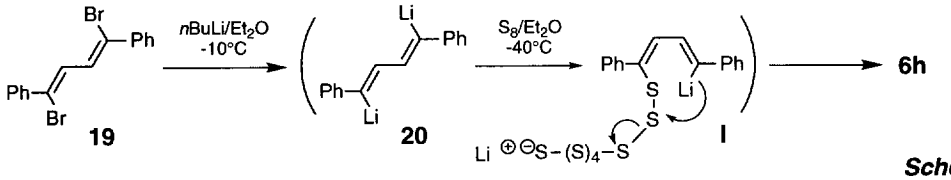
Scheme 5

By alkylation of the **14** with dimethyl sulfate (to disulfonium salts) and subsequent elimination by means of sodium hydroxide, the diacetylenes **1** can be obtained.[1e] Hence, the **14** also offer access to 1,2-dithiines **6** starting from 1,4-dicarbonyl compounds **17**, albeit in a circuitous manner.

On the other hand, the acid-catalyzed reaction of the **17** with benzylmercaptan did not yield the required 1,4-di(benzylthio)-1,3-butadienes **4** and only the thiophenes **12**, $R^1 = R^2 = Ar$, could be isolated. Here the initially produced **4** suffer cationic debenzylation. This was readily confirmed by the formation of **12**, $R^1 = R^2 = Ar$, from an authentic samples of **4** as well as from the mono-addition products **3**, $R^1 = R^2 = Ar$, under the above noted conditions.

An alternative approach to 3,6-disubstituted 1,2-dithiines **6** involves the successive functional conversion of a suitable butadiene precursor as previously reported for the di-anellated series:[1k] This is illustrated in *Scheme 6* where (*Z,Z*)-1,4-dilithio-1,4-diphenyl-butadiene (**20**), obtained from the corresponding dibromo-

compound **19** by halogen-metal exchange with *n*-butyllithium,[17] is treated (in situ) with elemental sulfur giving the 1,2-dithiine **6h** directly in a good over-all yield. In this case no final oxidation step is necessary, possibly due to an intramolecular nucleophilic attack on the sulfur chain by the remaining anionic centre as shown in **I**. This method is, of course, limited by the availability of the dibromo-precursors **19**.



Scheme 6

2. Structure and Reactivity

The surprising colour of the 1,2-dithiines **6** with absorptions up to nearly 500 nm[18] should be due to a n → σ* transition.[6g,i] This is undoubtedly due to the disulfide group.[19] By contrast the isomeric 1,4-dithiines[20] show no discrete absorption maximum in the visible region. A clear dependence of the wave length in the visible region of the electronic spectra of **6** on the subsituents is not recognizable at this time (see *Table 1*). The absorptiom maximum in the visible range appears to be bathochromicly shifted with increasing conjugative linking of the butadiene bridge. The UV absorption of the **6** (with two maxima at 230 - 250 and 310 - 350 nm) differs only slightly from those of the corresponding thiophenes **12**.

Table 1. Absorption maxima in the visible region

Entry	λ_{max} [nm] (lg ε)	Entry	λ_{max} [nm] (lg ε)	Entry	λ_{max} [nm] (lg ε)
6a	457(1.98)[a]	**6h**	468(3.51)[a]	**6n**	460(3.50)[b]
6b	440[b]		464(3.72)[b] 461(3.55)[d]	**6p**	465(3.26)[b]
6d	412(2.60)[b]	**6j**	464(3.42)[b]	**6q**	465(3.47)[b]
6e	423(2.19)[c]	**6k**	464(3.64)[b]	**6r**	460[b,e]
6f	425(2.31)[c]	**6l**	464(3.60)[b]	**6s**	453(3.27)[b]
6g	423(2.53)[c]	**6m**	463(3.65)[b]	**6t**	478(3.79)[b]

[a] in cyclohexane; [b] in MeCN; [c] in *n*-hexane; [d] in EtOH; [e] poorly soluble

Moreover, the (red) colour repeatedly caused doubts as to a cyclic disulfide structure corresponding to **A** and led us to re-examine the question of whether these molecules might exist as the open chain thioxo valence isomer form **B**, possibly in an equilibrium or in a no-bond resonance relationship (cf. ref.[4a,9c,18a]; concerning the influence of substituents on the stability of **A** and **B**, respectively: cf. ref.[6h,j]). It should be noted, however, that conjugated thiocarbonyl compounds, as in the case of **B**, usually exhibit their n → π* transitions at wave lengths substantially above 500 nm.

The cyclic disulfide structure **A** is unequivocally proved confirming our initial assertion (cf. ref.[1c,d,21a]). *Figure 1* illustrates the ^{1}H NMR 500 MHz spectrum of the parent compound **6a**, it is characterized by an AA'XX' type spectrum with chemical shifts exclusively in the olefinic region (cf. also ref.[1f,h-i,k,l,n]). In accord with this observation is the absence of any ^{13}C NMR indications for a thiocarbonyl group (δ > 200 ppm), as also stated in the spectra of the 3,6-disubstituted 1,2-dithiines. It should be emphasized that the ring-opened butadiene precursors **4** (as well as **10** and **11**) exist in the s-transoid conformation in solution, as concluded from a thorough NMR study.[1f] This conformation has been confirmed by X-ray crystallography.[21b]

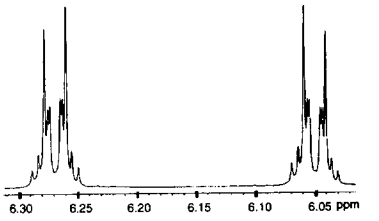


Figure 1. ^{1}H NMR spectrum of 1,2-dithiine (**6a**) (500 MHz; $CDCl_3$)

The X-ray analysis of 3,6-di(morpholinomethyl)-1,2-dithiine (**6g**)[22] and of 3,6-di(4-cyclohexylphenyl)-1,2-dithiine (**6p**)[23], shown in *Figures 2* and *3*, respectively, reveals a remarkable distortion of the 6-membered ring, as indicated by the C-S-S-C torsion angles of 52.6° (**6g**) and of 54.6° (**6p**), respectively. Further, by the twist of the C,C-double bonds against each other of 26.5° for **6g** and of 31.5° for **6p**, the repulsion of the adjacent S-p orbitals is minimized. The S-S distance of about 2 Å agrees with that of „normal" disulfides and excludes any consideration of a no-bond resonance with the ring-opened valence isomer of type **B**. These find-

ings are consistent with that from our X-ray elucidations in the di-anellated 1,2-dithiine series[24a] and of a tetrasubstituted 1,2-dithiine[24c] (see finally informations in ref.[24c]). The ring inversion barrier of the cyclic disulfide should be very low, as previously demonstrated by the fact that the ^{1}H NMR spectrum is unaltered up to -95°C in the case of the di-(*R*)borneno anellated 1,2-dithiine.[1i,n] Finally it should be noted that the geometry of the cyclic system agrees well with the results of *ab-initio* calculations.[6i,j]

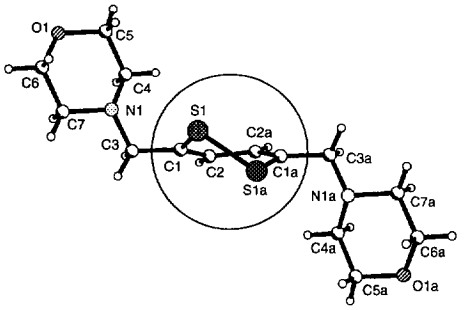


Figure 2. X-ray crystal structure[22] of 3,6-di(morpholinomethyl)-1,2-dithiine (**8g**). Selected data – *bond lengths*: S1-S1a = 2.0657(11), C1-S1 = 1.771, C1-C2 = 1.336(3), C2-C2a = 1.455(4) Å; *torsion angles*: C1a-S1a-S1-C1 = 52.6, S1a-S1-C1-C2 = -40.3, S1-C1-C2-C2a = 1.6, C1-C2-C2a-C1a = 26.5, C2-C2a-C1a-S1a = 1.6, C2a-C1a-S1a-S1 = 40.3°.

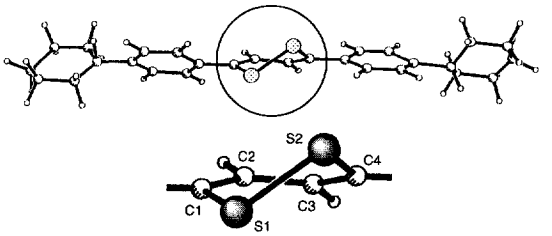


Figure 3. X-ray crystal structure[23] of 3,6-di(4-cyclohexylphenyl)-1,2-dithiine (**8p**). Selected data – *bond lengths*: S1-S2 = 2.503(5), C1-S1 = 1.780(10), C3-C4 = 1.337(15), C2-C3 = 1.420(20) Å; *torsion angles*: C1-S1-S2-C4 = -54.6), S2-S1-C1-C2 = 37.2, S1-S2-C4-C3 = 42.2, S1-C1-C2-C3 = 4.4, C1-C2-C3-C4 = -31.5, C2-C3-C4-S2 = -1.3°.

Thus the predominance of the cyclic disulfide structure **A** ≡ **6** versus its ring-opened valence isomer **B** seems comparable with the preference of the enthiols **10** versus the butane-1,4-dithiones for the same reasons.[15b] Alterations can be induced by π-donor groups in 3- and 6-position.[6h,j,25] A quite contrary situation exists in the oxygen series (cf. ref.[1o], and literature cited therein).

In accord with the rod-like shape of the 3,6-disubstituted 1,2-dithiines (cf. Figure 3), 3,6-di(4-*n*-butylphenyl)-1,2-dithiine (**6n**) displays liquid crystalline behaviour (nematic phase) on melting at 106°C for a short time prior to sulfur extrusion . By contrast the corresponding thiophene **12n** is inactive.

Table 2. Polarographic half wave potentials[26a]

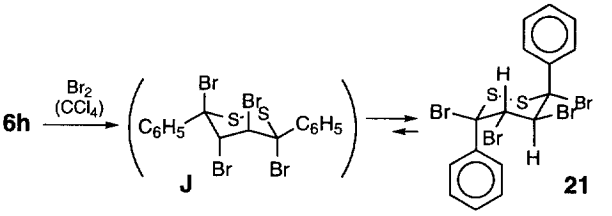
Entry	**6a**	**6h**	**6j**	**6k**	**6l**	**6m**	**6s**	**6t**
$E_{1/2}$ [V]	-0.67[a]	-0.70[a]	-0.68[c]	-0.66[a]	-0.65[c]	-0.63[a]	-0.57[c]	-0.73[a]
	-0.74[b]	-0.71[c]		-0.67[c]		-0.62[c]		-0.72[c]

[a] SCE, 90% EtOH, NEt_4I [b] SCE, 75% EtOH, NEt_4I [c] SCE, DMF, NEt_4ClO_4

The facile reduction of the 1,2-dithiines **6** to the dimercapto-precursors **5** or **10** (see above) is in line with polarographic studies.[26a] The half-wave potentials appear, as listed in *Table 2*, in the range of about -0.5 to -0.7 V. These values accord with those of diaryl disulfides (-1.4 to -1.8 V)[26b] rather than with those of dialkyl disulfides (-0.5 to -0.9 V)[26c]. The polarographic half wave potential of the known dibenzo-1,2-dithiine („*o*-diphenylene disulfide")[26d] was found to be $E_{1/2}$ = -0.56 V (SCE, DMF, NEt_4ClO_4).

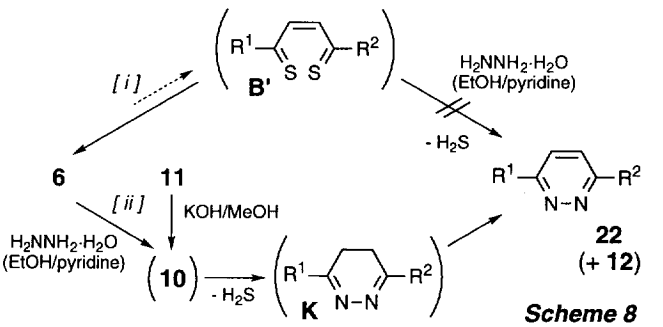
The olefinic character is demonstrated by the ready reaction of **6h** with bromine (*Scheme 7*). A tetrabromo adduct, stable only at low temperature and which decomposed to a compound of uncertain structure at room temperature, was produced. The structure assignment of the product as **21** is mainly based on the NMR indication of new sp^3-C atoms [^{1}H: CHBr 5.40 ppm; ^{13}C: CHBr 65.52, C(Br)Ph 81.77 ppm]. Moreover, no diastereomeric mixture could be observed. At -30°C the ^{1}H NMR spectrum ($CDCl_3$) indicates a rotation hindrance of the phenyl groups. This result could be expected from steric overcrowding between the *o*-H atoms of the phenyl groups and the other atoms at the 1,2-dithiacyclohexane ring assuming that the phenyl groups

take up axial and all bromo atoms equatorial position after ring flip of the primarily formed adduct **J**.



Scheme 7

If a ring-opened valence tautomer **B'** behaves as a reactive species, even in an extremely low equilibrium concentration, the 1,2-dithiines **6** should be able to condense with hydrazine hydrate with the formation of pyridazines **22** according to path *[i]* of *Scheme 8*. The formation of **22**, indeed takes place, e.g. in ethanol/pyridine along with the formation of thiophenes **12** in about equal amounts and hydrogen sulfide. Path *[i]*, however, seems not to be involved but path *[ii]*: The formation of the pyridazines **22** proceeds more likely via reduction of **6** to the (*Z*,*Z*)-1,4-dimercaptobutadienes **5** or **10**, respectively (as is known from non-cyclic disulfides)[27] followed by condensation to the dihydropyridazines **K** and final oxidation. Reaction of **10** with hydrazine hydrate gives **22** in even better yields. The additional formation of the thiophenes **12** in the reaction of **6** with hydrazine hydrate possibly results from a competing base-catalyzed sulfur extrusion (cf. below).



Scheme 8

More detailed information is provided by polarographic studies in dimethylformamide (SCE, NEt_4I). Under air exclusion the mixture of **6h** and hydrazine hydrate shows a polarographic half wave potential at $E_{1/2}$ = -1.95 V, corresponding to the reduction of **K** ($R^1 = R^2 = C_6H_5$). After admittance of air the latter half wave potential vanishes and that indicative of the reduction of **22** ($R^1 = R^2 = C_6H_5$) at $E_{1/2}$ = -1.51 V gradually appears. The latter value should correspond to attack at the „azo subunit" whereas the reduction of (*E*,*E*)-1,4-diphenylbutadiene appears under the same conditions at $E_{1/2}$ = -2.15 V (cf. half-wave potential of the S-S fission of **6h** in table 2). Analogous results were obtained using 1,2-dibenzoylethane, the oxygen counterpart of **10h**. On the other hand, (*Z*)-1,2-dibenzoylethene, the oxygen analogue of **B'** ($R^1 = R^2 = C_6H_5$), reacts immediately with hydrazine hydrate under the same conditions to produce **22** ($R^1 = R^2 = C_6H_5$), indicated as well by $E_{1/2}$ = -1.51 V.

This reaction represents rather a special instance in the transformation possibilities of the 1,2-dithiine ring. Normally the reaction potential of the 3,6-disubstituted 1,2-dithiines **6** is dominated by the propensity to extrude sulfur producing thiophenes. For example all attempts to use **6h** as diene or dienophile in Diels-Alder reactions or in addition reactions with nucleophiles (e.g. amines) failed due to the predominance of sulfur extrusion. The 3,6-disubstituted 1,2-dithiines **6** undergo this stabilization process smoothly in the solid state on heating near the melting point or in solution above 100°C. Sulfur extrusion from **6** in solution at room temperature under normal day-light is also an unusual feature of the chemistry of these compounds. Additionally, it should be emphasized that the parent compound **6a** undergoes polymerisation more readily, especially under base catalysis (possibly via ring-opening by S-S fission), whilst di-anellated 1,2-dithiines are surprisingly photochemically stable and require forcing thermal conditions for sulfur extrusion.[1i,k,n] Various more detailed results, obtained from our preliminary studies on the sulfur extrusion, are outlined below.

By monitoring the thermal sulfur extrusion process by ^1H NMR, it was possible to deduce that the reaction kinetics were (pseudo)first order.[28] The process is significantly influenced by the substituents, as demonstrated by some half-life values determined in dimethylsulfoxide-d_6: For **6f** $t_{1/2}$ = 6219 s (120°C), for **6g** $t_{1/2}$ = 2810 s (120°C), and for **6h** $t_{1/2}$ = 13562 (90°C), 3338 (105°C), 525 (120°C), and 203 s (135°C). The reaction

rate is significantly increased by additional conjugation, as exemplified by **6h**. From the temperature dependence of the extrusion of **6h** the values $\Delta H^{\ddagger} = 115.7$ kJ·mol^{-1} and $\Delta S^{\ddagger} = -10.2$ J·mol^{-1}·K^{-1} were deduced, indicating only a slight enhancement of order in the transition phase.

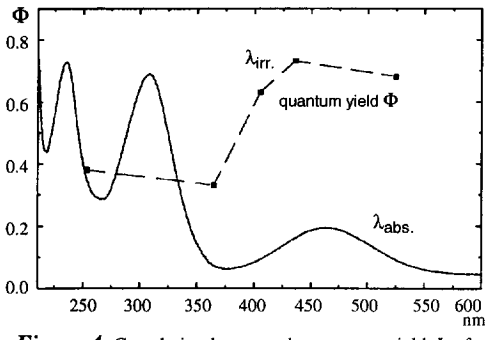
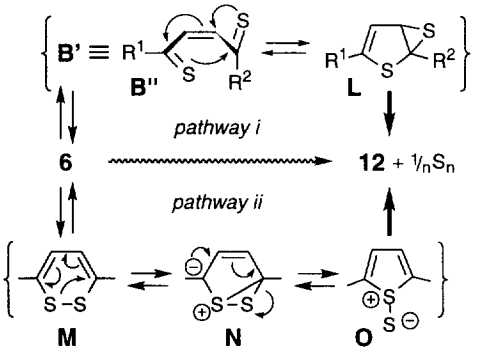


Figure 4. Correlation between the quantum yield Φ of the photolysis and the UV/Vis spectrum of **6h** in ethanol

On the other hand, the light-induced sulfur extrusion depends significantly on the wavelength $\lambda_{irr.}$ of the irradiated light and is unequivocally characterized by the quantum yields Φ as illustrated in *Figure 4* for the case of **6h** [determined at 20°C and based on the decrease of the extinction of the long wave absorption].[29a] Absorption in the visible region is chiefly responsible for this process. For example, the quantum yields Φ (in ethanol) are for **6d**: 0.56 ($\lambda_{irr.}$ = 365 nm), 0.77 ($\lambda_{irr.}$ = 436 nm); for **6f**: 0.14 ($\lambda_{irr.}$ = 405 nm), 0.21 ($\lambda_{irr.}$ = 436 nm), 0.14 ($\lambda_{irr.}$ = 525 nm); for **6g**: 0.30 ($\lambda_{irr.}$ = 405 nm), 0.47 ($\lambda_{irr.}$ = 436 nm), 0.41 ($\lambda_{irr.}$ = 525 nm) and for **6h**: 0.38 ($\lambda_{irr.}$ = 254 nm), 0.33 ($\lambda_{irr.}$ = 365 nm),[29b] 0.63 ($\lambda_{irr.}$ = 405 nm), 0.73 ($\lambda_{irr.}$ = 436 nm), 0.68 ($\lambda_{irr.}$ = 525 nm). These results are in line with an ab initio study.[6i,j] According to this study the determined n → σ* character of the longest wave transition should weaken the S-S bond and, hence, favour ring-opening, whilst the π → π* transitions in the short wave range should be less able to weaken the S-S bond and should be characterized, consequently, by smaller quantum yields. The influence of the substituents seems to be comparable with those in thermolysis (see above). Additionally, the choice of reaction solvent (e.g. heptane versus ethanol) had no significant influence on the quantum yield. Oxygen, known to be a good quencher of triplet states, did not influence the quantum yields (almost identical values under argon as under oxygen). Hence, the extrusion of sulfur appears to be due to an electronically excited singlet state.

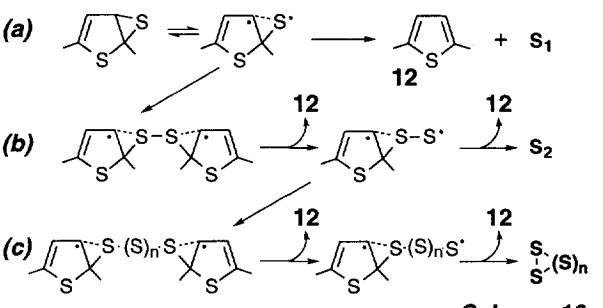


Scheme 9

A rationalization of the sulfur extrusion[30a] is shown in *Scheme 9* . On the basis of well documented valence isomerizations in the heterocyclohexa-1,3-diene series[31] the ring-opened valence isomer **B'** of **6** (analogous **B**) undergoes, in the twisted form **B''**, an intramolecular [π4+π2]-cycloaddition to the episulfide **L**[30b] which then extrudes sulfur affording the thiophenes **12** in an irreversible final step (*pathway i*). This stabilization process parallels the sulfur extrusion in thiepine[32] via thianorcaradien and 1,4-dithiocine[33] via benzenebisepisulfide.[34] Moreover, this sequence explains the amazing resistance of the di-anellated 1,2-dithiines to extrude sulfur under the above noted conditions due to the steric hindrance in **B''**. An intermediate ring opened thioxo isomer **B'**, however, could not be detected by flash photolysis in the microsecond range at room temperature. An alternative assumption according to *pathway ii* avoids an intermediate ring opening to **B'** but involves a 1,5-electrocyclization **M** → **N** [35] proceeding via the thiosulfoxide **O** (ref.[30], p. 172) as possibly competing precursor for **12**.

The final process from **L** or **O**, respectively, and the nature of the primarily extruded sulfur are still unclear. In preliminary attempts with **6h** to trap S_n (n = 1, 2) with excess cyclohexene (1:300 molar ratio) and with 2,3-dimethylbutadiene (1:2 molar ratio, benzene) in day-light at 20°C, a S_1 or S_2-adduct could be detected in traces only (≤ 1%; GC-MS). The major products were thiophene **12h** and oligomeric sulfur (mainly S_8). Moreover, in the ^{1}H NMR monitoring of an attempted reaction of **6h** with norbornene in DMSO-d_6 at 120°C (with exclusion of day-light) only the gradual formation of **12h** was observed. Thus, the attractive possibility that 1,2-dithiines could function as sulfur transfer reagents remains questionable. The primary extrusion or

transfer of singlet sulfur should require too much energy as suggested in ref.[36]. On the other hand, a sulfur transfer via addition of the supposed intermediates **L** or **O**, respectively, to the olefinic substrates is obviously minimized due to reactions of these intermediates with themselves. Thus, a successive concatenation of sulfur atoms and their final elimination in a thermodynamically favoured cyclic form according to the sequence *(a)-(c)* in *Scheme 10* (just as proposed for the sulfur extrusion from thiepine to benzene via thianorcaradiene)[37] should compete successfully.[38]



Scheme 10

Conclusions

The title system **A** represents formally an 8π-electron system, a sulfur-expanded thiophene and a butadiene-bridged disulfide. Special attention has been focussed on the parent compound and the 3,6-disubstituted derivatives **6**, which as *non-anellated* compounds differ essentially from their anellated counterparts in some fundamental aspects of their synthesis and behaviour. Unusual features are represented by the light absorption in the visible region, by the structure with respect to the questionable existence of the valence isomer **B** and by the tendency for the sulfur extrusion both under thermal and photochemical conditions.

A general synthesis, based on the base-assisted nucleophilic bis-addition of benzyl- or *t*-butylmercaptans, respectively, to butadiynes **1** forming the corresponding (*Z,Z*)-1,4-dithiobutadienes **3** , subsequent deprotection to (*Z,Z*)-butadiene-1,4-dithiols **10** and finally disulfide oxidation, was developed. An alternative approach, exemplified by the lithium-halogen exchange at (*Z,Z*)-1,4-dibromo-1,4-diphenylbutadiene (**19**) and successive sulfurization, was limited by the accessibility of the precursor.

The colour, arising from a $n \rightarrow \sigma^*$ transition, is influenced by the substituents and bathochromic shifts are especially caused by conjugation effects. The structure, a twisted cyclic disulfide, is well established in solution by NMR spectroscopy and in the solid state by X-ray analysis. The presence of any ring-opened thioxo valence isomer **B** is unequivocally excluded, unlike the situation in the 1,2-dithiete series. The structure **B**, however, can be involved as a transient species in thermally as well as photochemically induced sulfur extrusion with formation of the correspondingly substituted thiophenes. The quantum yields of the photo-induced sulfur extrusion depend crucially on the wave length of the light emloyed and attain their maximum value at about the absorption maximum in the visible region. A significant dependence on the substituents is also demonstrated from a consideration of the half-life values in the thermally induced process. Based on the activation parameters, a low ordered transition state is suggested. The extrusion process appears to involve a complex sequence of events prior to the expulsion of oligomeric sulfur. The use of these compounds as preparatively useful sulfur transfer reagents is excludedb at this time.

The high tendency to extrude sulfur under mild conditions predominates over the general reaction behaviour of the 1,2-dithiine ring. The 1,2-dithiine ring behaves preponderantly as an olefinic cyclic disulfide, and the compounds readily undergo reductive S-S ring fission. In the reaction with hydrazine hydrate, a primary reduction to (*Z,Z*)-butadiene-1,4-dithiols occurs which subsequently condense with excessive hydrazine to afford the pyridazines **22**. Bromine can be added to the C=C double bonds to form an unstable tetrabromo adduct.

Experimental Part

NMR spectra:Varian Unity 500 (^{1}H: 499.84 MHz, ^{13}C: 125.71 MHz), Bruker WP 200 (^{1}H: 200.13 MHz, ^{13}C: 50.3327 MHz), Bruker AC 80 (^{1}H: 80.13 MHz, ^{13}C: 20.149 MHz). ^{1}H and ^{13}C NMR spectra were recorded with TMS as internal standard. – MS: Varian MAT CH6, AMD Intectra 402 (70 eV). – IR: Carl Zeiss Jena Specord 71 and 75. – UV: Beckman DK-2A; Perkin-Elmer Lambda 16 – Column chromatography (CC): silica gel 60 [70-230 and 230-400 mesh (Merck)]. – HPLC: Merck Hitachi L-4000 (UV detector). – Melting points: Heating stage microscope (Boetius M; all temperatures quoted are not corrected). – X-ray analyses: Diffractometer STADI4 (Stoe, MoK$_\alpha$ radiation, $3 < 2\Theta < 54°$). – Elemental analyses: Carlo Erba (automatic apparatus).

***Nucleophilic addition of thiols* 2 and 7 *at butadiynes* 1**

(*Z,Z*)-1,4-Di(benzylthio)-1,3-butadiene (4a; cf. ref.[1a,c,f]). – ***Procedure I:*** A mixture of 252 g (2 mol) benzyl chloride, 152 g (2 mol) thiourea and 400 ml ethanol was heated at reflux with stirring 6 h, then treated with 320 g (8 mol) NaOH

and 2 l ethanol and the resulting mixture heated at reflux for further 3 h (generation of **2**) From a separate generator and under argon, a stream of **1a** (prepared by the dropwise addition of 600 g of a 40% aqueous NaOH solution to 200 (1.45 mol) 1,4-dichlorobutyne in 300 ml ethanol) was slowly (2-3 h) bubbled into the above solution of **2**. After 3-4 h the mixture was diluted with two volumes of water and the separated solid filtered and recrystallized from EtOH/AcOEt (1:1). – Colourless leaflets; yield 200-300 g (66-78%); m.p. 128-129°C. – ^{1}H NMR ($CDCl_3$): δ = 3.88 (s; 4H; 2 SCH_2), 6.00 (2 d; 2H; =C*H*-SCH_2); 6.29 (2 d; 2H; =C*H*-CH=; J^3 = 5.8, J^4 = 1.9 Hz), 7.28 (m; 10H; aromat. H); cf. data in ref.[1f]. – ^{13}C NMR ($CDCl_3$): δ = 38.2 (-SCH_2-), 123.2 (=*C*H-SCH_2), 126.9, 127.2 (=CH-, $C_{p\text{-aromat.}}$), 128.6, 128.8 ($C_{o,m\text{-aromat.}}$), 137.67 ($C_{i\text{-aromat.}}$); cf. data in ref.[1f]. – MS (70 eV) m/z = 298 (8 $[M]^+$), 207 (18 $[M^+ - C_7H_7]$), 175 (6 $[M^+ - C_7H_7 - S]$), 149 (17 $[M/2]^+$). – $C_{18}H_{18}S_2$ (298.5): calcd. C 72.44, H 6.08, S 21.48; found: C 72.54, H 5.94, S 21.40. – ***Procedure II*** (*in situ* reaction of **1a**): Analogous to procedure **I** using a 1 mole charge in 200 ml ethanol with stirring and under an inert atmosphere. After heating under reflux for 6 h, 280 g KOH was added, the mixture warmed until the commencement of reflux and 62 g (0.5 mol) 1,4-dichlorobutyne were added over a 1 h period. The mixture was then processed as above. 45-60 g (30-40%) yield.

(*Z,Z*)-5,8-Di(benzylthio)dodeca-5,7-diene (**4b**). – A solution of 5.6 g (100 mmol) KOH and 0.264 g (1 mmol) 18-crown-6 in 15 ml water was stirred 15 min under argon. Subsequently 1.5 g (12 mmol) **2** in 15 ml benzene and 0.81 g (5 mmol) **1b** in 20 ml benzene were added with stirring. The mixture was refluxed 20 h. After separation of the layers the aqueous phase was extracted with benzene. The combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified by CC (silica gel, benzene). – Pale yellow oil, yield: 1.9 g (93%). – ^{1}H NMR ($CDCl_3$): δ = 0.91-0.95 (t, 6 H, CH_3), 1.38-1.53 (m, 8 H, CH_2), 2.22-2.29 (t, 4 H, CH_2), 3.60 (s, 4 H, SCH_2), 7.21-7.36 (m, 12 H, C_6H_5, CH=). – ^{13}C NMR ($CDCl_3$): δ = 13.5 (CH_3), 18.9, 21.9, 30.4 (CH_2), 37.0 (SCH_2), 127.4, 128.5, 128.9, 129.4, 136.8, 137.5 (C_6H_5, =CH-, >C=). – MS (70 eV) m/z = 184 (10) $[M^+ - 2\ C_7H_7 - 2\ CH_3CH_2]$, 162 (100) $[M^+ - 2\ C_6H_5CH_2SH]$, 147 (26) $[M^+ - 2\ C_6H_5CH_2SH - CH_3]$, 133 (24) $[M^+ - 2\ C_6H_5CH_2SH - C_2H_5]$, 119 (62) $[M^+ - 2\ C_6H_5CH_2SH - C_3H_7]$, 105 (90) $[M^+ - 2\ C_6H_5CH_2SH - C_4H_9]$. – $C_{26}H_{34}S_2$ (410.7): calcd. C 76.04, H 8.35. S 15.61; found: C 76.29, H 8.06, S 15.62.

(*Z*)-3-Benzylthio-2,2,7,7-tetramethyl-3-octen-5-yne (**3c**). – A mixture of 2.56 ml (20 mmol) **2**, 300 mg powdered KOH, 1.62 g (10 mmol) **1c** and 40 ml DMF was stirred 2 h (solution). After 24 h the mixture was poured on to ice and the product was washed with water and the residue was recrystallized from ethanol. – Colourless needles; yield: 35%; m.p. 59-60°C. – ^{1}H NMR ($CDCl_3$): δ = 1.23 (s, 9 H, *t*-Bu), 1.35 (s, 9 H, *t*-Bu), 3.48 (s, 2 H, SCH_2), 6.48 (s, 1 H, =CH-), 7.26-7.32 (m, 5 H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 29.1, 30.8 [$C(CH_3)_3$], 28.4, 38.6 [$C(CH_3)_3$], 37.9 (SCH_2), 77.3 (≡*C*-CH=), 99.8 (≡*C*-*t*-Bu), 104.3 (=CH-), 127.4 ($C_{o\text{-aromat.}}$), 128.6 ($C_{m\text{-aromat.}}$), 129.1 ($C_{p\text{-aromat.}}$), 135.9 ($C_{i\text{-aromat}}$), 159.0 (=C-S). – MS (70 eV) m/z = 286 (55) $[M^+]$, 271 (21) $[M^+ - CH_3]$, 229 (39) $[M^+ - C_4H_9]$, 215 (11) $[M^+ - C_4H_9 - CH_2]$, 173 (8) $[M^+ - C_4H_9 - CH_2 - C_3H_6]$, 91 (100) $[C_7H_7^+]$, 57 (55) $[C(CH_3)_3^+]$. – $C_{19}H_{26}S$ (286.5): calcd. C 79.66, H 9.15, S 11.19; found: C 79.73, H 9.02, S 11.24.

(*Z,Z*)-3,6-Di(benzylthio)-2,7-dihydroxy-2,7-dimethyl-3,5-octadiene (**4d**). – A mixture of 2.9 ml (24.4 mmol) **2**, 332 mg KOH, 1.85 g (11.1 mmol) **1d** and 40 ml DMF was stirred 180 min at room temperature. The mixture was diluted with 150 ml water and extracted twice with AcOEt. The combined organic phases were washed with water and the residue obtained on concentration was recrystallized from *n*-hexane. – Colourless needles; yield 3.45 g (75 %); m.p. 95-96°C. – IR (KBr): $\tilde{\nu}$ = 3500-3140 cm^{-1} (s, OH, free and assoc.) – ^{1}H NMR ($CDCl_3$): δ = 1.36 (s, 12 H, CH_3), 2.16 (s, 2 H, OH), 3.81 (s, 4 H, SCH_2), 7.08 (s, 2 H, =CH-), 7.21-7.28 (m, 10 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 29.4 (CH_3), 41.6 (SCH_2), 74.7 [$C(CH_3)_3OH$], 127.3, 128.6, 129.1, 131.5, 140.0, 147.2 ($C_{olef.}$, $C_{aromat.}$). – MS (70 eV) m/z = 414 (1) $[M^+]$, 305 (2) $[M^+ - C_7H_7 - H_2O]$, 265 (19) $[M^+ - C_7H_7 - H_2O - C_3H_4]$, 247 (78.6) $[M^+ - C_7H_7 - 2\ H_2O - C_3H_4]$, 207 (16) $[M/2^+]$, 91 (100) $[C_7H_7^+]$. – $C_{24}H_{30}S_2O_2$ (414.5): calcd. C 69.56, H 7.25 S 15.46; found C 69.45, H 7.45, S 15.45.

(*Z,Z*)-2,5-Di(benzylthio)-1,6-dipyrrolidino-2,4-hexadiene (**4e**). – To a mixture of 2.56 ml (22 mmol) **2**, 56 mg powdered KOH and 50 ml dry diglyme 2.17 g (10 mmol) **1e** (m.p. 48-49°C) were added with stirring over 30 min. Stirring was continued 3 h at room temperature. The mixture was poured into 150-200 ml ice-water and then extracted twofold with AcOEt and once with Et_2O. After washing the combined organic layers with water (NaCl) and evaporation, the residue was recrystallized twice from ethanol. – Light beige needles; yield: 1.86 g (40%); m.p. 113-114°C. – ^{1}H NMR ($CDCl_3$): δ = 1.46 (m, 8 H, N-$CH_{2[cycl.]}$), 2.48 (m, 8 H, $CH_{2[cycl.]}$), 3.22 (s, 4 H, N-CH_2), 4.03 (s, 4 H, S-CH_2), 7.16-7.29 (m, 10 H, aromat.). – ^{13}C NMR ($CDCl_3$): δ = 23.7 ($[CH_2]_2$), 36.5 (S-CH_2), 53.8 (N-$CH_{2[cycl.]}$), 62.7 (N-CH_2), 126.9 (=CH-), 128.2 (>C=), 128.4 ($C_{o\text{-aromat.}}$), 128.8 ($C_{m\text{-aromat.}}$), 136.1 ($C_{p\text{-aromat.}}$), 138.5 ($C_{i\text{-aromat.}}$). – MS (70 eV) m/z = 464 (0.3) $[M^+]$, 373 (27) $[M^+ - CH_2C_6H_5]$, 302 (50) $[M^+ - CH_2C_6H_5 - HN(CH_2)_4]$, 270 (8) $[M^+ - CH_2C_6H_5 - HN(CH_2)_4 - S]$, 244 (6) $[M^+ - CH_2C_6H_5 - HN(CH_2)_4 - S - C_2H_5]$, 91 (53) $[C_7H_7^+]$, 84 (100) [pyrrolidino-CH_2^+]. – $C_{28}H_{36}N_2S_2$ (464.6): calcd. C 72.39, H 7.81, N 6.03, S 13.80; found C 72.22, H 7.84, N 6.13, S 13.82.

(*Z,Z*)-2,5-Di(benzylthio)-1,6-dipiperidino-2,4-hexadiene (**4f**). – As described for **4e** with 2.44 g (10 mmol) **1f** (m.p. 60°C). – Light beige needles; yield: 2.66 g (54%); m.p. 90-91°C. – ^{1}H NMR ($CDCl_3$): δ = 1.42-1.47 (m, 4 H, $CH_{2[cycl.C4]}$), 1.57-1.62 (m, 8 H, $CH_{2[cycl.C3/5]}$), 2.35-2.37 (m, 8 H, $CH_{2[cycl.C2/6]}$), 3.09 (s, 4 H, N-CH_2), 4.12 (s, 4 H,

S-CH_2), 6.73 (s, 2 H, =CH-), 7.19-7.33 (m, 10 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 24.6 ($CH_{2[cycl.C4]}$), 26.2 ($CH_{2[cycl.C3/5]}$), 36.3 (S-CH_2), 54.4 (N-$CH_{2[cycl.]}$), 126.8(3) (=CH-), 127.8(6) (>C=), 128.4 ($C_{o\text{-}aromat.}$), 128.8 ($C_{m\text{-}aromat.}$), 135.5 ($C_{p\text{-}aromat.}$), 138.6 ($C_{i\text{-}aromat.}$). – MS (70 eV) m/z = 492 (1) [M^+], 401 (22) [$M^+ - CH_2C_6H_5$], 316 (48) [$M^+ - CH_2C_6H_5$ – piperidine], 284 [$M^+ - CH_2C_6H_5$ – piperidine – S], 258 (4) [$M^+ - CH_2C_6H_5$ – piperidine – S – C_2H_2], 233 (6) [$M^+ - CH_2C_6H_5$ – piperidine – S – 2 C_2H_2], 98 (100) [piperidino-CH_2^+]. – $C_{30}H_{40}N_2S_2$ (492.8): calcd. C 73.14, H 8.18, N 5.69, S 13.02; found C 72.95, H 7.89, N 5.59, S 13.05.

(*Z,Z*)-2,5-Di(benzylthio)-1,6-dimorpholino-2,4-hexadiene (**4g**). – As described for **4e** with 2.48 g (10 mmol) **1g** (m.p. 107-108°C). – Light beige needles; yield: 2.08 g (42%); m.p. 116-117°C. – ^1H NMR ($CDCl_3$): δ = 2.39-2.41 (t, 8 H, N-$CH_{2[cycl.]}$), 3.10 (s, 4 H, N-CH_2), 3.68-3.70 (t, 8 H, O-$CH_{2[cycl.]}$), 4.07 (s, 4 H, S-CH_2), 6.72 (s, 2 H, =CH–), 7.18-7.30 (m, 10 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 36.1 (S-CH_2), 53.4 (N-$CH_{2[cycl.]}$). 65.1 (N-CH_2), 67.1 (O-$CH_{2[cycl.]}$), 127.1 (=CH-), 128.0 (>C=), 128.5 ($C_{o\text{-}aromat.}$), 128.7 ($C_{m\text{-}aromat.}$), 134.7 ($C_{p\text{-}aromat.}$), 138.2 ($C_{i\text{-}aromat.}$). – MS (70 eV) m/z = 496 (0.4) [M^+], 405 (20) [$M^+ - CH_2C_6H_5$], 318 (57) [$M^+ - CH_2C_6H_5 - C_4H_9NO$], 286 (9) [$M^+ - CH_2C_6H_5 - C_4H_9NO$ – S], 260 (3) [$M^+ - CH_2C_6H_5 - C_4H_9NO$ – S – C_2H_2], 234 (8) [$M^+ - CH_2C_6H_5 - C_4H_9NO$ – S – 2 C_2H_2], 100 (100) [morpholino-CH_2^+]. – $C_{28}H_{36}N_2O_2S_2$ (496.7): calcd. C67.72, H 7.31, N 5.64, S 12.91; found C 67.62, H 7.40, N 5.73, S 13.04.

(*Z,Z*)-1,4-Di(benzylthio)-1,4-diphenyl-1,3-butadiene (**4h**; cf. ref.[1c,f]). – ***Procedure I:*** After refluxing (1 h) a mixture of 30 g (0.15 mol) benzylisothiouronium chloride and 30 g (0.75 mol) NaOH in 160 ml ethanol, 10.1 g (0.05 mol) **1h** was gradually added (30 min) under argon and the mixture heated under reflux for a further 6 h. At 20°C 500 ml water was added; the isolated solid was crystallized from EtOH/AcOEt – Pale yellow needles; yield: 12.5 g (55%); m.p. 117-118°C. – ^1H NMR ($CDCl_3$): δ = 3.61 (s; 4H; S-CH_2), 7.04 (m; 4H; aromat. H), 7.13 (s; 2H; =C-H), 7.18 (m; 6H; aromat. H), 7.35 (m; 6H; aromat. H), 7.50 (m; 4H; aromat. H); cf. data in ref.[1f]. ^{13}C NMR ($CDCl_3$): δ = 37.7 (S-CH_2), 126.9 ($CH_2C_6H_{5[p]}$], 128.0(8) ($C_6H_{5[p]}$), 128.1(3), 128.2, 128.4, 128.7 ($C_6H_{5[o,m]}$), 132.2(7) (=CH-), 138.3(2), 139.2, 140.0 (>C=); cf. data in ref.[1f]. – MS (70 eV): m/z = 450 (13) [M]$^+$, 359 (80) [$M^+ - C_7H_7$], 237 (27), 236 (94) [$M^+ - C_7H_7 - SCH_2C_6H_5$], 91 (100) [$C_7H_7^+$]. – $C_{30}H_{26}S_2$ (450.7): calcd. C 79.95, H 5.82, S 14.23; found C 79.43, H 5.60, S 14.47. – ***Procedure II:*** To a mixture of 56 mg KOH or 112 mg KO-*t*Bu, respectively, and 50 ml diglyme under argon 2.56 ml (22 mmol) **2** was added drowise and, after stirring for 30 min at 20°C, the mixture was treated slowly with 2.02 g (10 mmol) **1b**. After further stirring at 20°C (2.5 h) the red coloured mixture was poured on ice-water, the separated yellow solid was extracted with AcOEt, and the organic layer evaporated i. vac.: 58% (using KOH), 61% (using KO-*t*Bu).

(*Z,Z*)-1,4-Di(benzylthio)-1,4-di-(4-bromophenyl)-1,3-butadiene (**4i**). – As described for **4h**/procedure I using **1i** (m.p. 269°C): Colourless prisms; yield: 56%; m.p. 191-192°C. – ^1H NMR ($CDCl_3$): δ = 3.58 (s, 4 H, CH_2), 6.96-7.50 (m, 20 H, aromat. H), 7.05 (s, 2 H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 37.7 (CH_2), 122.2 (C_i [C_6H_4Br], 127.0 (=CH-), 128.3, 128.7. 129.6, 131.6 (aromat. C), 132.9 (=CH-), 138.1, 138.4, 139.9 (>C=). – MS (70 eV): m/z = 608 (8), 517 (62) [$M^+ - C_7H_7$], 394 (100) [$M^+ - C_7H_7 - SCH_2C_6H_5$]. – $C_{30}H_{24}Br_2S_2$ (608.4): calcd. C 59.22, H 3.98, Br 26.26, S 10.54; found C 59.07, H 3.93, Br 26.38, S 10.22.

(*Z,Z*)-1,4-Di(benzylthio)-1-phenyl-4-(p-tolyl)-1,3-butadiene (**4j**; cf. ref.[1d]). – As described for **4h**/procedure I using **1j** (m.p. 110°C): Pale yellow needles; yield: 55%; m.p. 120-121°C. – ^1H NMR ($CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 3.60 (s, 4 H, S-CH_2), 7.10, 7.11 (s, s, 2 H, =CH-), 7.02 (m, 4 H, aromat. H), 7.18 (m, 7 H, aromat. H), 7.41 (m, 8 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_3), 37.7 (S-CH_2), 126.8 ($CH_2C_6H_{5[p]}$), 128.0 ($C_6H_{5[p]}$), 128.0, 128.1, 128.2, 128.4, 128.8, 129.1 (aromat. C), 131.7 (H-C^3=), 132.5 ((H-$C^{1'2}$=), 137.2, 138.1, 138.3(9), 138.4(4), 138.6, 139.3, 140.1 (>C=). – MS (70 eV): m/z = 464 (6) [M^+], 373 (56) [$M^+ - C_7C_7$], 296 (46) [$M^+ - C_7C_7 - C_6H_5$], 281 (31) [$M^+ - C_7C_7 - C_6H_5 - CH_3$], 251 (24), 250 (100) [$M^+ - C_7C_7 - SCH_2C_6H_5$], 91 (88) [$C_7H_7^+$]. – $C_{31}H_{28}S_2$ (464.7): calcd. C 80.12, H 6.08; found C 79.87, H 5.99.

(*Z,Z*)-1,4-Di(benzylthio)-1,4-di(p-tolyl)-1,3-butadiene (**4k**; cf. ref.[1c]). – As described for **4h**/procedure I with 11.5 g (0.05 mol) **1k** (m.p. 183°C) resulting in 6.5 g (27%) product. The evaporation of the mother liquor gave 14.35 g of an oily product (mono-adduct **3k**) which was subsequently treated with 5.46 g (0.044 mol) **2** and 600 mg KOH in 120 ml DMF under stirring 2 h at 46°C. After addition of water further 7.8 g (40.5%) product was isolated and recrystallized from EtOH/AcOEt (1:1): Pale yellow needles; yield (total): 14.3 g (59.7%); m.p. 135-136°C. –^1H NMR ($CDCl_3$): δ = 2.38 (s, 6 H, CH_3), 3.61 (s, 4 H, S-CH_2), 7.03 (m, 4 H, $CH_2C_6H_{5[o]}$), 7.11 (s, 2 H, =CH-), 7.22 (m, 10 H, aromat. H), 7.41 (m, 4 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_3), 37.7 (S-CH_2), 126.8 (aromat. $C_{[p]}$), 128.0, 128.2, 128.8, 129,1 (aromat. $C_{[o,m]}$), 131.8 (=CH-), 137.2, 138.0, 138.5, 138.7 (>C=). – MS (70 eV): m/z = 478 (9) [M^+], 387 (55) [$M^+ - C_7H_7$], 264 (100) [$M^+ - C_7H_7 - SCH_2C_6H_5$], 91 (41) [$C_7H_7^+$]. – $C_{32}H_{32}S_2$ (478.7): calcd. C 80.29, H 6.32; found C 79.93, H 6.42. – From the oily intermediate the mono-adduct [**(*Z*)-1-benzylthio-1,4-di(p-tolyl)-1-buten-3-yne** (**3k**; cf. ref.[1c])] could be isolated by crystallization from ethanol: Colourless needles, m.p. 90-91°C; MS (70 eV): m/z = 354 (12) [M^+]; $C_{25}H_{22}S$ (354.5): calcd. C 84.70, H 6.26; found 84.28, 6.36.

(*Z,Z*)-1,4-Di(benzylthio)-1-(p-methoxyphenyl)-4-phenyl-1,3-butadiene (**4l**; cf. ref.[1d]). – As described for **4h**/procedure I using **1l** m.p. (110°C): Pale yellow needles; yield: 55%; m.p. 108°C. – ^1H NMR ($CDCl_3$): δ = 3.61 (s, 4 H, S-

CH_2), 3.85 (s, 3 H, CH_3), 6.91 (m, 2 H, aromat. H), 7.04 (d, 1H, J = 6.56 Hz, -C^2H=), 7.05 (m, 4 H, aromat. H), 7.11 (d, 1H, J = 6.56 Hz, -C^3H=), 7.20 (m, 6 H, aromat. H), 7.30-7.54 (m, 7 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 37.6(5), 37.6(9) (S-CH_2), 55.4 (O-CH_3), 113.8, 126.8, 127.9(4), 128.0(7), 128.2(1), 128.2(5), 128.4, 128.7(4), 128.7(5), 129.3 (aromat. CH), 131.0 (=CH-), 132.5 (C_i[$C_6H_4OCH_3$]), 132.6 (=CH-), 138.2, 138.4(1), 138.4(4), 139.0, 140.2 (>C=), 159.8 (*C*-OCH_3). – MS (70 eV): m/z = 480 (9) [M^+], 389 (74) [$M^+ - C_7H_7$], 267 (38), 266 (99) [$M^+ - C_7H_7$ - $SCH_2C_6H_5$], 251 (33) [$M^+ - C_7H_7$ - $SCH_2C_6H_5 - CH_3$], 91 (100) [$C_7H_7^+$]. – $C_{31}H_{28}OS_2$ (480.7): calcd. C 77.46, H 5.90; found C 76.92, H 6.12.

(*Z,Z*)-1,4-Di(benzylthio)-1,4-di(p-methoxyphenyl)-1,3-butadiene (4m; cf. ref.[1c]). – A mixture of 5.24 g (0.02 mol) **1m** (m.p. 140°C), 5.1 g (0.041 mol) **2**, 0.5 g (1.9 mmol) 18-crown-6 (1.9 mmol), 1.12 g (0.02 mol) KOH, 30 ml water and 60 ml benzene was refluxed for 5 h with stirring. The oily evaporation residue obtained from the organic layer was again treated with 3.6 g (0.029 mol) **2** and 0.56 g (0.01 mol) KOH in 60 ml DMF and stirred for 90 min at 50-60°C. After the addition of 15 ml water to the red-orange solution the product was separated and recrystallized from EtOH/AcOEt (1:1). – Pale yellow needles; yield: 3.9 g (38%); m.p. 156-157°C. – ^{1}H NMR ($CDCl_3$): δ = 3.61 (s, 4 H, S-CH_2), 3.84, (s, 6 H, OCH_3), 6.89 (m, 4 H, o-H [$C_6H_4OCH_3$]), 7.04 (m, 4 H, phenyl-H), 7.06 (s, 2 H, =CH-), 7.20 (m, 6 H, phenyl-H), 7.43 (m, 4 H, m-H [$C_6H_4OCH_3$]). – ^{13}C NMR ($CDCl_3$): δ = 37.7 (S-CH_2), 55.3 (OCH_3), 113.9 (o-C [$C_6H_4OCH_3$]), 126.8 (p-C [phenyl]), 128.2, 128.7, 129.3 (o-C, m-C [phenyl]; m-C [$C_6H_4OCH_3$]), 131.3 (=CH-), 132.7, 137.9, 138.5 (>C=), 159.6 (*C*-OCH_3). – MS (70 eV): m/z = 510 (3%) [M^+], 419 (24) [$M^+ - C_7H_7$], 296 (100) [$M^+ - C_7H_7 - SCH_2C_6H_5$], 281 (32) [$M^+ - C_7H_7 - SCH_2C_6H_5 - CH_3$], 91 (37) [$C_7H_7^+$]. – $C_{32}H_{30}O_2S_2$ (510.7): calcd. C 75.26, H 5.92, S 12.56; found C 75.00, H 6.10, 12.50. – From the oily intermediate the mono-adduct **[(*Z*)-1-benzylthio-1,4-di(p-methoxyphenyl)-1-buten-3-yne (3m**; cf. ref.[1c])] could be separated by fractional crystallization from ethanol: Colourless needles, m.p. 72-73°C; MS (70 eV): m/z = 386 (8) [M^+]; $C_{25}H_{22}O_2S$ (386.5): calcd. C 77.69, 5.74; found C 78.10, H 6.12.

(*Z,Z*)-1,4-Di(benzylthio)-1,4-di(p-*n*-butylphenyl)-1,3-butadiene (4n). – As described for **4h**/procedure I using 15.7 g (0.05 mol) **1n** (m.p. 72°C): Pale yellow needles (EtOH/AcOEt); yield: 7.6 g (27%); m.p. 79-80°C. – ^{1}H NMR ($CDCl_3$): δ = 0.96 (t, 6 H, CH_3), 1.30-1.71 (m, 8 H, CH_2), 2.64 (t, 4 H, CH_2), 3.62 (s, 4 H, CH_2), 7.02-7.45 (m, 20 H, aromat. H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.4, 33.6, 35.4 (CH_2), 37.7 (S-CH_2), 126.8, 128.0, 128.2, 128.5, 128.8, 131.8, 137.4, 138.5, 138,8, 143.0 (aromat. C, =CH-, >C=). – MS (70 eV): m/z = 562 (10), [M^+], 471 (51) [$M^+ - C_7H_7$], 438 (8) [$M^+ - SCH_2C_6H_5$], 348 (100) [$M^+ - C_7H_7 - SCH_2C_6H_5$], 305 (27) [$M^+ - C_4H_9C_6H_5 - HSCH_2C_6H_5$]. – $C_{38}H_{42}S_2$ (562.8): calcd. C 81.09, H 7.52, S 11.39; found C 80.77, H 7.51, S 11.33.

(*Z,Z*)-1,4-Di(benzylthio)-1,4-di(p-*t*-butylphenyl)-1,3-butadiene (4o). – As described for **4h**/procedure I using 15.7 g (0.05 mol) **1o** (m.p. 90°C): Pale yellow needles (EtOH/AcOEt[1:1]; yield: 22.5 g (80%); m.p. 166-167°C. – ^{1}H NMR ($CDCl_3$): δ = 1.45 (s, 18 H, CH_3), 3.73 (s, 4 H, CH_2), 7.13, 7.58 (m, 20 H, aromat. H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 31.3 (CH_3), 34.6 (>C<), 37.7 (CH_2), 125.3, 126,5, 127,7, 127,8, 128,2, 128.8, 131,2, 131,7, 138.5, 138.7 (aromat. C, =CH-, >C=). – MS (70 eV): m/z = 562 (14) [M^+], 471 (50) [$M^+ - C_7H_7$], 438 (11) [$M^+ - HSCH_2C_6H_5$], 380 (4) [$M^+ - 2\ C_7H_7$], 348 (100) [$M^+ - C_7H_7 - SCH_2C_6H_5$], 333 (28) [$M^+ - C_7H_7 - SCH_2C_6H_5 - CH_3$]. – $C_{38}H_{42}S_2$ (562.8): calcd. C 81.09, H 7.52, S 11.39; found C 81.31, H 7.50, S 11.21.

(*Z,Z*)-1,4-Di(benzylthio)-1,4-di(p-cyclohexylphenyl)-1,3-butadiene (4p). – As described for **4h**/procedure I using 18.3 g (0.05 mol) **1p** (m.p. 232°C) and 28 h reaction time: Pale yellow prisms (EtOH/AcOEt/benzene [1:1:1]); yield: 15.6 g (51%); m.p. 172°C. – ^{1}H NMR ($CDCl_3$): δ = 1.29-1.89 (m, 22 H, cyclohexyl), 3.62 (s, 4 H, S-CH_2), 7.02-7.46 (m, 20 H, aromat. H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 26.2, 26.9, 34.4 (CH_2), 37.7 (S-CH_2), 44.3 (CH), 126.8, 128.0, 128.2, 128.8, 131.8, 137.6, 138.6, 138.8, 148.2 (aromat. C, =CH-, >C=). – MS (70 eV): m/z = 614 (24) [M^+], 523 (76) [$M^+ - C_7H_7$], 490 (35) [$M^+ - HSCH_2C_6H_5$], 400 (100) [$M^+ - C_7H_7 - SCH_2C_6H_5$]. – $C_{42}H_{46}S_2$ (614.9): calcd. C 80.03, H 7.54, S 10.43; found C 80.03, H 7.43, S 10.40. – By fractional crystallization (EtOH/AcOEt [1:1]) the mono-addition product **[(*Z*)-1-benzylthio-1,4-di(p-cyclohexylphenyl)-1-buten-3-yne (3p)**] could also be separated: Pale yellow needles; yield 6.8 g (28%); m.p. 117°C (EtOH/AcOEt [1:1]). – IR (KBr):$\tilde{\nu}$ = 2160 cm^{-1} (C≡C). – ^{1}H NMR ($CDCl_3$): δ = 1.24-2.48 (m, 22 H, cyclohexyl), 3.90 (s, 2 H, S-CH_2), 7.05-7.45 (m, 14 H, aromat. H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 26.1, 26.3, 26.9, 34.2, 34.3, 34.4 (CH_2), 37.5 (S-CH_2), 44.3, 44.5 (CH), 87.2, 110.0 (-C≡), 120.9, 126.9, 127.9, 128.0, 128.2, 128.8, 128.9, 131.4, 132.5, 136.5, 138.0, 148.4, 148.5, 148.9, (aromat. C, =CH-, >C=). – MS (70 eV): m/z = 490 (90) [M^+], 366 (100) [$M^+ - HSCH_2C_6H_5$]; $C_{35}H_{38}S$ (490.7): calcd. C 85.66, H 7.81, S 6.53; found C 85.49, H 7.85, S 6.72.

(*Z,Z*)-1,4-Di(benzylthio)-1,4-di[2-(5,6,7,8-tetrahydronaphthyl)]-1,3-butadiene (4q; cf. ref.[1d]). – As described for **4h**/procedure I using 15.5 g (0.05 mol) **1q** (m.p. 163°C) and 40 h reaction time: Pale yellow needles (EtOH/ AcOEt [3:2]); yield: 17.8 g (64%); m.p. 152°C. – ^{1}H NMR ($CDCl_3$): δ = 1.53-2.78 (m, 16 H, C_4H_8), 3.61 (s, 4 H, S-CH_2), 6.99-7.29 (m, 18 H, aromat. H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 23.2, 29.3, 29.5 (CH_2), 37.8 (S-CH_2), 125.3, 126.8, 128.2, 128.7, 128.8, 129.0, 129.1, 137.1, 137.4, 138.7, 138.8, 141.6 (aromat. C, =CH-, >C=). – MS (70 eV): m/z = 558 (3) [M^+], 434 (73) [$M^+ - HSCH_2C_6H_5$], 344 (100) [$M^+ - C_7H_7 - SCH_2C_6H_5$]. – $C_{38}H_{38}S_2$ (558.8): calcd. C 81.67, H 6.85, S 11.48; found C 81.45, H 6.92, S 10.94.

(*Z,Z*)-1,4-Di(benzylthio)-1,4-di(4-biphenylyl)-1,3-butadiene (**4r**; cf. ref.[1d]). – ***Procedure I:*** 3.54 g (0.01 mol) **1r** (m.p. 231°C), 3.5 g (0.025 mol) **2**, 2.4 g (0.06 mol) NaOH and 26 ml dry ethanol were heated at 80°C for 40 h in a sealed tube. Isolation as described for **4h**/procedure I. – Yellow needles (benzene; very poorly soluble); yield: 1.99 g (33%); m.p. 213-214°C. – ^{1}H NMR ($CDCl_3$): δ = 3.67 (s, 4 H, S-CH_2), 7.06, 7.21, 7.45, 7.64 (m, aromat. H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 37.9 (S-CH_2), 126.9, 126.9(9), 127.0(9), 127.4, 128.3, 128.5, 128.7(9), 128.8(3) (aromat. C), 132.5 (=CH-), 138.4, 138.8(7), 139.0(3), 140.6, 140.9 (>C=). – MS (70 eV): m/z = 602 (4) [M^+], 511 (21) [$M^+ - C_7H_7$], 389 (53), 388 (100) [$M^+ - C_7H_7 - S\text{-}CH_2C_6H_5$], 91 (78) [$C_7H_7^+$]. – $C_{42}H_{34}S_2$ (602.8): calcd. C 83.67, H 5.68; found C 83.42, H 6.06. – ***Procedure II:*** A mixture of 1.28 g (10.32 mmol) **2**, 0.16 g (2.85 mmol) KOH and 20 ml dry DMF was stirred 30 min. After the addition of 1.6 g (4.5 mmol) **1r** stirring was continued 3 h at room temperature. The precipitate was filtered by suction and recrystallized from benzene, 0.7 g (26%).

(*Z,Z*)-1,4-Di(benzylthio)-1,4-di(1-naphthyl)-1,3-butadiene (**4s**; cf. ref.[1d]). – ***Procedure I:*** As described for **1r**/procedure I using 3.02 g (0.01 mol) **1s** (m.p. 177°C): Colourless needles; yield 1.71 g (31%); m.p. 189-190°C. – ^{1}H NMR ($CDCl_3$): δ = 3.39 (s, 4 H, S-CH_2), 6.87 (m, 4 H, o-H [benzyl]), 7.07 (m, 8 H, aromat. H, =CH-), 7.49 (m, 8 H), 7.85 (m, 4 H), 8.26 (m, 2 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 36.6 (S-CH_2), 125.1, 125.9, 126.0, 126.1, 126.8, 127.4 (aromat. C), 128.1 (phenyl $C_{o/m}$), 128.2, 128.4 (aromat. C), 128.7 (phenyl $C_{o/m}$), 129.3 (aromat. C), 131.8, 133.7 (>C=), 137.5(8), 137.6(0), 137.6(3) (>C= [naphthyl]). – MS (70 eV): m/z = 550 (26) [M^+], 459 (24) [$M^+ - C_7H_7$], 336 (100) [$M^+ - C_7H_7 - SCH_2C_6H_5$], 91 (79) [$C_7H_7^+$]. – $C_{38}H_{30}S_2$ (550.8): calcd. C 82.87, H 5.49; found C 82.82, H 5.71. – ***Procedure II:*** A mixture of 2.8 g (9.3 mmol) **1s**, 3.0 g (24 mmol) **2**, 11 g (196 mmol) KOH, 0.52 g (2 mmol) 18-crown-6, 30 ml water and 60 ml benzene was heated under reflux for 7 h. The organic phase was washed with water and concentrated. The resulting oily layer was again treated with 2.0 g (15.9 mmol) **2** and 300 mg (5.35 mmol) KOH in 10 ml dry DMF and stirred at 40°C for 1 h. The precipitated solid was recrystallized from benzene, yield: 2.25 g (44%).

(*Z,Z*)-1,4-Di(benzylthio)-1,4-di(2-thienyl)-1,3-butadiene (**4t**; cf. ref.[1c]). – As described for **4h**/procedure I using 10.7 g (0.05 mol) **1t** (m.p. 92°C): Yellow needles; yield: 13.4 g (58%); m.p. 115-116°C. – ^{1}H NMR ($CDCl_3$): δ = 3.81 (s, 4 H, S-CH_2), 7.00-7.28 (m, 18 H, aromat. H, thienyl H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 39.2 (S-CH_2), 125.6, 126.2, 127.0, 127.8 (aromat. C, thienyl C), 128.3, 128.8 (phenyl $C_{o/m}$), 131.1 (>C=), 131.9 (=CH-), 138.1, 146.2 (>C=). – MS (70 eV): m/z = 462 (14) [M^+], 371 (72) [$M^+ - C_7H_7$], 248 (100) [$M^+ - C_7H_7 - SSCH_2C_6H_5$], 91 (89) [$C_7H_7^+$]. – $C_{26}H_{22}S_4$ (462.7): calcd. 67.48, H 4.79; found C 66.97, H 4.82.

(*Z,Z*)-1,4-Di(*t*-butylthio)-1,4-diphenyl-1,3-butadiene (**8h**). – A mixture of 1.8 g (20 mmol) **7**, 300 mg KOH and 40 ml dry DMF was stirred at room temperature for 30 min and then treated slowly with 2.02 g (10 mmol) **1h**. Stirring was continued 30 min (after 10 min a solid precipitates), then 200 ml water were added. The product was filtered by suction and recrystallized from trichloroethene or EtOH/$CHCl_3$. – Colourless needles; yield:3.35 g (87.7%); m.p. 238-239°C. – ^{1}H NMR ($CDCl_3$): δ = 1.15 (s, 18 H, *t*-Bu), 7.73 (s, 2 H, =CH-), 7.32-7.70 (m, 10 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 31.8 (C[CH_3]$_3$), 48.2 (*C*[CH_3]$_3$), 127.8 (=CH-), 128.0(5), 128.1(2) (aromat. $C_{o,m}$), 138.0 (>C=), 138.9 (aromat. C_p), 144.0 (aromat. C_i). – MS (70 eV): m/z = 382 (33.5) [M^+], 325 (16) [$M^+ - C_4H_9$], 269 (58) [$M^+ - C_4H_9 - C_4H_8$], 237 (100) [$M^+ - C_4H_9 - S\text{-}C_4H_8$], 204 (11) [$M^+ - C_4H_9 - S\text{-}C_4H_8 - SH$]. – $C_{24}H_{38}S_2$ (382.6): calcd. C 75.34, H 7.90, S 16.76; found C 75.16, H 7.71, S 17.25.

(*Z,Z*)-1,4-Di(*t*-butylthio)-1,4-di(p-tolyl)-1,3-butadiene (**8k**). – As described for **8h** using 2.3 g (10 mmol) **1k**: Colourless needles (AcOEt); yield: 3.4 g (83.2%); m.p. 244-245°C. – ^{1}H NMR ($CDCl_3$): δ = 1.17 (s, 18 H, *t*-Bu), 2.37 (s, 6 H, $CH_3C_6H_5$], 7.77 (s, 2 H, =CH-), 7.15 (*pseudo*-d, J = 8 Hz, 4 H, aromat. H [C_oH]), 7.60 (*pseudo*-d, 4 H, J = 8 Hz, aromat. H [CH_m]). – ^{13}C NMR ($CDCl_3$): δ = 21.1 (CH_3-C_6H_5), 31.7 (C[CH_3]$_3$), 47.9 (*C*[CH_3]$_3$), 127.8, 128.7 ($C_{o,m}$ [tolyl]), 137.4 (=CH-), 137.5 (>C=), 138.2 (C_i [tolyl]), 141.1 (C_i [phenyl]). – MS (70 eV): m/z = 410 (21) [M^+], 353 (18) [$M^+ - C_4H_9$], 297 (55) [$M^+ - C_4H_9 - C_4H_8$], 265 (100) [$M^+ - C_4H_9 - S\text{-}C_4H_8$], 232 (8) [$M^+ - C_4H_9 - S\text{-}C_4H_8 - SH$]. – $C_{26}H_{34}S_2$ (410.7): calcd. C 76.04, H 8.34, S 15.62; found C 76.02, H 8.26, S 15.70.

(*Z,Z*)-1,4-Di(*t*-butylthio)-1,4-di(p-methoxyphenyl)-1,3-butadiene (**8m**). – As described for **8h** using 2.62 g (10 mmol) **1m**: Colourless needles (trichloroethene); yield: 3.60 g (81.5%); m.p. 137-138°C. – ^{1}H NMR ($CDCl_3$): δ = 1.16 (s, 18 H, *t*-Bu), 3.82 (s, 6 H, OCH_3), 7.71 (s, 2 H, =CH-), 6.87 (2 d, 4 H, J = 2 Hz, aromat. H_o [CH_3O-C_6H_4]), 6.30 (2 d, 4 H, J = 2 Hz, aromat. H_m [CH_3O-C_6H_4]). – ^{13}C NMR ($CDCl_3$): δ = 31.8 (C[CH_3]$_3$), 48.0 (*C*[CH_3]$_3$), 55.3 (OCH_3), 113.5, 129.2 (aromatic. $C_{o,m}$), 136.6 (=CH-), 136.8 (>C=), 137.4 (aromat. C_i {=C[S]–*C*=}), 159.5 (aromat. C_i [=*C*–OCH_3]). – $C_{26}H_{34}O_2S_2$ (442.7): calcd. C 70.54, H 7.74, S 14.49; found C 70.68, H 7.58, S 14.51.

***Transformation to 1,2-dithiines* 6** (all preparative and isolation steps must be carried out with the exclusion of air):

1,2-Dithiine (**6a**; cf. ref.[1a,c]). – To a solution of 50 g (308 mmol) anhydrous $FeCl_3$ in 250 ml dry methanol was dropped (2 h; 20°C) with stirring a solution of 15.4 g (130 mmol) **10a** (see below) in 100 ml dry methanol. The mixture was diluted with 1.5 l water and extracted twice with 300 ml petroleum ether (b.p. 30-50°C; stabilization with a small amount of N-cyclohexylmaleinimide). After careful evaporation i. vac. (bath temp. at -10 till -20°C) the residue was distilled i. vac. (to reduce polymerization caused by alkali traces the apparatus was previously treated with conc. H_2SO_4 at 200°C, washed with water and dryed at 150°C). – Dark red oil; yield: 1,2 g (8%; a major part remains in the flask as viscous

material [polymer or polydisulfide?]). – UV/Vis (cyclohexane): λ_{max} (lg ε) = 222 (3.22), 267 (3.18), 274 (3.20), 355 (2.25; sh), 457 (1.98) nm. – IR ($CHCl_3$): $\tilde{\nu}$ = 620, 1300 (s, m; cis-HC=CH), 1300, 1540 (w-m; C=C), 3005 (m; =CH) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 6.05 (m, 2 H, $C^3 \equiv {}^6H$), 6.27 (m, 2H, $C^4 \equiv {}^5H$); AA'BB'-type: $^3J_{3,4 \equiv 6,5}$ = 9.4, $^4J_{3,5 \equiv 6,4}$ = 0, $^3J_{4,5}$ = 5.5, $^5J_{3,6}$ = 2.0 Hz. – ^{13}C NMR ($CDCl_3$): δ = 119.5 ($C^3 \equiv {}^6H$; $^1J_{C,H}$ = 176.2 Hz), 129.8 ($C^4 \equiv {}^5H$; $^1J_{C,H}$ = 162.9 Hz). – MS (70 eV): m/z = 116 (100) [M^+], 84 (81) [M^+ – S], 71 (66) [M^+ – S – CH], 58 (30) [M^+ – S - 2 CH]. – $C_4H_4S_2$ (116.2): calcd. C 41.35, H 3.47, S 55.18; found C 41,45, H 3.80, S 54.92.

3,6-Di(*n*-butyl)-1,2-dithiine (6b). – To 11.1 g (27 mmol) powdered **4b** in 200 ml liquid ammonia was added 2.53 g (110 mmol) Na at -70°C over 90 min. Solid NH_4Cl was added until the blue colour of the solution had disappeared. After evaporation, the residue was dissolved in 200 ml of water and washed twice with two 20 ml portions of Et_2O. The resulting aqueous solution of **5b** was covered with 100 ml portions of Et_2O and acidified at -5°C with 25% aqueous HCl solution. The organic phase **10b** was evaporated under reduced pressure (bath temp. < 15°C), the resulting pale yellow oil dissolved in 30 ml MeOH and a solution of $FeCl_3$ in 20 ml MeOH slowly added with stirring under an argon atmosphere. The mixture was stirred for a further 2 h at room temperature, diluted with 100 ml water and extracted with cyclohexane. On concentration 4.0 g (65%) of a deep red oil was obtained (R_f = 0.65 [silica gel, benzene]) which had a high tendency for sulfur extrusion. – UV/Vis (MeCN): λ_{max} = 246, 440 nm (compare, however, the product in ref.[10]). – ^1H NMR ($CDCl_3$): δ = 0.92 (t_c, 6 H, CH_3), 1.01-1.83 (m, 8 H, CH_2), 2.06-2.41 (m, 4 H, CH_2), 6.62 (s, 2 H, =CH-). – $C_{12}H_{20}S_2$ (228.4): calcd. C 63.10, H 8.83, S 28.07; found C 62.86, H 8.89, S 27.90.

3,6-Di(2-hydroxy-2-propyl)-1,2-dithiine (6d). – Approximately 1 g (43 mmol) of Na was added slowly to a solution 0f 3.32 g (8 mmol) **4d** in 120 ml liquid ammonia at -70°C until a deep blue colour persisted. After 2 h further stirring at this temperature the mixture was neutralized by the addition of NH_4Cl (decolourization) and the solution allowed to evaporate. The resulting residue was dissolved in 40 ml 2N NaOH solution, insoluble material removed by filtration and the product purified by extraction with Et_2O. The orange aqueous phase **5d** was slowly added with stirring to a 5% aqueous solution of $K_3[Fe(CN)_6$ (6.6 g [20 mmol]) and the precipitated product recrystallized from *n*-hexane/$CHCl_3$ (3-4:1). – Yellow-orange needles; yield: 1.1 g (59.1%); m.p. 108-109°C. – UV/Vis (MeCN): λ_{max} (lg ε) = 262 (3.44), 412 (2.60) nm. – ^1H NMR ($CDCl_3$): δ = 1.49 (s, 12 H, CH_3), 1.74 (s, 2 H, OH), 6.39 (s, 2 H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 29.0 (CH_3), 73,4 (-*C*$[CH_3]_2$OH), 122.6 (=CH-), 144.2 (>C=). MS (70 eV): m/z = 232 (57) [M^+], 200 (11) [M^+ – S], 185 [M^+ – S – CH_3], 167 (13) [M^+ – S – CH_3 – H_2O], 159 (100) [M^+ – S – CH_3 – H_2O – C_2H_2], 59 (56) [$C(CH_3)_2OH^+$]. – $C_{10}H_{16}O_2S_2$ (232.4): calcd. C 51.69, H 6.94, S 27.60; found 51.89, H 7.20, S 27.27.

3,6-Di(pyrrolidinomethyl)-1,2-dithiine (6e). – As described for **6d** using 2.10 g (4.5 mmol) **4e**, 75 ml liquid NH_3, 529 mg (23 mmol) Na, 25 ml 2N NaOH solution and 3.95 g (12 mmol) $K_3[Fe(CN)_6$ (in a 5% aqueous solution), recrystallization from AcOEt. – Bright yellow needles; yield: 661 mg (52%); m.p. 72-73°C;[39] R_f = 0.18 (silica gel, *n*-hexane(AcOEt [1:1]). – UV/Vis (*n*-hexane): λ_{max} (lg ε) = 268 (3.67), 4.23 (2.19) nm. – ^1H NMR ($CDCl_3$): δ = 1.69-1.85 (m, 8 H, $CH_{2[cycl.C3/4]}$), 2.46-2.54 (m, $CH_{2[cycl.C2/5]}$), 3.31 (s, 4 H, >N-CH_2), 6.05 (s, 2 H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 23.7 ($CH_{2[cycl.C3/4]}$), 54.0 ($CH_{2[cycl.C2/5]}$), 61.4 (>N-CH_2), 125.1 (=CH-), 134.4 (>C=). – MS (70 eV): m/z = 282 (12) [M^+], 250 (4) [M^+ – S], 180 (11) [M^+ – S – C_4H_8N], 111 (7) [M^+ – S – 2 C_4H_8N], 84 (100) [pyrrolidino-CH_2^+]. – $C_{14}H_{22}N_2S_2$ (282.5): calcd. C 59.53, H 7.85, N 9.92, S 22.70; found C 59.42, H 7.93, N 9.80, S 22.85.

3,6-Di(piperidinomethyl)-1,2-dithiine (6f). – As described for **6d/6e** using 2.22 g (4.5 mmol) **4f**; recrystallization from AcOEt – Bright yellow needles; yield: 800 mg (55%); m.p. 112-113°C;[39] R_f = 0.42 (*n*-hexane/AcOEt [1:1]). – UV/Vis (*n*-hexane): λ_{max} (lg ε) = 282 (3.64), 425 (2.31) nm. – ^1H NMR ($CDCl_3$): δ = 1.38-1.40 (m, 4 H, $CH_{2[cycl.C4]}$), 1.51-1.57 (m, 8 H, $CH_{2[cycl.C3/5]}$), 2.37-2.39 (m, 8 H, $CH_{2[cycl.C2/6]}$), 3.15 (s, 4 H, >N-CH_2), 6.12 (s, 2 H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 24.3 ($CH_{2[cycl.C4]}$), 26.0 ($CH_{2[cycl.C3/5]}$), 54.4 ($CH_{2[cycl.C2/6]}$), 64.7 (>N-CH_2), 125.3 (=CH-), 134.3 (>C=). – MS (70 eV): m/z = 310 (23) [M^+], 278 (5) [M^+ – S], 194 (14) [M^+ – S – $C_5H_{10}N$], 111 (6) [M^+ – S – 2 $C_5H_{10}N$], 98 (100) [piperidino-CH_2^+]. – $C_{16}H_{26}N_2S_2$ (310.5): calcd. C 61.88, H 8.44, N 9.02, S 20.65; found C 61.14, H 8.31, N 9.11, S 20.64.

3,6-Di(morpholinomethyl)-1,2-dithiine (6g). – As described for **6d/6e** using 2.24 g (4.5 mmol) **4g**; recrystallization from AcOEt. – Bright yellow needles; yield: 849 mg (60%); m.p. 159-160°C;[39] R_f = 0.24 (*n*-hexane/AcOEt [1:1]). – UV/Vis (*n*-hexane): λ_{max} (lg ε) = 280 (3.53), 423 (2.53) nm. – ^1H NMR ($CDCl_3$): δ = 2.40-2.51 (m, 8 H, $CH_{2[cycl.C2/6]}$), 3.21 (s, 4 H, >N-CH_2), 3.64-3.75 (m, 8 H, $CH_{2[cycl.C3/5]}$), 6.17 (s, 2 H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 53.3 ($CH_{2[cycl.C2/6]}$), 64.3 (>CH_2), 67.0 ($CH_{2[cycl.C3/5]}$), 126.0 (=CH-, $J^1_{C,H}$ = 159.6 Hz), 133.5 (>C=). – MS (70 eV): m/z = 314 (40) [M^+], 282 (6) [M^+ – S], 196 (14) [M^+ – S – C_4H_8NO], 111 (7), [M^+ – S – 2 C_4H_8NO], 100 (100) [morpholino-CH_2^+]. – $C_{14}H_{22}N_2O_2S_2$ (314.5): calcd. C 53.47, H 7.05, N 8.91, S 20.39; found C 53.42, H 7.08, N 8.37, S 20.41.

3,6-Diphenyl-1,2-dithiine (6h; cf. ref.[1c,f]). – ***Method I:*** A solution of 2.25 g (5 mmol) of **4b** in 100 ml liquid ammonia was treated slowly with about 0.5 g (22 mmol) of Na, then stirred for a further 2 h, neutralized by the addition of NH_4Cl (disappearance of the blue colour) and the solution evaporated. The residue was dissolved in 25 ml 2N NaOH under an argon atmosphere and filtered to remove insoluble material. The resulting solution of **5h** was added drowise with stirring to a 5% aqueous solution of $K_3Fe(CN)_6$ (4.5 g [13.5 mmol]) . The product precipitated immediately. Alternatively

if a current of air was passed through the above alkaline solution (3 h), the product separated as a fine crystalline material. – Purple leaflets (AcOEt); yield: 724 mg (54%); m.p. 144-145°C;[39] R_f = 0.77 (*n*-hexane/AcOEt [3:1]). – UV/Vis (cyclohexane): λ_{max} (lg ε) = 237 (4.23), 312 (4.13), 468 (3.51) nm; (MeCN): 241 (4.15), 310 (4.19), 464 (3.72) nm; (EtOH): 233 (4.25), 307 (4.22), 461 (3.55) nm. – ^{1}H NMR ($CDCl_3$): δ = 6.90 (s, 2 H, =CH-), 7.29-7.82 (m, 10 H, aromat. H). – ^{13}C NMR ($CDCl_3$): see data in ref.[1f], p. 606. – MS (70 eV): m/z = 268 (100) [M^+], 236 (31) [M^+ – S], 202 (9) [M^+ – H_2S], 147 (7) [M^+ – C_6H_5CS], 121 (19) [$C_6H_5CS^+$]. – $C_{16}H_{12}S_2$ (268.4): calcd. C 71.60, H 4.51, S 23.89; found C 71.43, H 4.54, S 23.32; molar weight (cryoscopic in benzene: 256). – ***Method II:*** A mixture of 1.91 g (5 mmol) **8h**, 25 ml trichloroethene and 25 ml AcOH was stirred and treated portionwise with 11.89 g 2-nitrophenylsulfenyl chloride and the resulting pale yellow solution stored at 60°C for 6 h. After concentration at reduced pressure, the solids obtained were washed with water, dried and the crude **9h** used for subsequent transformations to **6h**: **(*Z,Z*)-1,4-Di(o-nitrophenyldithio)-1,4-diphenyl-1,3-butadiene (9h)**. – Yellow leaflets; yield: 2.55 g (92%); m.p. 185-186°C (rapid heating); very poorly soluble in most solvents; in trichloroethene, DMF and DMSO colour change to red occurs with precipitation of **6h**. – MS (70 eV): m/z = 268 (25) [**6h**$^+$], 308 (25) [di(2-nitrophenyl) disulfide$^+$], 236 (100) [**6h**$^+$ – S], 154 (100) [di(2-nitrophenyl) disulfide/2$^+$]; no molpeak recognizable. – [$C_{28}H_{20}N_2O_4S_4$ (576.7)]. – To a suspension of **9h** in 20 ml dry THF was added with stirring 8 mg (0.08 mmol) NEt_3 and 6 mg (0.08 mmol) 2-mercaptoethanol. A red solution was obtained after 20 min. The mixture was allowed to stand at room temperature for a further 30 min, the solvents removed at reduced pressure and the residue dissolved in Et_2O. The solution was washed twice with 5% $NaHCO_3$ solution and then with water to remove any thiol. The etheral solution was concentrated and the residues recrystallized from AcOEt to eliminate the co-produced di(2-nitrophenyl) disulfide. Yield of **6h**: 300 mg (58%). – ***Method III:*** A suspension of 0.72 g (2 mmol) **19** in 30 ml dry diethyl ether was treated dropwise at -10°C with 3 ml (4.8 mmol) of a 1.6M *n*-BuLi solution in 20 ml diethyl ether under an argon atmosphere. After stirring for 30 min at -10°C and 20 min at room temperature the mixture was cooled to -40°C and an excess of finely powdered elemental sulfur (0.32 g) was added. Stirring was continued at the same temperature for 2 h. After standing overnight at room temperature, 40 ml of a 10% NaOH solution was added at 0 to 5°C. The residue obtained after evaporation of the solvents was washed with *n*-hexane and recrystallized from EtOAc; yield of **6h**: 0.376 g (70%).

3-Phenyl-6-(p-tolyl)-1,2-dithiine (6j; cf. ref.[1d]). – As described for **6h**/method I using 2.32 g (5 mmol) **4j**: Purple needles (AcOEt); yield: 1.0 g (71%); m.p. 126-127°C.[39] – UV/Vis (MeCN): λ_{max} (lg ε) = 238 (4.09), 316 (4.14), 464 (3.42) nm. – ^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 3 H, CH_3), 6.85, 6.90 (2 d [J = 6.7 Hz], 2 H, =CH-), 7.18-7.70 (m, 4 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_3), 125.1 (=CH-), 126.2, 127.7, 128.7, 128.8, 129.4 (aromat. CH), 133.7 (>C^1= [tolyl]), 134.0 (>C^6= [dithiine]), 135.1 (>C^3= [dithiine]), 136.8 (>C= [phenyl]), 139.1 (>C^4= [tolyl]). – MS (70 eV): m/z = 282 (M^+], 250 (100) [M^+ – S], 267 (8) [M^+ – CH_3], 216 (8) [M^+ – S – H_2S]. – $C_{17}H_{14}S_2$ (282.4): calcd. C 72.30, H 5.00, S 22.70; found C 72.24, H 5.12, S 23.16.

3,6-Di(p-tolyl)-1,2-dithiine (6k; cf. ref.[1c]). – ***Method I:*** As described for **6h**/method I using 2.39 g (5 mmol) **4k**: Purple prisms (AcOEt); yield: 711 mg (48%); m.p. 161-162°C[39]; R_f = 0.60 (benzene/*n*-hexane 1:1). – UV/Vis (MeCN): λ_{max} (lg ε) = 241 (4.23), 316 (4.25), 464 (3.64). – ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 6 H, CH_3), 6.85 (s, 2 H, =CH-), 7.19, 7.56 (2 d [J = 8 Hz)], 8 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_3), 125.3 (=CH-), 127.7, 129.4 (aromat. CH), 133.4 (>C^1= [tolyl]), 134.4 (>C= [dithiine]), 139.1 (>C^4= [tolyl]). – MS (70 eV): m/z = 296 (35) [M^+], 264 (100) [M^+ – S], 248 (28), [M^+ – S – CH_4], 215 (28), [M^+ – S – CH_4 – SH]. – $C_{18}H_{16}S_2$ (296.4): calcd. 72.93, H 5.44, S 21.63; found C 73.01, H 5.50, S 21.50. – ***Method II:*** As described for **6h** /method II using 2.05 g (5 mmol) **8k** and yielding first **(*Z,Z*)-1,4-Di(o-nitrophenyldithio)-1,4-di[p-tolyl]-1,3-butadiene (9k)**. – Yellow leaflets; yield: 2.8 g (93%); m.p. 179-181°C (rapid heating up); very poorly soluble in most solvents. – MS (70 eV): m/z = 308 (10) [di(2-nitrophenyl) disulfide$^+$], 296 (32) [**6k**$^+$], 264 (100) [**6k** – S], 154 (15) [di(2-nitrophenyl) disulfide/2$^+$]; no molpeak recognizable. – [$C_{30}H_{24}N_2O_4S_4$ (604.8)]. – Transformation using 1.2 g (2 mmol) **9k**; yield of **6k**: 361 mg (61%).

3-(p-Methoxyphenyl)-6-phenyl-1,2-dithiine (6l; cf. ref.[1d]). – As described for **6h**/method I using 2.40 g (5 mmol) **4l**: Dark-red needles (AcOEt); yield: 985 mg (66%); m.p. 140-141°C.[39] – UV/Vis (MeCN): λ_{max} (lg ε) = 241 (4.15), 320 (4.19), 464 (3.60) nm. – ^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 3 H, CH_3), 6.80, 6.89 (2 d [J = 6.7 Hz], 2 H, =CH-), 6.93, 7.62 (2 d [J = 8.9 Hz], 2 H, aromat. H [$C_6H_4OCH_3$]), 7.31-7.70 (m, 7 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 55.38 (CH_3), 114.2, 124.2, 126.4, 127.6, 128.7 (aromat. C), 129.2 (=CH- [dithiine]), 129.2 (>C= [phenyl]), 133.1 (>C^6= [dithiine]), 135.1 (>C^1= [methoxyphenyl]), 136.9 (>C^3= [dithiine]), 160.4 (>C^4= [methoxyphenyl]). – MS (70 eV): m/z = 298 (29) [M^+], 266 (100) [M^+ – S], 283 (14) [M^+ – CH_3], 251 (90) [M^+ – S – CH_3], 223 (40) [M^+ – S – CH_3 – CO]. – $C_{17}H_{14}OS_2$ (298.4): calcd. C 68.42, H 4.73, S 21.49; found C 68.44, H 5.03, S 21.85.

3,6-Di(p-methoxyphenyl)-1,2-dithiine (6m; cf. ref.[1c]). – ***Method I:*** As described for **6h**/method I using 2.55 g (5 mmol **4m**: Purple needles (AcOEt); yield: 1.18 g (72%); m.p. 177-178°C.[39] – UV/Vis (MeCN): λ_{max} (lg ε) = 244 (4.15), 324 (4.31), 463 (3.65) nm. – ^{1}H NMR (acetone-d_6): δ = 3.84 (s, 6 H, CH_3), 6.98 (s, 2 H, =CH- [dithiine]), 6.68 (2 pseudo-d [J = 2 H], 4 H, aromat. H), 7.01 (2 pseudo-d [J = 2 Hz], 4 H, aromat. H). – ^{13}C NMR (acetone-d_6): δ = 55.8 (CH_3), 115.2 (aromat. C^3), 125.6 (aromat. C^2), 127.4 (=CH- [dithiine]), 129.7 (aromat. C^1), 133.6 (>C= [dithiine]), 162 (aromat. C^4). – MS (70 eV): m/z = 328 (38) [M^+], 313 (11) [M^+ – CH_3], 296 (100) [M^+ – S], 281 (96) [M^+ – S – CH_3],

266 (11) [$M^+ - S - 2\ CH_3$], 238 (11) [$M^+ - S - 2\ CH_3 - CO$]. – $C_{18}H_{16}O_2S_2$ (328.4): calcd. C 65.82, H 4.91, S 19.52; found C 66.10, H 4.85, S 19.20. – ***Method II:*** As described for **6h**/method II using 2.21 g (5 mmol) **8m** and yielding first **(*Z,Z*)-1,4-Di(2-nitrophenyldithio)-1,4-di[p-methoxyphenyl]-1,3-butadiene (9m)**. – Yellow leaflets; yield: 2.8 g (89.7%); m.p. 168-172°C (rapid heating). – MS (70 eV): m/z = 328 (17) [**6m**$^+$], 308 (10) [di(2-nitrophenyl) disulfide$^+$], 296 (100) [**6m**$^+ - S$], 154 (65) [di(2-nitrophenyl) disulfide/2^+]; no molpeak recognizable. – [$C_{30}H_{24}N_2O_6S_4$ (636.8)]. – Transformation using 637 mg (1 mmol) **9m**; yield of **6m**: 185 mg (57%).

3,6-Di(p-*n*-butylphenyl)-1,2-dithiine (6n). – As described for **6h**/method I using 2.81 g (5 mmol **4n**: Felted purple needles (AcOEt); yield: 875 mg (46%); m.p. 105-108°C (nematic phase at 106°C); R_f = 0.76 (benzene) – UV/Vis (MeCN): λ_{max} (lg ε) = 230 (4.11), 328 (4.30), 460 (3.50) nm. – ^{1}H NMR ($CDCl_3$): δ = 0.93 (t_c, 6 H, CH_3), 1.27-1.68 (m, 8 H, CH_2), 2.63 (t_c, 4 H, CH_2), 6.87 (s, 2 H, =CH-), 7.17-7.62 (m, 8 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 13.94 (CH_3), 22.3, 33.5, 33.5, 35.4 (CH_2), 125.5, 127.7, 128.9, 142.3, 144.0 (aromat. C, =CH-, >C=). – MS (70 eV): m/z = 380 (8) [M^+], 348 (100) [$M^+ - S$], 305 (53) [$M^+ - C_3H_7$]. – $C_{24}H_{28}S_2$ (380.6): calcd. C 75.74, H 7.42, S 16.85; found C 75.36, H 7.36, S 16.58.

3,6-Di(p-*t*-butylphenyl)-1,2-dithiine (6o). – As described for **8h**/method I using 2.81 g (5 mmol **4o**: Rectangular purple leaflets (AcOEt); yield: 818 mg (43%); m.p. 160-161°C;[39] R_f = 0.72 (benzene). – ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 18 H, CH_3), 6.87 (s, 2 H, =CH-), 7.23-7.64 (m, 8 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 31.2 (CH_3), 34.7 (>C<), 125.4, 125.7, 127.5, 128.3, 134.0, 143.2 (aromat. C, =CH-, >C=). – MS (70 eV): m/z = 380 (48) [M^+], 365 (16) [$M^+ - CH_3$], 348 (100) [$M^+ - S$], 333 (60) $M^+ - S - CH_3$]. – $C_{24}H_{28}S_2$ (380.6): calcd. C 75.74, H 7.42, S 16.85; found C 75.34, H 7.27, S 16.43.

3,6-Di(p-cyclohexylphenyl)-1,2-dithiine (6p). – As described for **6h**/method I using 3.07 g (10 mmol) **4p**: Rectangular purple leaflets ($CHCl_3$, also crystals for X-ray analysis[23] [cf. Figure 3]); yield: 104 mg (48%); m.p. 221°C;[39] R_f = 0.70 (benzene). – UV/Vis (MeCN): λ_{max} (lg ε) = 239 (4.14), 300 (3.93), 465 (3.26) nm. – ^{1}H NMR ($CDCl_3$): δ = 1.21-1.84 (m, 22 H, C_6H_{11}), 6.85 (s, 2 H, =CH-), 7.21-7.81 (m, 8 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 26.1, 26.8, 34.3 (CH_2), 44.4 (>CH), 125.4, 127.2, 127.8, 134.4, 149.1 (aromat. C, =CH-, >C=). – MS (70 eV): m/z = 432 (8), [M^+], 399 (100) [$M^+ - SH$], 357 (15) [$M^+ - S - C_3H_7$], 331 (10) [$M^+ - S - C_5H_9$]. – $C_{28}H_{32}S_2$ (432.7): calcd. C 77.73. H 7.45, 14.82; found C 77.22, H 7.35, S 14.52.

3,6-Di[2-(5,6,7,8-tetrahydronaphthyl]-1,2-dithiine (6q). – As described for **6h**/method I using 2.79 g (5 mmol) **4q**: Rectangular purple leaflets (AcOEt); yield: 979 mg (52%); m.p. 165°C;[39] R_f = 0.83 (benzene). – UV/Vis (MeCN): λ_{max} (lg ε) = 239 (4.14), 300 (3.93), 465 (3.26) nm. – ^{1}H NMR ($CDCl_3$): δ = 1.53-2.91 (m, 16 H, CH_2), 6.83 (s, 2 H, =CH-), 7.09-7.40 (m, 6H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 23.1, 29.3, 29.5 (CH_2), 124.8, 125.2, 128.6, 129.4, 134.1, 134.4, 137.5, 139.4 (aromat. H, =CH-, >C=). – MS (70 eV): m/z = 376 (7) [M^+], 344 (15) [$M^+ - S$], 256 (100) [S_8^+]. – $C_{24}H_{24}S_2$ (376.6): calcd. C 76.55, 6.42, S 17.03; found C 76.36, H 6.47, S 17.42.

3,6-Di(p-biphenylyl)-1,2-dithiine (6r; cf. ref.[1d]). – As described for **6h**/method I using 3.01 g (5 mmol) **4r**; major amount of unsoluble solid after evaporation of NH_3: Reddish brown needles (dissolution in benzene and reprecipitation by AcOEt); yield: 533 mg (25%); m.p. 229-230°C.[39] – UV/Vis (MeCN): λ_{max} (lg ε) = 277, 350, 460 nm (poorly soluble). – ^{1}H NMR (DMSO-d_6): δ = 6.88 (2 H, =CH-), 7.39-7.85 (m, 18 H, aromat. H). – ^{13}C NMR ($CDCl_3$; 12 h accumulated): δ = 126.0, 127.1, 127.4, 127.7, 128.2, 128.9 (aromat. C, =CH-), 134.4, 135.7, 140.3, 141.7 (>C=). – MS (70 eV): m/z = 420 (18) [M^+], 388 (100) [$M^+ - S$], 354 (5) [$M^+ - S - H_2S$], 195 (65) [$M^+ - S - C_6H_5$-C_6H_4 – CSH]. – $C_{28}H_{20}S_2$ (420.6): calcd. C 79.96, H 4.79, S 15.25; found C 79.32, H 4.99, S 14.86.

3,6-Di(1-naphthyl)-1,2-dithiine (6s; cf. ref.[1d]). – As described for **6h**/method I using 2.75 g (5 mmol) **4s**: Orange red prisms (coformed thiophene **12s** was precipitated by addition of AcOEt to the solution of the crude product in few benzene and precpitating with AcOEt (isolation of **6s** from the mother liquor); yield: 655 mg (35%); m.p. 148-149°C.[39] – UV/Vis (MeCN): λ_{max} (lg ε) = 317 (3.94), 453 (3.06) nm. – ^{1}H NMR (DMSO-d_6): δ = 6.71 (s, 2 H, =CH-), 7.36-8.55 (m, 14 H, aromat. H). – ^{13}C NMR ($CDCl_3$; 12 h accumulated): δ = 125.3, 126.1, 126.3, 126.6, 127.4, 128.5, 129.4, 130.2 (aromatic C, =CH- [dithiine]), 131.1, 132.8, 133.9, 136.2 (>C=). – MS (70 eV): m/z = 368 (31) [M^+], 336 (100) [$M^+ - S$], 302 (16) [$M^+ - S - H_2S$]. – $C_{24}H_{16}S_2$ (368.5): calcd. C 78.22, H 4.38, S 17.40; found C 77.95, H 4.48, S 17.56.

3.6-Di(2-thienyl)-1,2-dithiine (6t; cf. ref.[1c]). – As described for **6h**/method I using 2.31 g (5 mmol) **4t**: Violet needles (AcOEt); yield: 101 mg (72%); m.p. 122-123°C.[39] – UV/Vis (MeCN): λ_{max} (lg ε) = 252 (3.87), 339 (4.23), 477 (3.79). – ^{1}H NMR (DMSO-d_6): δ = 6.83 (s, 2 H, =CH-), 7.03-7.07 (m, 2 H, thienyl-H), 7.31-7.35 (m, 4 H, thienyl-H). – ^{13}C NMR ($CDCl_3$): δ = 124.0 (=CH- [dithiine]), 126.5, 126.9, 127.5 (thienyl-CH), 127.9 (>C= [dithiine]), 141.1 (>C= [thienyl]). – MS (70 eV): m/z = 280 (30) [M^+], 248 (100) [$M^+ - S$], 214 (10)[$M^+ - S - H_2S$], 203 (20) [$M^+ - S - H_2S$ – CSH]. – $C_{12}H_8S_4$ (280.4): calcd. C 51.39, H 2.88, S 45.73; found C 51.54, H 2.88, S 46.00.

***Access to 1,3-butadiene-1,4-dithiols* 10 *and 1,4-di(acetylthio)-1,3-butadienes* 11**

A) By reductive fission of (Z,Z)-1,4-Di(benzylthio)-1,3-butadienes **4** *via 1,4-dithiolates* **5**: **(*Z,Z*)-1.3-Butadiene-1,4-dithiol (10a**; cf. ref.[1a,c,f]). – A mixture of 40 g (134 mmol) **4a** and 1 l liquid ammonia was cautiously treated with Na (maximum 15.4 g [670 mmol]) at -70°C over a 2 h period and then with NH_4Cl until the blue colour of the solution was

discharged. After evaporation of the solvent, the product was dissolved in 500 ml water and washed repeatedly with Et_2O. The resulting aqueous solution of **5a** was covered with 200 ml of Et_2O, and acidified at -20°C with 25% aqueous HCl. The aqueous phase was extracted several times with Et_2O, the combined extracts dried (Na_2SO_4), the solvents removed at reduced pressure (receiver at -70°C) and the residue distilled under vacuum (reveiver at -70°C). – Pale yellow lachrymatory liquid with a highly disagreeable odour; yield: 8.2 g 52%; b.p. 38°C/0.3 Torr. (m.p. ≈ -30°C) – ^{1}H NMR ($CDCl_3$): δ = 2.92 (d, 2H SH; J = 9 Hz), 6.17 (m, 2H; =C*H*SH), 6.41 (d, 2H, -C*H*=CHSH; J = 8.3 Hz). – ^{13}C NMR ($CDCl_3$): δ = 118.3 (=CHSH), 122.8 (*H*C=C). – MS (70 eV): m/z = 118 (46) [M$^+$], 116 (35) [M$^+$ – 2 H], 85 (100) [M$^+$ – SH], 84 (48) [M$^+$ – H_2S], 71 (32) [M$^+$ – H_2S – CH], 58 (23) [M$^+$ – H_2S – 2 CH]. – $C_4H_6S_2$ (118.2); calcd. C 40.64, H 5.12, S 54.24; found C 40.63, H 5.46, S 55.05; molar weight (cryoscopic in benzene: 126). – Conversion into **(*Z,Z*)-1,4-di(acetylthio)-1,3-butadiene** (**11a**; cf. ref.[1a,c,f]): A) An aqueous solution of **5a** (obtained as above) was treated dropwise at 0°C with Ac_2O until precipitation of the product took place (acidification). – B) A solution, prepared from 1.18 g (0.01 mol) **10a** and 15 ml 2N NaOH, was treated with Ac_2O at 0°C as described above. – Colourless needles (EtOH/AcOEt [1:1]); yield: 19 g (70%); m.p. 147-148°C. – IR (KBr):$\bar{\nu}$ = 1700 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 6 H, CH_3), 6.33-6.37 (2 d, 2 H, =CH-CH=; J^1 = 2.1 Hz, J^2 = 8.75 Hz), 6.74-6.78 (2 d, 2 H, =C*H*-SCOCH$_3$; J^1 = 2.1 Hz, J^2 = 8.76 Hz); cf. data in ref.[1f]. – ^{13}C NMR ($CDCl_3$): δ = 30.8 (CH_3), 121.0 (=CH-), 124.8 (=CH-S), 190.4 (C=O). – MS (70 eV): m/z = 202 (10) [M$^+$], 160 (10) [M$^+$ – $COCH_2$], 118 (30) [M$^+$ – 2 $COCH_2$], 85 (24) [M$^+$ – 2 $COCH_2$ – HS], 84 (21) [M$^+$ – 2 $COCH_2$ – H_2S], 43 (100) [$COCH_3^+$]. – $C_8H_{10}O_2S_2$ (202.3): calcd. C 47.50, H 4.98, S 31.70; found C 47.56, H 4.98, S 31.67.

(*Z,Z*)-1,4-Diphenyl-1,3-butadiene-1,4-dithiol (**10h**; cf. ref.[1c]). – A 2N NaOH-solution (containing **5h**), obtained by the procedure for **6h**/method I, was covered with 60 ml Et_2O and carefully acidified with 25% HCl-solution; the aqueous solution was washed twice with 20 ml Et_2O and the combined organic phases were dried with Na_2SO_4 and evaporated. The residue was recrystallized from petroleum ether: Pale yellow needles; yield: 1.11 g (82%); m.p. 99-100°C.[39] – ^{1}H NMR ($CDCl_3$): δ = 3.13 (s; 2H, SH), 6.89 (s, 2H; =CH-), 7.25-7.72 (m, 10H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 125.4, 127.1, 128.5, 128.5 (aromat. C), 134.0, 142.5 (>C=); cf. data in ref.[1f]. – MS (70 eV): m/z = 270 (9) [M$^+$], 237 (100) [M$^+$ – SH], 236 (89) [M$^+$ – H_2S], 204 (25) [M$^+$ – H_2S – S], 202 (15) [M$^+$ – 2 H_2S]. – $C_{16}H_{14}S_2$ (270.4): calcd. C 71.06, H 5.22, S 23.71; found C 71.30, H 5.22, S 23.62. – Conversion into **(*Z,Z*)-1,4-di(acetylthio)-1,4-diphenyl-1,3-butadiene** (**11h**; cf. ref.[1c]): The above noted alkaline solution of **5b** was stirred and treated dropwise with AcCl until neutral: Colourless needles (benzene); yield: 1.10 g (62%); m.p. 158-159°C. – ^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 6 H, CH_3), 7.48 (s, 2 H, =CH-), 7.32-7.62 (m, 10 H, aromat. H). – IR (KBr):$\bar{\nu}$ = 1690 cm^{-1}. – ^{13}C NMR ($CDCl_3$): δ = 30.5 (CH_3), 127.2, 128.5, 128.7, 134.5 (aromat. C, =CH-), 134.8, 140.36 (>C=), 192.4 (C=O); cf. data in ref.[1f]. – MS (70 eV): m/z = 354 (5) [M$^+$], 311 (28), [M$^+$ – $COCH_3$], 268 (32) [M$^+$ – 2 $COCH_3$], 236 (100) [M$^+$ – 2 $COCH_3$ – S]. – $C_{20}H_{18}O_2S_2$ (354.5): calcd. C 67.76, H 5.12, S 18.09; found 67.60, H 5.20, S 18.12.

(*Z,Z*)-1,4-Di(p-tolyl)-1,3-butadiene-1,4-dithiol (**10k**; cf. ref.[1c]). – As described for **10h** using 2.39 g (5 mmol) **4k**: Pale yellow leaflets (Et_2O); yield: 925 mg (62%); m.p. 137-138°C[39]. – ^{1}H NMR ($CDCl_3$): δ = 2.35 (s, 6 H, CH_3), 3.07 (s, 2 H, SH), 6.83 (s, 2 H, =CH-), 7.15-7.54 (2 d, 8 H, aromat. H; J = 8.2 Hz). – ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_3), 124.9, 127.0, 129.1, 133.5, 138.5, 139.7 (aromat. C, =CH-). – MS (70 eV): m/z = 298 (3) [M$^+$], 264 (100) [M$^+$ – H_2S], 249 (5) [M$^+$ – H_2S - CH_3]. – $C_{18}H_{18}S_2$ (298.5): calcd. C 72.47, H 6.08, S 21.49; found C 72.47, H 6.08, S 21.52. – Conversion into **(*Z,Z*)-1,4-di(acetylthio)-1,4-di(p-tolyl)-1,3-butadiene** (**11k**; cf. ref.[1c]) as described for **11h**: Colourless needles (benzene); m.p. 192-193°C. – IR (KBr):$\bar{\nu}$ = 1730 cm^{-1}. – $C_{22}H_{22}O_2S_2$ (382.6): calcd. C 69.07, H 5.79; found C 69.33, H 5.66.

(*Z,Z*)-1-(p-Methoxyphenyl)-4-phenyl-1,3-butadiene-1,4-dithiol (**10l**). – As described for **10h** using 2.4 g (5 mmol) **4l**: Pale yellow needles (petroleum ether in the presence of some $NaBH_4$); yield: 901 mg (60%); m.p. 97-98°C[39]. – ^{1}H NMR ($CDCl_3$): δ = 3.80 (s, 2 H, SH), 3.82 (s, 3H, OCH_3), 6.84-6.90 (2 d, 2 H, =CH-; J = 2.76 Hz), 7.31-7.62 (m, 9 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 55.4 (OCH_3), 124.2, 125.7, 127.1, 127.7, 128.3, 128.4, 132.9 (aromat. C, =CH-), 132.9, 133.7, 134.9, 142.5, 160.0 (>C=). – MS (70 eV): m/z = 300 (4) [M$^+$], 266 (100) [M$^+$ – H_2S], 251 (77) [M$^+$ – H_2S – CH_3]. – $C_{17}H_{16}OS_2$ (300.4): calcd. C67.96, H 5.37, S 21.34; found C 68.06, H 5.29, S 21.29. – Conversion into **(*Z,Z*)-1,4-di(acetylthio)-1-(p-methoxyphenyl)-4-phenyl-1,3-butadiene** (**11l**) as described for **11h**: Pale yellow needles (benzene); m.p. 132-133°C. – IR (KBr):$\bar{\nu}$ = 1710 cm^{-1}. – $C_{21}H_{20}O_3S_2$ (384.5): calcd. C 65.59, H 5.24; found C 65.92, H 5.58.

(*Z,Z*)-1,4-Di(p-methoxyphenyl)-1,3-butadiene-1,4-dithiol (**10m**; cf. ref.[1c]). – As described for **10h** using 2.55 g (10 mmol) **4m**: Pale yellow needles (petroleum ether); yield: 122 mg (74%); m.p. 147-148°C[39]. – ^{1}H NMR ($CDCl_3$): δ = 3.05 (s, 2 H, SH), 3.82 (s, 6 H, OCH_3), 6.79 (s, 2 H, =CH-), 6.87-7.59 (m, 8 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 55.4 (OCH_3), 113.8, 124.5, 128.3 (aromat. C, =CH-), 132.6, 135.0 (>C=), 159.9 (*C*-OCH_3). – MS (70 eV): m/z = 330 (5) [M$^+$], 296 (100) [M$^+$ – H_2S], 281 (93) [M$^+$ – H_2S – CH_3], 266 (18) [M$^+$ – H_2S – 2 CH_3]. – $C_{18}H_{18}O_2S_2$ (330.5): calcd. C 65.42, H 5.49, S 19.41; found C 65.33, H 5.45, S 19.50. – Conversion into **(*Z,Z*)-1,4-di(acetylthio)-1,4-di(p-methoxyphenyl)-1,3-butadiene** (**11m**; cf. ref.[1c]) as described for **11h**: Pale yellow needles (benzene); m.p. 166-167°C. – IR (KBr): $\bar{\nu}$ = 1695 cm^{-1}. $C_{22}H_{22}O_4S_2$ (414.6): calcd. C 63,72, H 5.35; found C 63.30, H 5.31.

B) By reduction of 1,2-dithiines **6**: A solution of 1 mmol **6** in 5ml benzene/20ml EtOH/1ml H_2O was treated at room temperature with 380 mg (10 mmol) $NaBH_4$. The colour of the reaction mixture changed from red to yellow. The mixture was carefully acidified with 2N H_2SO_4, 15 ml benzene added and the organic phase recovered and concentrated. The residue was recrystallized from petroleum ether, isolated yields ≈85% (examples: **10h,k,l,m**).

***Transformation to thiophenes* 12.**

A) By action of acids on **4** (cf. ref.[1e]): A solution of 3 mmol **4** in 20 ml dioxane was treated with a current of dry HCl gas for 2 h. The mixture was allowed to stand overnight, the solvents evaporated and the residue recrystallized from EtOH or AcOH. – Examples: **2,5-Diphenylthiophene (12h)**, 65%, m.p. 152-153°C; **2-phenyl-5-(p-tolyl)thiophene (12j)**, 63%, m.p. 148-149°C; **2,5-di(p-tolyl)thiophene (12k)**, 61%, m.p. 173-174°C; **2-phenyl-5-(p-methoxyphenyl)thiophene (12l)**, 52%, m.p. 165-166°C, **2,5-di(p-methoxyphenyl)thiophene (12m)**, 50%, m.p. 218-219°C. – The same reaction with **3k** yields 55% **12k**. – *B) By sulfur extrusion from* **6**: A solution of 100 mg **6** in 30 ml AcOEt was exposed for 4-5 h at room temperature to day-light whereupon complete decolouration occurs (cf. also the thermal sulfur extrusion, e.g in DMSO above 100°C in »Results and Discussion« and ref.[28]). After evaporation the residue was recrystallized in order to separate the product from coformed sulfur: Yields almost quantitative. Examples: **2,5-Di(p-*n*-butylphenyl)thiophene (12n)**, m.p. 142°C (no occurrence of a nematic phase in opposite to **6n**), R_f = 0.79 (silica gel, benzene); UV/ Vis (MeCN): λ_{max} (lg ε) = 233 (4.11), 327 (4.40) nm; ^1H NMR ($CDCl_3$): δ = 0.93 (t_c, 6 H, CH_3), 1.24-1.45 (m, 4 H, CH_2), 1.53-1.68 (m, 4 H, CH_2), 2.61 (t_c, 4 H, CH_2), 7.15-7.54 (m, 10 H, aromat. H, =CH-); ^{13}C NMR ($CDCl_3$): δ = 13.9 (CH_3), 22.3, 35.3, 37.5 (CH_2), 125.4, 127.3, 128.2, 131.5, 138.7, 143.3 (aromat. C, =CH-, >C=); MS (70 eV): m/z = 348 (100) [M^+], 306 (43) [$M^+ - C_3H_6$]; $C_{24}H_{28}S$ (348.5): calcd. C 82.70, H 8.10, S 9.20; found H 82.91, H 8.43, S 9.36. – **2,5-Di(p-*t*-butylphenyl)thiophene (12o)**, m.p. 164°C, R_f = 0.77 (silica gel, benzene); UV/ Vis (MeCN): λ_{max} (lg ε) = 235 (4.15), 326 (4.47) nm; ^1H NMR ($CDCl_3$): δ = 1.33 (s, 18 H, CH_3), 7.22-7.57 (m, 10 H, aromat. H, =CH-); ^{13}C NMR ($CDCl_3$): δ = 31.3 (CH_3), 34.6 (>C<), 123.5, 125.3, 125.8, 131.6, 143.2, 146.9 (aromat. C, =CH-, >C=); MS (70 eV): m/z = 348 (100) [M^+], 333 (55) [$M^+ - CH_3$]; $C_{24}H_{28}S$ (348.5): calcd. C 82.70, H 8.10, S 9.20; found C 82.71, H 7.84, S 9.24. – **2,5-Di(p-cyclohexylphenyl)thiophene (12p)**, m.p. 233°C, R_f = 0.86 (silica gel, benzene); UV/ Vis (MeCN): λ_{max} (lg ε) = 232 (4.20), 330 (4.44) nm; ^1H NMR ($CDCl_3$): δ = 1.30-2.50 (m, 22 H, C_6H_{11}), 7.19-7.55 (m, 10 H, aromat. H, =CH-); ^{13}C NMR ($CDCl_3$): δ = 26.2, 26.9, 34.4 (CH_2), 44.3, (>CH-), 123.4, 125.6, 127.3, 132.0, 143.3, 147 .5, (aromat. C, =CH-, >C=); MS (70 eV): m/z = 400 (100) [M^+], 331 (13) [$M^+ - C_5H_9$]; $C_{28}H_{32}S$ (400.6): calcd. C 83.94, H 8.05, S 8.01; found C 83.87, H 7.98, S 8.06. – **2,5-Di[2-(5,6,7,8-tetrahydronaphthyl]thiophene (12q)**, m.p 164°C, R_f = 0.77 (silica gel, benzene); UV/ Vis (MeCN): λ_{max} (lg ε) = 231 (4.28), 328 (4.54); ^1H NMR ($CDCl_3$): δ = 1.22-1.51 (m, 16 H, C_4H_8), 7.23-7.63 (m, 8 H, aromat. H, =CH-); ^{13}C NMR ($CDCl_3$): δ = 22.0, 30.6, 30.8, 36.7 (CH_2), 127.0, 127.3, 128.3, 128.6, 128.8, 129.3, 137.8, 149.9 (aromat. C, =CH-, >C=); MS (70 eV): m/z = 344 (100) [M^+], 310 (17) [$M^+ - H_2S$]; $C_{24}H_{24}S$ (344.5): calcd. C 83.67, H 7.03, S 9.30; found C 83.07, H 7.70, S 9.81.

C) By thermolysis of **10** (H_2S-elimination): Heating of **10** for several minutes at the melting point or refluxing a solution of **10** in a high-boiling solvent (e.g. xylene) for 5-10 min gave almost quantitative yields (examples: **12h,j**).

***Alkylation of 5 and* 10 (11)**

A) The alkaline aqueous solution of **5** or **10**, obtained from the reductive debenzylation of **4** (described in the procedure for **6h**) was diluted with the equal amount EtOH and subsequently treated with two molar equivalents of the organic halide (benzyl chloride, methyl iodide, ethyl iodide). The precipitated products (**4**, **13**, **14**) were filtered by suction and recrystallized; yield: 70-90%. – B) 10 mmol **11** were dissolved (saponified) in a solution of 3.4 g (60 mmol) KOH in 20 ml MeOH, after addition of the organic halide at elevated temperature (≈40°C) the products precipitate; yield: 80-95%. – **(*Z,Z*)-1,4-Di(methylthio)-1,4-diphenyl-1,3-butadiene (13h)**, m.p. 134°C (EtOH/AcOEt [1:1]), R_f = 0.68 (benzene); ^1H NMR ($CDCl_3$): δ = 2.03 (s, 6 H, CH_3), 7.23-7.63 (m, 12 H, aromat. H, =CH-); ^{13}C NMR ($CDCl_3$): δ = 16.4 (CH_3), 128.0, 128.1, 128.4, 129.4, 139.6. 140.9 (aromat. C, =CH-, >C=); MS (70 eV): m/z = 298 (21) [M^+], 251 (56) [$M^+ - CH_3S$], 236 (85) [$M^+ - CH_3S - CH_3$], 202 (51) [$M^+ - CH_3S - CH_3 - H_2S$], 121 (100) [$C_6H_5CS^+$], 77 (81) [$C_6H_5^+$]; $C_{18}H_{18}S_2$ (298.4): calcd. C 72.44, H 6.07, S 21.49; found C 72.41, H 6.19, S 21.55; identical with product obtained by thiol addition to **1h** using 16.1 g (75 mmol) S-methylisothiouronium sulfate according to procedure for **4h**/method I (yield: 64%). – Further examples: **13a**, b.p. 93-94°C/3 Torr [$C_6H_{10}S_2$ (146.3)]; **13j**, m.p. 140-141°C [$C_{19}H_{20}S_2$ (312.5)]; **13k**, m.p. 187-188°C [$C_{20}H_{22}S_2$ (326.5)]; **13l**, m.p. 106-107°C [$C_{19}H_{20}OS_2$ (328.5)]; **13m**, m.p. 163-164°C [$C_{20}H_{22}O_2S_2$ (358.5)]; **13t**, m.p. 111-112°C [$C_{14}H_{16}S_4$ (312.5)]. – **(*Z,Z*)-1,4-Di(ethylthio)-1,4-diphenyl-1,3-butadiene (14h)**, m.p. 99-100°C (EtOH), R_f = 0.72; ^1H NMR ($CDCl_3$): δ = 1.09 (t_c, 6 H, CH_3), 2.48 (q_c, 4 H, CH_2), 7.32-7.68 (m, 12 H, aromat. H, =CH-); ^{13}C NMR ($CDCl_3$): δ = 15.1 (CH_3), 27.1 (CH_2), 128.1, 128.5, 131.5, 138.4, 139.6, 140.3 (aromat. C, =CH-); MS (70 eV): m/z = 326 (10) [M^+], 265 (25) [$M^+ - C_2H_5S$], 236 (100) [$M^+ - C_2H_5S - C_2H_5$], 202 (33) [$M^+ - C_2H_5S - C_2H_5 - H_2S$], 121 (89) [$C_6H_5CS^+$]; $C_{20}H_{22}S_2$ (326.5): calcd. C 73.57, H 6.79, S 19.64; found C 73.96, H 6.78, S 19.36; identical with product obtained by thiol addition to **1h** using 27.75 g (150 mmol) S-ethylisothiouronium bromide according to procedure for **4h**/method I (yield: 76%). – Further examples: **14a**, b.p. 95-96°C/0.9 Torr [$C_8H_{12}S_2$ (174.3)]; **14j**, m.p. 96-97°C [$C_{21}H_{24}S_2$ (340.6)]; **14k**, m.p. 140-141°C [$C_{22}H_{26}S_2$ (354.6)]; **14l**, m.p. 76-

78°C [$C_{21}H_{24}OS_2$ (356.6)]; **14m**, m.p. 113-114°C [$C_{22}H_{26}O_2S_2$ (386.6)]; **14t**, m.p. 108-109°C [$C_{16}H_{18}S_4$ (338.6)]. – Compounds **14h**, **14j**, **14k**, **14l**, **14m** and **14t** were also produced by reaction of the corresponding 1,2-diaroylethenes with EtSH under acidic conditions (1,4-dioxane/HCl; p-toluenesulfonic acid, Δ) as previously described in ref.[1e].

(*Z*,*Z*,*Z*,*Z*)-1,4-Diphenyl-1,4-di(β-styrylthio)-1,3-butadiene (15). – A solution of 540 mg (2 mmol) **10h**, 225 mg (4 mmol) KOH and 408 mg (4 mmol) phenylacetylene in 6 ml MeOH was refluxed 7 h. Oily droplets gradually separated and crystallized. The hot methanolic solution was decanted and the residue after washing with H_2O and MeOH recrystallized from AcOEt/EtOH (1:1). – Yellow needles; yield: 500 mg (52%); m.p. 159-160°C. – UV/Vis (EtOH): λ_{max} (lg ε) = 257 (4.47), 292 (4.55), 381 (4.53) nm. – ^{1}H NMR ($CDCl_3$): δ = 6.02 (d, 2 H), 6.37 (d, 2 H; H^α, H^β; J = 10.8 Hz), 7.23 (m, 2H, aromat. H), 7.31 (s, 2 H, -C*H*=C[S]-C_6H_5), 7.36 (m, 10 H, aromat. H), 7.50, 7.54, 7.61 (m, 8 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 125.1, 126.4, 127.1 (=CH-), 128.4, 128.6, 128.7, 129.5 (aromat. C), 136.4, 139.3, 139.4 (>C=). – MS (70 eV): m/z = 474 (40) [M^+], 339 (100) [$M^+ - C_6H_5CHCHS$], 261 (44) [$M^+ - C_6H_5CHCHS - C_6H_6$], 236 (34) [$M^+ - C_6H_5CHCHS - C_6H_5CHCH$], 121 (31) [$C_6H_5CS^+$]. – $C_{32}H_{26}S_2$ (474.7): calcd. C 80.97, H 5.52, S 13.51; found C 81.10, H 5.73, S 13.89.

7,10-Diphenyl-3,4-benzo-1,6-dithiacyclododeca-3,7,9-triene (16). – A solution of 840 mg (15 mmol) KOH in 4 ml MeOH and 300 ml DMF was treated dropwise with solutions of 900 mg (2.5 mmol) **11h** in 50 ml DMF and of 660 mg (2.5 mmol) o-di(bromomethyl)benzene in 50 ml DMF at 55°C with stirring under an argon atmosphere. After further stirring at this temperature for 3 h, the solvents were evaporated, the residues dissolved in 50 ml water and the solution extracted three times with 30 ml portions of CH_2Cl_2. The combined extracts were concentrated and the residue was recrystallized from AcOEt. – Pale yellow leaflets; yield: 100 mg (11%); m.p. 142°C; R_f = 0.67 (silica gel, benzene). – UV/Vis (MeCN): λ_{max} (lg ε) = 268 (4.21), 343 (4.25) nm. – ^{1}H NMR ($CDCl_3$): δ = 3.44 (s, 4 H, CH_2), 7.09-7.22 (m, 16 H, aromat. H, =CH-). – ^{13}C NMR ($CDCl_3$): δ = 36.5 (CH_2), 126.9, 127.2, 128.2, 130.7, 134.7, 138.0, 138.5, 139.9 (aromat. C, =CH-, >C=). – MS (70 eV): m/z = 273 (10) [M^+], 236 (96) [$C_6H_5CCHCHCSC_6H_5^+$], 136 (68) [$SCH_2C_6H_4CH_2^+$ (dihydroisothionaphthene)], 121 (100) [$C_6H_5CS^+$], 104 (69) [$CH_2C_6H_4CH_2^+$]. – $C_{24}H_{20}S_2$ (372.5): calcd. C 77.38, H 5.41, S 17.21; found C 77.28, H 5.22, S 17.23. – From the mother liquor **12h** (32%) and dihydroisothionaphthene were isolale (TLC, R_f = 0.59 [silica gel, benzene]).

Reductive defunctionalization of **14h** *to* **(*E*)-1,4-Diphenyl-2-butene (18)**: 6.53 g (20 mmol) **14h** was treated with 2.0 g (87 mmol) Na in 120 ml liquid NH_3 at -70°C and worked up as described for **6h**/method I. After addition with 100 ml 2N NaOH to the evaporation residue, the precipitated white solid was removed by suction filtration and recrystallized from EtOH (the filtrate shows no reaction with $FeCl_3$). – White needles; yield: 2.8 g (67%); m.p. 43-44°C (ref.[40a]: 43-45°C; ref.[40b]: 45.5-46°C); identical with the product obtained from the analogous treatment of (*Z*,*Z*)-1,4-diphenyl-1,3-butadiene (72%). – IR (nujol): $\tilde{\nu}$ = 970 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 3.35-3.41 (m, 4 H, CH_2), 5.64-5.73 (m, 2 H, =CH-), 7.13-7.28 (m, 10 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 39.0 (CH_2), 126.0, 128.4, 128.6, 130.5, 140.8 (aromat. C, =CH-). – MS (70 eV): m/z = 208 (36) [M^+], 117 (100) [$C_6H_5CH_2CHCH^+$], 91 (35) [$C_7H_7^+$]. $C_{16}H_{16}$ (208.3).

Bromine addition: **3α,4β,5α,6β-Tetrabromo-3,6-diphenyl-1,2-dithiane (21)**. – A suspension of 0.27 g (1 mmol) **6h** in 4 ml CCl_4 was treated at -5°C with 0.32 g (2 mmol) Br_2. A clear solution was obtained and a solid precipitated. The solid was collected, washed with ice-cold CCl_4 and quickly dried i. vac. – Buff-coloured crystals; yield: 0.38 g (65%); m.p. 83-84°C (dec., from 77°C formation of gas and colour change to orange red). – ^{1}H NMR ($CDCl_3$): δ = 5.40 (s, 2 H, >CHBr), 7.47 m_c, 6 H aromat. $H_{[m,p]}$), 7.88 (m_c[broad, hindrance of rotation], 4 H, aromat. $H_{[o]}$). – ^{13}C NMR ($CDCl_3$): δ = 65.5 (>CHBr), 81.8 >CBrPh), 127.7 (aromat. $C_{[p]}$), 128.9, 130.2 (aromat. $C_{[o,m]}$), 138.8 (aromat. $C_{[i]}$). – $C_{16}H_{12}Br_4S_2$ (588.0); storage stability even at -20°C only 3-4 d.

Condensation reaction to 3,6-disubstituted pyridazines 22. – A) To a mixture of 3 ml EtOH and 5 ml pyridine (liberated from oxygen by previous heating under an argon atmosphere) was added 0.27 g (1 mmol) **6h** and 0.12 ml (2.4 mmol) 98% hydrazine hydrate. The mixture was heated under exclusion of day-light and oxygen 2 h on a wather bath (yellow brown solution). After chilling **3,6-diphenylpyridazine (22h)** precipitated which was separated and recrystallized from EtOH. – Colourles leaflets; yield: 100 mg (43%); m.p. 223°C (ref.[41a]: 219-220°C); $C_{16}H_{12}N_2$ (232.3). – The residues were concentrated and treated with water to afford a solid which was recrystallized from a little EtOH to give 110 mg (47%) 2,5-diphenylthiophene (**12h**) (pale yellow plates; m.p. 148-149°C). – Further examples: **22j** (48%; m.p. 185-186°C [ref.[41a]: 185-186°C]; $C_{17}H_{14}N_2$ [246.3]), **22k** (38%; m.p. 233-234°C [ref.[41b]: 231-232°C]; $C_{18}H_{16}N_2$ [260.3]), **22l** (45%); m.p. 195-196°C [ref.[41a]: 195-196°C]; $C_{17}H_{14}N_2O$ [262.3]). – B) As described precedingly with 1 mmol **10** or **11**, 0.5 ml EtOH, 1.5 ml pyridine and 75 mg (1.5 mmol) hydrazine hydrate. Hydrogen sulfide was produced and the reaction was completed by heating on a wather bath for 1 h. The product was obtained by dilution of the solution with water: Yields 75-85% (from 10), 70-75% (from **11**), examples: **22h**, **22j**, **22k**, **22l**, **22m** (m.p. 236-237°C [ref.[41a]: 234-235°C]; $C_{18}H_{16}ON_2$ [276.3]), **22t** (m.p. 178-179°C; $C_{12}H_8N_2S_2$ [244.3]).

Acknowledgements: Financial support by the Fonds der Chemischen Industrie, Frankfurt/Main, and the Deutsche Forschungsgemeinschaft is acknowledged. We are very grateful to Dr. Allan Dunn, Frankfurt/Main, for editorial assistance.

References and Notes

☆ *Dedicated to Professor Siegfried Hünig on the occasion of his 75th birthday*

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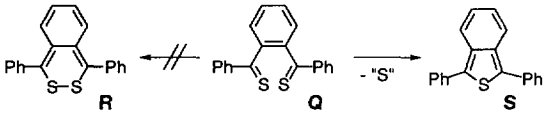

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(*Received in Germany* 27 *June* 1996; *accepted* 9 *August* 1996)