THE CONVERSION OF THIOKETONES TO 1,2,4,5-TETRATHIANES AND ITS MECHANISM

Rolf Huisgen* and Jochen Rapp

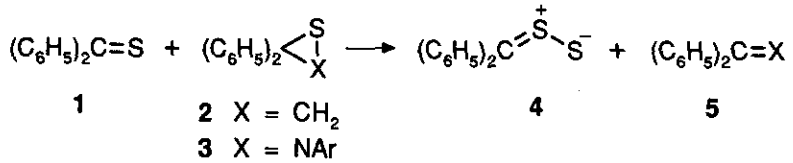
Institut für Organische Chemie der Universität München
Karlstr. 23, D-80333 München, Germany

Dedicated to Professor Teruaki Mukaiyama, Tokyo, on the occasion of his 70th birthday

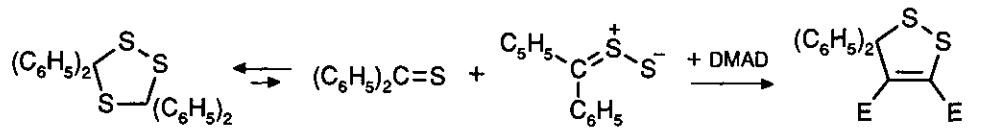
Abstract - Thiobenzophenone and adamantanethione react with sulfur (1:1) under catalysis by sodium thiophenoxide in acetone at rt furnishing 1,2,4,5-tetrathianes (**9** and **43**) in high yields. An attack of the oligothiolate ($R\text{-}S_x^-$) on the C-atom of $>C=S$ is proposed as initiating step. Thione *S*-sulfides ($R_2C=S^+-S^-$, thiosulfines) cannot be intermediates, since they combine fast with thiones affording 1,2,4-trithiolanes. With more sulfur, adamantanethione produces the 1,2,3,5,6-pentathiepane-*bis*(*spiroadamantane*) (**44**) which interconverts with the tetrathiane, but not with the 1,2,4-trithiolane, in an equilibrium catalyzed by $R\text{-}S_x^-$. According to ^{13}C NMR evidence, the tetrathiane-bis(spiroadamantane) occurs in a twist conformation which inverts with $\Delta G^{\neq}$ 16.0 kcal mol^{-1}.

INTRODUCTION

We reported on the conversion of aromatic and alicyclic thioketones into thione *S*-sulfides (thiosulfines) of type (**4**) by sulfur transfer from 2,2-diphenylthiirane (**2**) at rt;[1,2] the reaction is formulated for thiobenzophenone (**1**). 1,3-Dipoles of type (**4**) are not isolable; in a fast subsequent 1,3-cycloaddition, they combine *in situ* with a second molecule of thione furnishing 1,2,4-trithiolanes. Tetraphenyltrithiolane (**6**) – in contrast to alkylated trithiolanes – equilibrates above rt with a small concentration of thiobenzophenone *S*-sulfide (**4**) and **1**, making **6** a useful storage form of **4**. The latter can be intercepted by activated acetylenes providing 1,2-dithioles of type (**7**).[2] 2-Aryl-3,3-diphenylthiaziridines (**3**) were proposed to be intermediates in the reaction of aryl azides with **1** at 80 °C; **3** transfers a formal sulfur atom to **1**, even faster than **2**, and **6** is again the product.[3]



1 **2** X = CH_2, **3** X = NAr **4** **5**



6 **1** **4** **7** E = CO_2CH_3

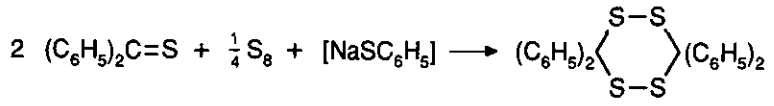
Although phenylated thiiranes are capable of converting thiones into thione *S*-sulfides (**2**) and related compounds are not the most rational reagents for a larger preparative scale. Can elementary sulfur serve as an equivalent of the formal sulfur atom ?

On treating adamantanethione with sulfur in refluxing xylene, Wai and Sammes obtained the corresponding 1,2,4-trithiolane.[4] However, this reaction was not observed with other thioketones. We found that thiones do not react with S_8 at temperatures < 100 °C. Furthermore, aromatic trithiolanes of type (**6**) decompose above rt *via* **4** into thione + elemental sulfur.[2]

Various nucleophilic reagents are known to open the ring of cyclooctasulfur.[5] We chose a catalytic amount of sodium thiophenoxide. Although our goal, the conversion of thiones into thione *S*-sulfides, was not achieved, the results are surprising and mechanistically enlightening.

3,3,6,6-TETRAPHENYL-1,2,4,5-TETRATHIANE

Flowers of sulfur partially dissolved in acetone, when stirred with sodium thiophenoxide (**8**, 1.3 mol% based on "S", 10 mol% based on S_8), a deep-redbrown suspension resulted. Thiobenzophenone (**1**/"S" = 1:2) was added and the blue color disappeared on stirring for 3 d at rt; 95% of the colorless, crystalline tetrathiane (**9**) was isolated.[6] Since the solubility of **9** in acetone is not high, the reaction mixture remains heterogeneous. When the amount of sulfur was diminished to 1 g-atom equiv, *i.e.*, the stoichiometric requirement for the formation of **9**, 81% of **9** was isolated after refluxing with 2.5 mol% of **8** in acetone for 1.5 h.

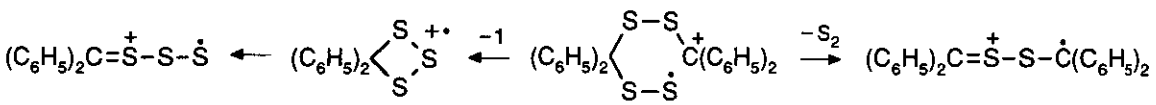


1 **8** **9**

It is not a farfetched idea, that **9** might come from the *dimerization* of thiobenzophenone *S*-sulfide (**4**). However, this cannot be correct. If the amount of sulfur was reduced to 1 g-atom per 2 mol of **1**, the overall stoichiometry would be just right for the formation of the 1,2,4-trithiolane (**6**) by fast 1,3-cycloaddition of **4** to **1**; it should be recalled that thiones are *superdipolarophiles*.[7] Nevertheless, the 1:2 reaction at rt still yielded 77% of **9**, now based on S_8. Much of the thione remained unconsumed, and TLC of the mother liquor revealed only a tiny amount of **6**.

As we reported, the reaction of **1** with 0.5 equiv of thiirane (**2**) in pentane at rt (24 d) afforded 92% each of trithiolane (**6**) and 1,1-diphenylethylene;[1,2] no tetrathiane (**9**) was observed. In an additional experiment, **1** and 0.5 equiv of **2** were heated to 100 °C for 1 h; 1,1-diphenylethylene was quantitatively formed, but neither **6** nor **9** showed up; the thermal sulfur loss from **4** furnished **1** and elementary sulfur.[2] The overall effect is a catalysis of the cleavage of **2** into olefin + S_8 by thione (**1**). *Thus, the formation of the 1,2,4,5-tetrathiane* (**9**) *in the thiolate-catalyzed reaction of* **1** *with sulfur does not involve the thione S-sulfide* (**4**) *as an intermediate.*

The ^{13}C NMR spectrum of **9** reveals the equivalence of the four phenyl groups. The high symmetry either points to a twist conformation (D_2 symmetry) or is the result of fast conformational equilibration (see later section).



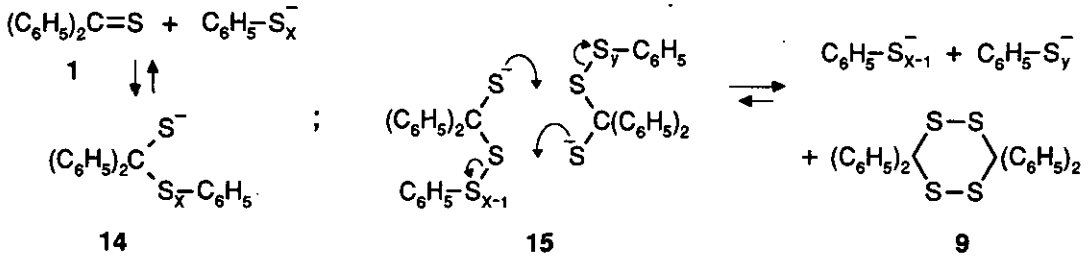
10 *m/z 262* (3.4%) **11** **12** *m/z 460* (0.1%) **13** *m/z 396* (4.5%)

The radical cation of thiobenzophenone, the 9-fluorenyl cation, and $C_6H_5-C\equiv S^+$ constitute the most populous peaks in the MS of **9**. The molecular peak – perhaps the *distonic* radical ion (**12**) – is tiny, but $[M^+ - 2S]$ demands interest as a thiobenzophenone dimer; we prefer the open-chain resonance hybrid (**13**) to a dithietane radical ion. The likewise small peak *m/z* 262 is $C_{13}H_{10}S_3^{+\cdot}$; again the distonic species (**10**) appears more attractive than the cyclic **11**. In the MS of the tetrathiane-bis(spiroadamantane) (**43**), $C_{10}H_4S_3^+$ $[M^+ - R_2S]$ is even the base peak (*vide infra*). The molecular formulae were secured by the intensities of ^{13}C and ^{34}S isotope peaks and by high resolution. A recent compilation of literature data [8] revealed that the MS of the tetrathiane parent and its alkylated derivatives likewise show strong peaks for $RR'CS_3^{+\cdot}$ and $RR'CS^{+\cdot}$; the loss of S_2 may be suggested.

MECHANISM OF TETRATHIANE FORMATION

The thiocarbonyl group is an ambident electrophile. Organometallic compounds preferentially attack at sulfur (*thiophilic*), but some at carbon, the ratio depending on the nature of

the reactants and the conditions.[9,10] The dual regiochemistry in the cycloadditions of diazomethane to thioketones offers another illustration.[11-13] The sulfurization by thiirane (**2**) giving thione *S*-sulfides [2] parallels the thiophilic reactivity. We propose that *nucleophilic attack on the carbon atom* of the thione initiates the formation of 1,2,4,5-tetrathianes.



14 **15** **9**

The ring opening of S_8 by sodium thiophenoxide (**8**) gives rise to an equilibrium mixture of oligothiolates of different chain length, $C_6H_5\text{-}S_x^-$. The latter adds to the carbon atom of **1**, and the anionic sulfur of adduct (**14**) attacks the S – S bond of another anionic adduct. The rapid and reversible metathesis reaction of thiolates with disulfides (or higher oligosulfides, R-S_n-R') is well known.[14,15] The interaction according to formula (**15**) does not mean a straightforward (or even concerted) double nucleophilic attack, but may rather be regarded as the book-keeping for the formation of the thermodynamically favored tetrathiane (**9**). The thiolate anion enters into S_N2 type substitutions only at the sulfur atoms in the oligothiolate chain and not at the central C-atom of **14**. Therefore, the trithiolane (**6**) is not a constituent of the established equilibria. The tetraphenyl-1,2,3,5,6-pentathiepane, the 7-membered ring, appears likewise not to be involved in the equilibrium, in contrast to the sulfurization of adamantanethione (**41**) which will be discussed below.

It is conceivable that the oligothiolate does not monopolize on the *C-attack* of the C=S double bond. However, the thione *S*-sulfide originating from an eventual *S-attack*, is unstable in the presence of $R\text{-}S_x^-$ functions. Nucleophilic reagents initiate the sulfur loss from thione *S*-sulfides. In the formal equilibrium,

thione + 1/8 S_8 ⇆ thione *S*-sulfide,

the left side is favored. The sleight-of-hand in the preparation of thione *S*-sulfide (**4**) by S transfer from thiirane (**1**) consists in immobilizing the above equilibrium by capturing **4** with the cycloaddition to **1** and precipitation of the scarcely soluble trithiolane (**6**).[2] In the presence of oligothiolates, $C_6H_5\text{-}S_x^-$, however, even an excess of **1** cannot save more than a trace of **4**, if it should occur alongside with **14**.

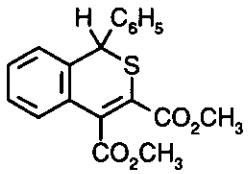
THERMOLYSIS OF TETRATHIANE 9

The colorless tetrathiane (**9**) turns blue at the mp 209 °C indicating thiobenzophenone (**1**) as cleavage product. When **9** – stable yet in boiling benzene – was refluxed in mesitylene (150 °C) for 15 h, the degradation was complete; we isolated **1** nearly quantita-

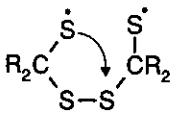
tively; the residue of the distillation consisted mainly of elementary sulfur. Tetraphenyl-1,2,4-trithiolane (**6**) decomposes into **1** + 1/8 S_8 at much lower temperature (refluxing chloroform) and slowly even at rt.[2]

When the thermolysis of **9** in mesitylene was carried out in the presence of dimethyl acetylenedicarboxylate (DMAD) which is a scavenger for thione *S*-sulfide (**4**), the 1*H*-2-benzothiopyran derivative (**16**), *i.e.*, the Diels-Alder product of **1** and DMAD,[16] was found (44%); the dithiole (**7**) was missing.

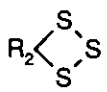
A reservation: On repeating the interception experiment by heating **9** and DMAD *in chloroform* in the sealed tube at 150 °C, we isolated 26% of dithiole (**7**) besides 36% of **16**. We cannot exclude a competing acid-catalyzed pathway. On sealing the glass tube containing a $CHCl_3$ solution, the occurrence of some HCl can hardly be avoided. Recently we secured an acid catalysis under the same conditions in another context.[2]



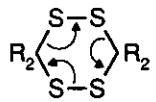
16



17



18



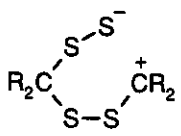
19

The 1,3-dipolar cycloreversion of 1,2,4-trithiolanes, *e.g.*, **6** → **4** + **1**, is allowed to be *concerted* by orbital control. In contrast, the cleavage of the tetrathiane into 2 molecules of thione *S*-sulfide should be a twostep process and is perhaps less advantageous. The breaking of a S–S bond in the initiating step requires less activation energy than that of a C–S bond. A homolysis of the S–S bond of **9** may open other channels, even chain reactions. It is imaginable, that the ring-opened diradical (**17**) undergoes a cleavage to thione + trithietane (**18**), the latter as an intermediate. Furthermore, a symmetry-allowed 6π fragmentation according to **19** is conceivable, leading to 2 molecules of thione + S_2. The process should be endothermic, and becomes energetically feasible by 4 S_2 → S_8. Since the dienophilic activity of S_2 is known,[17] tetrathianes might be precursors of S_2. The thermolysis of tetrathianes will be a rewarding subject for further studies.

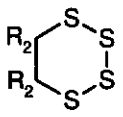
DO THIONE *S*-SULFIDES DIMERIZE ?

Repeatedly, the elusive thione *S*-sulfides have been claimed to be precursors of 1,2,4,5-tetrathianes. A twostep dimerization (and cycloreversion) *via* **20** is *a priori* conceivable, as long as the substituents R stabilize positive charge or a radical. A dimerization leading to the 1,2,3,4-tetrathiane (**21**) cannot be ruled out either; for thiobenzophenone *S*-methylide (**22**) such a head-head dimerization was observed.[18] On the other hand, *S*-oxides of

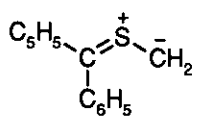
thioaldehydes prefer a dimerization pathway giving rise to the 5-membered *S*-oxide (**23**) which, in turn, rearranges to the dithietane *S*-dioxide (**24**).[19,20]



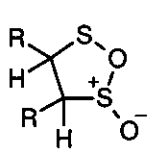
20



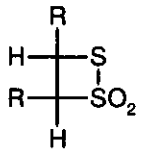
21



22

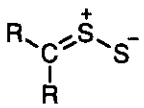


23

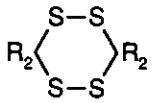


24

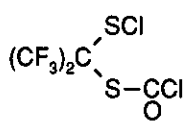
However, the various dimerization schemes are rather hypothetical. If we accept the scavenging by cycloaddition to dipolarophiles as a good criterion for the presence of thione *S*-sulfides (recently reviewed),[2] then we must state that *for none of these examples a dimerization has been observed*. In the absence of intercepting reagents, the thione *S*-sulfides lose sulfur; a reasonable mechanism which avoids the intermediacy of the sulfur atom has been proposed.[2] Wherever a thione *S*-sulfide was assumed as a precursor of a 1,2,4,5-tetrathiane, a confirmation by a mechanistic study would be desirable. Doubts are appropriate, especially when the medium contains nucleophiles or thiones.



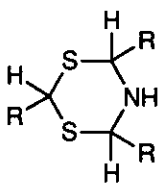
25 R = $CONHCH_3$
26 R = $CO_2C_2H_5$
27 R = CF_3



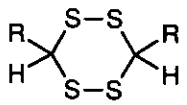
28
29
30



31

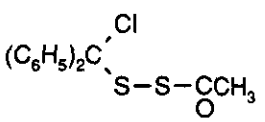


32 R = Aryl, CH_3

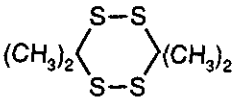


33

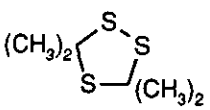
Thiosulfine (**25**) was proposed for a product obtained from *N,N'*-dimethylmalonamide and S_2Cl_2.[21] Kutney and Still recognized it as the tetrathiane (**28**) and suggested a pathway which shuns **25**.[22] Saalfrank and Rost converted 1,1,3,3-tetraethoxyallene to **29** by S_2Cl_2,[23] but the conjectured occurrence of thione *S*-sulfide (**26**) is not mandatory. On heating **31** to 110 °C, Sundermeyer *et al.* isolated **30**; a dimerization of the dithiirane – in equilibrium with **27** – was supposed.[24] The oxidation of dihydro-1,3,5-dithiazines (**32**) gives rise to *cis,trans*-isomeric tetrathianes (**33**);[25] since the interception by CC double or triple bonds was not successful, the invoking of thione *S*-sulfides as intermediates lacks conviction. In the search for thiosulfines, Senning *et al.* treated **34** with morpholine and discussed that a product with mp 110-112 °C might be the formal dimer (**9**);[26] however, **9** has mp 209 °C.



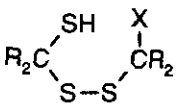
34



35



36

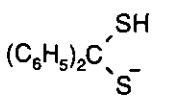


37 X = NHR'
38 X = SH

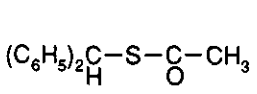
In 1887, Willgerodt reacted acetone with aqueous ammonium oligosulfide and described the product as "duplodithioacetone"(**35**);[27] the optimized procedure gave 32%, based on the oligosulfidic sulfur.[28] Various cyclic ketones likewise afforded tetrathiane-bis-spiranes in moderate yield.[29,30] According to Asinger *et al.*, the combined treatment of ketones with hydrogen sulfide, amines, and S_8 afforded 1,2,4-trithiolanes, 1,2,4,5-tetrathianes, and pentathiepanes.[31] The nature of the primary or secondary amine had a stunning influence on the product yield. Under the best conditions with acetone and diisobutylamine, the yield of trithiolane (**36**) reached 45%, based on S_8. On doubling the amount of elemental sulfur, the authors isolated 50% of the tetrathiane (**35**) instead. Though mechanistically not clarified, sequences of addition and elimination reactions with intermediates of type (**37**) and **38** were assumed. The involment of an equilibrium system was underlined by the conversion of trithiolanes with butylamine into ketimines.[31]
It is rather improbable that thione *S*-sulfides play a role in these reactions. The function of S_8 in the mix was ascribed to a dehydrogenation of thiols to disulfides (like **37**, **38**).[31] In our opinion, the superior nucleophilicity of S_2^{--}, compared with S^{--}, is important here.

REACTIONS OF TETRATHIANE (9)

Franek's recent fine review [8] leaves no doubt that the reactions of 1,2,4,5-tetrathianes have not been studied systematically. By reduction of **9** with lithium aluminum hydride and subsequent acetylation, we obtained diphenylmethyl thioacetate (**40**, 62%). Probably, the hydridic cleavage of the disulfide bonds is followed by an elimination of HS^- from **39**, and **1** consumes another hydride equivalent. The blue color of **1** was observed for a while, and the evolution of H_2 demonstrated the interaction of hydride with HS^- or R-SH. The $LiAlH_4$ reduction of tetraalkyltetrathianes to monothiols has been described before.[32]
Copper powder at 180 °C desulfurized **9** to afford tetraphenylethylene (98%).



39



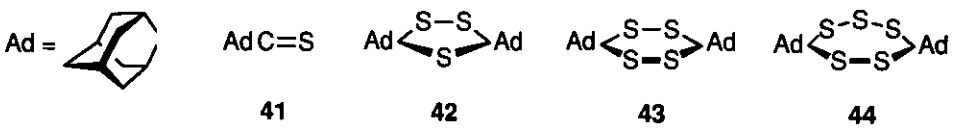
40

As for the interrelations of polysulfide rings, it should be mentioned that neither triethyl phosphite nor triphenylphosphane in refluxing THF converted **9** to the 1,2,4-trithiolane (**6**);

we doubt that thermodynamic reasons block this desulfurization. A reservation: we are dealing here with the sterically hindered tetraphenyltetrathiane. Takikawa *et al.* reported that the *cis,trans* mixture of 3,6-diphenyltetrathiane (**33**) was transformed to the 1,2,4-trithiolane "in good yield" by triphenylphosphane or KCN in DMF.[25]

SULFURIZATION OF ADAMANTANETHIONE

Treatment of adamantanethione (**41**) with 1.0 g-atom of sulfur (S_8) and a few percent of sodium thiophenoxide (**8**) in acetone furnished the 1,2,4,5-tetrathiane-bis(spiroadamantane) (**43**) in 80-83% yield. The reaction proceeded in suspension; before the sulfur was completely dissolved, the colorless **43** precipitated. The sulfurization of **41** was faster than that of **1**, *e.g.*, 3 h *vs.* 3 d at rt and 15 min *vs.* 1.5 h in refluxing acetone.



41 **42** **43** **44**

The dichotomy of the sulfurization pathways with S_8 and [$NaSC_6H_5$] on one side and with diphenylthiirane (**2**) on the other is the same for **1** and **41**. The reaction of **41** with 0.5 g-atom of sulfur – the correct stoichiometry for the formation of the trithiolane (**42**) – produced 98% of the tetrathiane (**43**), based on sulfur (S_8); only a trace of **42** was observed by TLC. On the other hand, the 2:1 interaction of **41** with thiirane (**2**) gave rise to 80% of **42** and no **43**.[1,2]

Whereas the sulfurization of **1** reached its end in the tetrathiane (**9**), that of **41** went beyond that stage. Interaction of **41** with 1.8 g-atom of sulfur and 3 mol% of **8** in acetone at rt furnished 88% of the crude pentathiepane-bis(spiroadamantane) **44** (78% after purification). Since the intermediate tetrathiane (**43**) is only scarcely soluble, the suspension had to be stirred for 7 h. Of course, the isolated **43** was likewise converted to **44** with an excess of sulfur and catalysis by **8**.

After heating of the pentathiepane (**44**) with 32 mol% of $NaSC_6H_5$ (**8**) in acetone at 60°C, a substantial conversion to **43** and sodium benzeneoligothiolate was observed. In a similar experiment with **43** + **8**, the tetrathiane remained unchanged, and the redbrown color of the oligothiolate did not develop. Obviously, the thermodynamic stability of the tetrathiane is especially high.

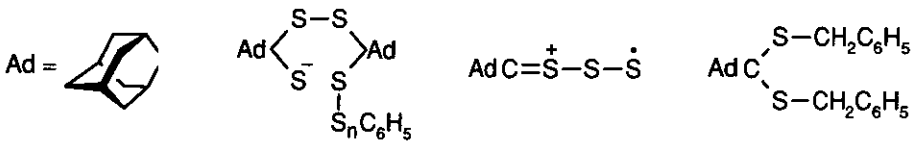
In the presence of 10 mol% of **8**, the comproportionation

2 pentathiepane (**44**) + 2 thione (**41**) → 3 tetrathiane (**43**)

took place and yielded 95% of **43** (10 d at rt).

All these interconversions require thiolate catalysis. The S–S bond of **43** is attacked by the oligothiolate anion and the ring-opened species (**45**) is the key intermediate for ring

enlargement and ring contraction. The equilibria are mobile and are influenced by the concentration of elementary sulfur.



45 46 47

Houk and Whitesides compared the stabilities of cyclic disulfides with respect to two properties, ring-opening polymerization and redox potential of the disulfide/dithiol system.[33] The 6-membered disulfide exceeded the 5-, 7-, and 8-membered ring in stability.

The ring enlargement of tetrathianes by sulfur is not new. The tetrathiane parent was transformed by Na_2S_4 in DMF into 30% of the pentathiepane;[25] the latter is lenthionine, the aroma constituent of the Shiitake mushroom.[34]

The conversion of **43** or **44** into the trithiolane (**42**) did not succeed – apart from traces observed by TLC. Neither was the sulfurization of **42** with sulfur + **8** achieved. Thus, our experiments in the adamantanethione series parallel those with thiobenzophenone. The formation of the 1,2,4-trithiolane (**42**) from the intermediate (**45**) would require an intramolecular S_N2 reaction at the *tert*-C-atom which ranks in rate below the attack on sulfur.

The MS of tetrathiane (**43**) shares some features with that of **9**. The molecular peak is 16%, and the interesting radical ion $C_{10}H_{14}S_3^{+\cdot}$ (**46** or cyclic species) corresponding to **10** (3.5%) is the 100% peak here. The radical cation of **41** ($C_{10}H_{14}S^+$) occurs with 88% whereas $C_{10}H_{13}^+$, i.e., $[41^+ - HS^{\cdot}]$, is small (3.4%). In the MS of all thioketones, aromatic, open-chain, cyclic or bicyclic, $[M^+ - HS]$ appears, in the MS of cyclopentanethione and cyclohexanethione even as the base peak.[35-37]

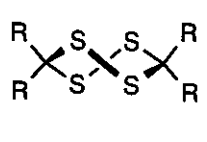
Magnusson cleaved the disulfide bonds of **35** with sodium in liquid ammonia, followed by benzylation. We applied this protocol to **43** and **44**; the dibenzyldithioacetal (**47**) was the product.

CONFORMATION OF 1,2,4,5-TETRATHIANE-BIS(SPIROADAMANTANE) (43)

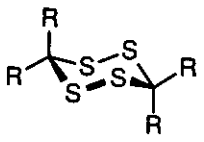
In 1969, Bushweller elegantly established by dynamic NMR that 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane (**35**) occurs in a *twist* conformation (**48a**) with equivalent methyl groups, and a *chair* form (**49a**) (*equatorial* and *axial* CH_3 groups) in 72:28 ratio (CS_2, −15 °C).[38] The substantial barrier of $\Delta H^{\neq}$ = 16.5 kcal mol^{-1} for twist → chair was evaluated by line shape analysis.[39] Force field calculations by Allinger *et al.* reproduced equilibrium and barrier height – the TS corresponds to the half-chair conformation – surprisingly well.[40]

The repulsion of lone pairs generates rotational barriers of 6-8 kcal mol^{-1} in disulfides, RS-SR [41,42]. This phenomenon stabilizes the twist conformer (**48a**) which has the high tor-

sion angle of 80° (X-ray analysis of **35**) [43] at the S–S bonds. The chair form (**49a**) suffers from a lower torsion angle and *syn-axial* repulsion (S_1/S_5, S_2/S_4).



48



49

a R = CH_3

b R,R = 

The equilibrium concentration of the twist form (**48**) becomes greater with increasing volume of the substituents R. The free energy change ΔG° (kcal mol^{-1}) for chair **49** → twist **48** amounts to +1.4 for R = H,[44] −0.5 for R = CH_3,[39] and −0.7 for R_2 = $(CH_2)_5$ [45] (CS_2, −15 °C).

How can information be gathered on the conformation of the tetrathiane-bis(spiroadamantane) (**43**) ? The ^1H NMR spectrum is less helpful than the ^{13}C NMR data which reveal elements of symmetry from number and multiplicity of the signals. The point group of symmetry for the tetrathiane with adamantyl is the same as for *gem*-dimethyl, *i.e.*, D_2 for the twist form (**48**) and C_{2h} for the chair conformer (**49**).

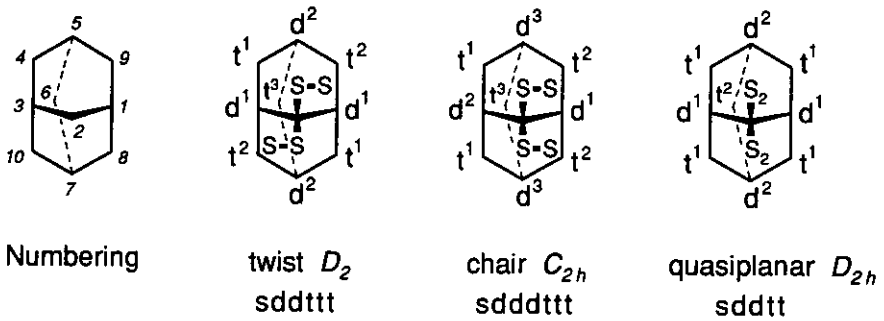


Figure 1. Symmetry considerations and expected ^{13}C NMR data of various conformations of tetrathiane-bis(spiroadamantane) (**43**) (see text)

Since the two adamantyl residues are chemically equivalent in each of the two conformations, the "counting" of nonequivalent C-atoms can be limited to *one* adamantyl. In the schematic projections of Figure 1 we are looking from the tetrathiane ring towards the adamantyl system. The dithioacetalic C-2 in front gives rise to a singlet; C-6 (in the background) spans the distance between C-5 and C-7, and its triplet is nonequivalent to all others.

With the annellation of the tetrathiane ring (jutting out in front in our diagrams), the relevant symmetry element enters, C_2 for the twist and C_s for the chair conformation. Positi-

ons C-1 and C-3 are equivalent in the twist and nonequivalent in the chair conformation. The diagrams show the number of doublets and triplets expected by symmetry considerations. A stereomutation interconverts the enantiomeric twist conformers *via* the chair form; when this process becomes fast on the NMR time scale with increasing temperature, the *quasiplanar* time average reduces the number of nonequivalent triplets to two.

The comparison of the H-decoupled and the off-resonance ^{13}C NMR spectrum of **43** results in the 6 signals (sddttt) anticipated for the twist form (**48b**). The pattern was the same in [D_2]1,1,2,2-tetrachloroethane (s-TC) and [D_6]benzene at +32 °C, as well as in $CDCl_3$ at −33 °C, thus ruling out an accidental coincidence.

The chemical shifts of the adamantane parent come at δ_C 28.5 for the CH and 37.9 for CH_2. The sulfur functions deshield not only C-2 (s δ 74.2, s-TC, 32 °C), but also the adjacent C-1/C-3 (d 36.5); the second doublet at 27.2 is assigned to C-5/C-7. A minor concentration of the chair conformer could have easily escaped attention. Thus, the trend to greater preference for the twist form with increasing bulk of the substituents appears to be valid for the dispiro-tetrathiane (**43**) .

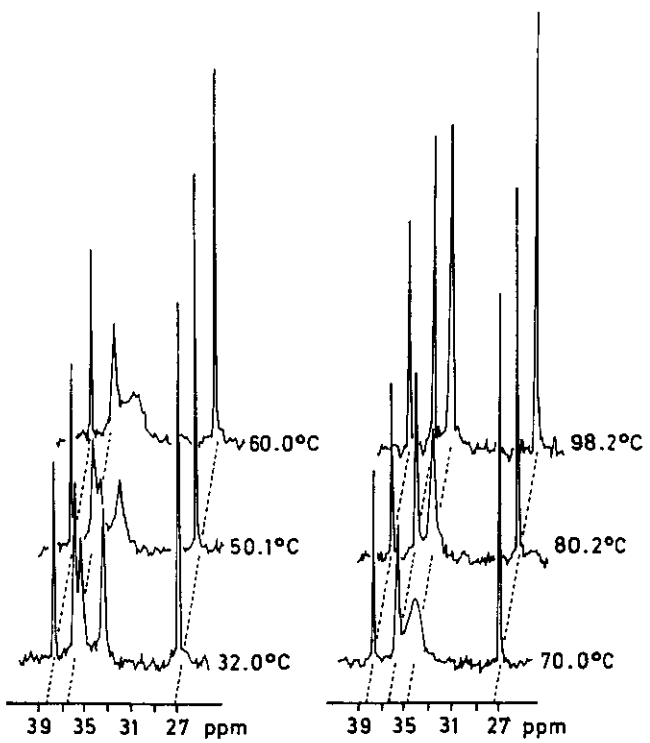


Figure 2. Temperature dependence of the H-decoupled ^{13}C NMR spectrum of **43** at 25.2 MHz in [D_2]1,1,2,2-tetrachloroethane

Of the three triplets (δ 34.0, 35.6, 38.4, s-TC, 32 °C), the first two are broadened on increasing the measuring temperature; they coalesce at 60 °C and the new triplet at δ 34.9 gains in sharpness at 98 °C. Now the ^{13}C NMR spectrum assumes the characteristics anticipated for the quasiplanar tetrathiane ring (D_{2h} symmetry), *i.e.*, the rate of stereomutation leaves the ^{13}C NMR time scale towards fast exchange. Our estimate of $\Delta G^{\neq}$ = 16.0

± 1.0 kcal mol^{-1} cannot claim high precision, but closely approaches the values reported for other 1,2,4,5-tetrathianes.

A quasiplanar 1,2,3,5,6-pentathiepane-bis(spiroadamantane) (**44**) would correspond to C_{2v} symmetry, and sdddttt should be the set of ^{13}C NMR signals. However, one expects for the nonplanar 7-membered ring of **44** a higher barrier to inversion than for the 6-membered **43**. The ^{13}C NMR spectrum of **44** shows 8 signals, one triplet in excess. At higher temperature, 81 °C and 118 °C in s-TC, not coalescence, but decomposition was observed.

EXPERIMENTAL

General Methods. IR spectra were obtained with a Bruker FT model IFS 45. ^1H NMR spectra were recorded with Bruker WP80CW (80 MHz) and ^{13}C NMR spectra with Bruker WP80DS (20 MHz), routinely using decoupled and off-resonance spectra. The NMR spectra were taken in $CDCl_3$ (if not otherwise stated) with TMS as internal standard; the $CDCl_3$ was kept acid-free by storing over dry K_2CO_3. For quantitative ^1H NMR analysis, a weighed amount of 1,1,2,2-tetrachloroethane (s-TC, δ 5.92) was added as internal standard, after the reaction was finished; the machine integrals were compared. – The MS (electron impact) were run on Finnigan MAT 90. The intensities of isotope peaks turned out to be valuable in the assignment of fragments. They were calculated on the basis of the main isotopic composition, and results are reported in the form, *e.g.*, % ^{13}C calcd/found. MS high resolution (HR) data were acquired with the program CMASS on Finnigan MAT 95Q; resolution 4500. – Preparative layer chromatography (PLC): 2 mm silica gel 60 PF (Merck) on glass plates. – Melting points are uncorrected.

Materials. Thiobenzophenone,[46] adamantanethione.[47]

Sodium thiophenoxide (**8**) was prepared from sodium in abs. ethanol and 1.04 mol-equiv. of thiophenol. After evaporation (bath up to 40 °C), the colorless **8** was stored under argon in a Schlenk flask at -20 °C. The activity was checked iodometrically; good specimens show 93-97%.

SULFURIZATION OF THIOBENZOPHENONE

3,3,6,6-Tetraphenyl-1,2,4,5-tetrathiane (9). (a) *2 Equiv of "S":* 500 mg (1.95 mmol of S_8, 15.6 mg-atom) of flowers of sulfur and 28.1 mg (0.21 mmol, 1.3 mol% of "S") of sodium thiophenoxide (**8**) were stirred in 10 ml of abs. acetone for 30 min at rt under argon; part of the sulfur dissolved with deep-redbrown color. 1.55 g (7.82 mmol) of **1** was added, and after stirring for 3 d the deep-blue color of **1** had nearly vanished; the system remained heterogeneous throughout. The filtered colorless solid was washed with acetone: 1.88 g, mp 207.5-209 °C, still containing some S_8. Dissolving in hot $CHCl_3$ and adding methanol gave 1.71 g (95%) of **9** in colorless crystals, mp 209-209.5 °C (decomp, blue). IR (KBr): ν 696 cm^{-1}, 727, 748 (C_6H_5 wagg.); 1442, 1490 st. – ^{13}C NMR: δ 71.5

(s, C-3, C-6); 127.7, 128.5 (2 d, 20 arom. CH), 141.1 (s, 4 arom. C_q); 2 of the expected 3 d are isochronous. – MS (70 eV, 180 °C); *m/z* (%): 460 (0.1) [M^+, **12**], 396 (4.5) [$M^+ - 2S$, **13**; ^{13}C 1.30/1.31; $^{34}S + {}^{13}C_2$ 0.58/0.57], 262 (3.4) [$C_{13}H_{10}S_3^+$, **10**; ^{13}C 0.50/0.57; $^{34}S + {}^{13}C_2$ 0.49/0.49], 198 (100) [$C_{13}H_{10}S^+$, **1**$^+$; ^{13}C 14.6/13.6; $^{34}S + {}^{13}C_2$ 5.2/4.6], 165 (87) [$C_{13}H_9^+$, fluorenyl; ^{13}C 12.7/11.6], 121 (40) [C_6H_5-C≡S^+; ^{13}C 3.1/3.3; $^{34}S + {}^{13}C_2$ 2.1/2.1], 77 (7) [$C_6H_5^+$]. – Anal. Calcd for $C_{26}H_{20}S_4$: C 67.78, H 4.38, S 27.84. Found C 67.56, H 4.36, S 27.89. – Mol. Mass 446 (vapor-phase osmometry, $CHCl_3$, 37 °C, calcd 460.7).

(b) *1 Equiv of "S"*: 1.59 g (8.02 mmol) of **1**, 256 mg (7.98 mg-atom) of sulfur, and 26.2 mg (0.20 mmol, 2.5 mol% of "S") of **8** in 10 ml of acetone (procedure as above) were refluxed for 1.5 h; the blue color nearly disappeared. Work-up as above gave 1.49 g (81%) of **9**, mp 209-209.5 °C.

(c) *0.5 Equiv of "S"*: 395 mg (2.0 mmol) of **1**, 32.1 mg (1.0 mg-atom) of sulfur, and 5.10 mg (0.039 mmol, 3.8 mol% of "S") of **8** in 5 ml of acetone were stirred for 5 d at rt; the crude **9**, still tinted blue by the excess of **1**, was washed with acetone: 178 mg (77%, based on S_8), mp 209 °C. The residue of the mother liquor was analyzed by TLC (pentane/CH_2Cl_2 10:1); besides **9** (R_f 0.25), a small amount of trithiolane (**6**) was identified by R_f 0.31 with an authentic sample.

Reaction with 2,2-Diphenylthiirane at 100 °C. 212 mg (1.0 mmol) of **2** and 397 mg (2.0 mmol) of **1** were heated for 1 h without solvent in a sealed tube to 100 °C; the deep-blue color persists. Quantitative ^1H NMR analysis in $CDCl_3$ with s-TC as internal standard indicated the complete conversion of **2** (s δ 3.34) to 1,1-diphenylethylene (s δ 5.41). According to TLC (pentane/CH_2Cl_2 10:1), only sulfur and **1** were present besides the olefin. Trithiolane (**6**) was probably formed, but decomposed at 100 °C *via* its equilibrium concentration of **4**. Tetrathiane (**9**) should have survived, if formed, but was not found.

Reactions of 3,3,6,6-Tetraphenyl-1,2,4,5-tetrathiane. (a) *With lithium aluminum hydride*. The solution of 460 mg (1.0 mmol) of **9** in 20 ml of abs. THF was introduced dropwise into the stirred suspension of $LiAlH_4$ (102 mg, 2.7 mmol) in 10 ml of THF. The reaction mixture turned blue-violet and H_2 was evolved. After 30 min 2 ml of ethyl acetate was added, followed 10 min later by 1.57 g (20 mmol) of acetyl chloride. After 2 h, work-up with water/CH_2Cl_2 gave an oil which was purified by PLC (CH_2Cl_2-ethyl acetate 5:1); the fraction with R_f 0.82 contained 302 mg (62%) of **diphenylmethyl thioacetate (40)**, a colorless oil. – IR (film): ν 699 cm^{-1}, 749, 955 (C_6H_5 wagg.), 1449, 1494 (arom. C=C), 1695 (C=O). – ^1H NMR: δ 2.22 (s, CH_3), 5.87 (s, *tert*-CH), 7.18 (br s, 2 C_6H_5). – MS (20 eV, 150 °C); *m/z* (%): 242 (11) [M^+; ^{13}C 1.9/1.9; $^{34}S + {}^{13}C_2$ 0.63/0.67], 199 (2.1) [$C_{13}H_{11}S^+$, ^{13}C 0.3/0.4], 167 (100) [$C_{13}H_{11}^+$, benzhydryl$^+$; ^{13}C 15/16], 121 (1.4) [C_6H_5-C≡S^+], 91 (0.7) [tropylium]. – Anal. Calcd for $C_{15}H_{14}OS$: C 74.34, H 5.82, S 13.23. Found C 73.99, H 5.80, S 13.37.

(b) *Triethyl phosphite* (1.66 g, 10 mmol) and 460 mg (1.0 mmol) of **9** in 10 ml of THF were refluxed for 24 h under argon and with exclusion of light. After evaporating the solvent, the residue crystallized from THF-pentane: 390 mg (85%) of **9**, mp and mixed mp 209-209.5 °C. – No reaction with triphenylphosphane (1 equiv) under the same conditions. – No reduction of **9** with sodium borohydride in methanol.

(c) *Desulfurization.* Copper powder (300 mg) and 190 mg (0.41 mmol) of **9** in 30 ml of diglycol diethyl ether were refluxed for 1 h; the hot solution was filtered and worked up with water/$CHCl_3$. Colorless tetraphenylethylene (134 mg, 98%), mp 221 °C (222 °C),[48] crystallized from $CHCl_3$-methanol.

(d) *Thermolysis.* 1.0 mmol of **9** was refluxed in 10 ml of mesitylene for 15 h; after several min the formation of **1** began (blue color). The solvent was removed in vacuum, and the deep-blue residue was distilled at 120-140 °C (bath)/10^{-3} torr: 388 mg (98%) of **1**, mp 52-53 °C; the specimen did not show the IR absorptions of phenyl dithiobenzoate (see lit. 2). TLC (cyclohexane) of the residue showed S_8.

(e) *Thermolysis in the presence of dimethyl acetylenedicarboxylate.* 1.0 mmol of **9** and 1.20 g (8.4 mmol) of DMAD in 10 ml of mesitylene were heated to 150 °C for 20 h. After removing the solvent in vacuum, a weighed amount of s-TC was added, and the comparison of the ^1H NMR integrals ($CDCl_3$) indicated 0.873 mmol (44%, s δ 5.14, 1-H) of **16**.[16] The NMR signals of the 1,2-dithiole (**7**) [2] were absent and TLC (petrol ether-ethyl acetate 5:1) did not show **7**.

(f) 923 mg (2.0 mmol) of **9** and 915 mg (6.44 mmol) of DMAD in 10 ml of $CHCl_3$ were heated in a sealed tube to 150 °C for 5 h; **9** was dissolved after 5 min, and the colorless solution turned yellow-brown. On cooling, 145 mg (16%) of **9** crystallized, mp 209-209.5 °C. PLC (petrol ether-ethyl acetate 5:1) of the mother liquor allowed to separate 191 mg (26%) of dimethyl 3,3-diphenyl-3*H*-1,2-dithiole-4,5-dicarboxylate (**7**), yellow crystals of mp 105 °C (mp 104 °C,[2] mixed mp), and 243 mg (36%) of the colorless dimethyl 1-phenyl-1*H*-2-benzothiopyran-4,5-dicarboxylate (**16**), mp 90-91 °C (91-92 °C,[16] mixed mp.). The participation of an acid-catalyzed pathway is conceivable.

(g) *Attempted ring enlargement to pentathiepane.* 461 mg (1.0 mmol) of **9**, 66 mg (2.1 mg-atom) of sulfur, and 61.4 mg (0.46 mmol, 22 mol% of "S") of **8** in 3 ml of abs. acetone were refluxed for 3 h under argon. The redbrown suspension was freed from the solvent; recrystallization from $CHCl_3$-methanol gave 386 mg (84%) of unchanged **9**.

SULFURIZATION OF ADAMANTANETHIONE

Dispiro[adamantane-2,3'-(1,2,4,5)-tetrathiane-6',2''-adamantane] (43). (a) Flowers of sulfur (346 mg, 10.8 mg-atom) and 29.8 mg (0.225 mmol, 2.1 mol% of "S") of **8** in 10 ml of acetone were stirred at rt for 30 min under argon. When adamantanethione (**41**, 1.79 g, 10.8 mmol) was added, the deep-redbrown color of the benzeneoligothiolate disappeared rapidly, and the orangered color of **41** nearly vanished on stirring at rt for 3 h. Filtering

and washing with acetone gave 1.77 g (83%) of crude **43**, mp 264-266 °C. Recrystallization from $CHCl_3$-methanol afforded 1.38 g of colorless **43**, mp 289-290 °C (decomp).
(b) Analogously, 1.33 g (8.00 mmol) of **41**, 256 mg (8.00 mg-atom) of sulfur and 20.2 mg (0.153 mmol) of **8** in 10 ml of acetone were refluxed; within 15 min the orange-red color of **41** almost disappeared, but the mixture remained heterogeneous. Filtering provided 1.27 g (80%) of crude **43**; the residue of the mother liquor (310 mg) showed by TLC (cyclohexane) besides **43** some pentathiepane (**44**) as well as small amounts of **41** and trithiolane (**42**).
(c) 1.55 g (9.32 mmol) of **41**, 145 mg of sulfur (4.5 mg-atom, 0.5 equiv based on **41**), and 30.3 mg (0.23 mmol) of **8** in 10 ml of acetone were stirred for 3 d. The orange color of **41** persisted and 878 mg (98% based on S_8) of **43** were isolated. TLC (cyclohexane) of the mother liquor indicated traces of **42** and **44** besides the dominant **41**.
Spectroscopic properties of **43**. IR (KBr): ν 1096 cm^{-1}, 1450, 2854, 2908. – ^{13}C NMR in various solvents (refers to two equivalent adamantyl residues):

		s C-2	d C-5/C-7	C-1/C-3	t C-4/C-8	C-9/C-10	C-6
$CDCl_3$, −33 °C	δ	74.3	26.4	35.9	33.3	35.5	37.6
C_6D_6, 32 °C		74.7	27.2	36.7	33.8	35.9	38.2
Cl_2CD-$CDCl_2$, 32 °C		74.2	27.2	36.5	34.0	35.6	38.4
" 98 °C		74.2	27.4	36.4	34.9		38.6

Determination of barrier height. Figure 2 shows the temperature dependence of the H-decoupled ^{13}C NMR spectrum in s-TC. $\Delta\nu$ = 46 Hz was extrapolated to 60 °C (coalescence temperature) for the signals at δ 34.0 and 35.6; we approximated $k_c = 2.22\,\Delta\nu$ = 102 s^{-1} at 333 K. The half-chair (conformation at saddle point) can form both enantiomeric twist forms with equal chance; 2 k_c corresponds to $\Delta G^{\neq}$ = 16.0 kcal mol^{-1}.
MS of **43** (70 eV, 35 °C, HR); *m/z* (%): calcd 396.1068/found 396.1072 (15.6) [M^+, ^{13}C 3.3/3.5; ^{34}S + $^{13}C_2$ 2.6/3.1], 230.0255/.0234 (100) [$C_{10}H_{14}S_3^+$, **46**; ^{13}C 9.7/11.2; ^{34}S + $^{13}C_2$ 13.2/13.9], 198.0534/.0543 (0.7) [$C_{10}H_{14}S_2^+$], 166.0813/.0830 (88) [$C_{10}H_{14}S$, **41**$^+$; ^{13}C 8.7/9.3], 133.1014/.1011 (3.4) [166 − SH, $C_{10}H_{13}^+$], 125.0423/.0406 (1.0) [$C_7H_9S^+$], 124.0345/.0324 (1.8) [C_7H_8S], 105.0702/.0685 (0.6) [$C_8H_9^+$, methyltropylium], 91.0546/.0541 (4.9) [$C_7H_7^+$, tropylium]. In a MS (120 °C), *m/z* 166 was the base peak, and the lower masses have stronger peaks. – Anal. Calcd for $C_{20}H_{28}S_4$: C 60.55, H 7.12, S 32.33. Found C 60.41, H 7.00, S 32.55. – Mol. Mass 386 (vapor phase osmometry, $CHCl_3$, 37 °C, calcd 396.7).

Dispiro[adamantane-2,4'-(1,2,3,5,6)-pentathiepane-7',2''-adamantane] (**44**). 1.45 g (8.72 mmol) of **41**, 500 mg of sulfur (15.6 mg-atom, 1.8 equiv), and 35 mg (0.26 mmol) of **8** in 10 ml of abs. acetone were stirred at room temp.; due to the low solubility of the intermediate (**43**), the disappearance of the thione color required 7 h. The colorless crude **44**

(1.65 g, 88%), mp 229-231°C, still contained some S_8. Repeated recrystallization (dissolving in hot $CHCl_3$ and addition of methanol) furnished 1.46 g (78%) of pure **44**, mp 236 °C (decomp). – IR (KBr): *v* 1095 cm^{-1}, 1448, 1636; 2854, 2909 (C-H). – ^{13}C NMR (32 °C): δ 27.1, 34.7, 37.7 (3 d, 8 CH); 33.8, 34.2, 35.4, 38.7 (4 t, 10 CH_2), 84.0 (weak s, C-4', C-7'). – MS (20 eV, 110-120 °C); *m/z* (%): 428 (1.2) [M^+; ^{13}C 0.26/0.25; $^{34}S+^{13}C_2$ 0.29/0.22], 396 (6.4) [M^+-S; ^{13}C 1.4/1.6; $^{34}S+^{13}C_2$ 1.3/1.4], 364 (1.9) [M^+-2S; ^{13}C 0.44/0.48; $^{34}S+^{13}C_2$ 0.39/0.38], 262 (10) [$M^+-C_{10}H_{14}$, $C_{10}H_{14}S_4^+$; ^{13}C 1.1/1.5; $^{34}S+^{13}C_2$ 1.8/2.3], 230 (17) [$C_{10}H_{14}S_3^+$, **46**; ^{13}C 1.9/2.4; $^{34}S+^{13}C_2$ 2.3/2.6], 198 (5.8) [$C_{10}H_{14}S_2^+$; ^{13}C 0.7/0.9; $^{34}S+^{13}C_2$ 0.9/0.8], 166 (100) [$C_{10}H_{14}S^+$, 41^+; ^{13}C 11/13; $^{34}S+^{13}C_2$ 5.0/4.7], 133 (10) [$C_{10}H_{13}^+$, 41^+-SH; ^{13}C 1.1/1.6], 125 (10) [$C_7H_9S^+$], 91 (15) [$C_7H_7^+$]. – Anal. Calcd for $C_{20}H_{18}S_5$: C 56.02, H 6.58, S 37.39. Found C 56.21, H 6.61, S 37.51. – Mol. Mass: 424 (vapor phase osmometry, $CHCl_3$, 37 °C, calcd 428.8).

Interconversions of Tetrathiane and Pentathiepane. (a) Tetrathiane (**43**) (401 mg, 1.01 mmol), 70.5 mg of sulfur (2.2 mg-atom), and 16.2 mg (0.12 mmol) of **8** in 4 ml of acetone were refluxed under argon for 4 h; the suspension retained the redbrown color of the oligothiolate anion. Work-up by PLC (cyclohexane) furnished 356 mg (82%) of the colorless pentathiepane (**44**), mp 234-235 °C (mixed mp); **42** and **43** were not observed.

(b) 397 mg (1.0 mmol) of **43** and 26.5 mg (0.20 mmol) of **8** in 4 ml of acetone were refluxed for 12 h under argon; the redbrown color of the oligothiolate did not appear: Work-up of the suspension gave back 321 mg of **43**, mp 289-290 °C. TLC did not show a disproportionation into trithiolane (**42**) and pentathiepane (**44**).

(c) Pentathiepane (**44**) (300 mg, 0.70 mmol), 116 mg (0.70 mmol) of thione (**41**), and 9.8 mg (0.074 mmol) of **8** were stirred in 3.5 ml of acetone at rt under argon for 10 d; the orange color of **41** disappeared. Filtering gave 351 mg of **43**, mp 285-290 °C. PLC (cyclohexane) of the residue of the mother liquor afforded further 25 mg of **43** (R_f 0.67), 15 mg of unconsumed **44** (R_f 0.54), and a tiny amount of **42** (R_f 0.73). Based on consumed **44**, the yield of **43** in the comproportionation reaction was 95%.

(d) 300 mg (0.70 mmol) of **44** and 116 mg (0.70 mmol) of **41** were stirred in 3.5 ml of acetone for 24 h without **8**; the educts were almost completely recovered.

(e) 428 mg (1.0 mmol) of pentathiepane (**44**) and 42 mg (0.32 mmol) of **8** in 4 ml of acetone were sealed under argon in a tube and heated to 60 °C for 12 h. After 2 min the deep-redbrown color of the oligothiolate anion was observed. The content of the tube was diluted with 15 ml of methanol; the off-white solid was filtered and washed with methanol: 341 mg (86%) of crude tetrathiane (**43**), mp 257-265 °C. TLC revealed the admixture of some sulfur and **44**; recrystallization from $CHCl_3$-methanol afforded the pure sample of **43**, mp 289-290 °C (dec, mixed mp). Regrettably, we did not find a reliable method for the quantitative analysis of mixtures of **43** and **44**.

(f) 430 mg (1.0 mmol) of pentathiepane (**44**) and 262 mg (1.0 mmol) of triphenylphos-

phane in 4.0 ml of THF were refluxed under argon for 19 h. TLC disclosed that both educts were unchanged.

2,2-Bis(benzylthio)adamantane (47). (a) We introduced 500 mg (1.26 mmol) of solid tetrathiane **43** into the deep-blue solution of 116 mg (5.04 mg-atom) of freshly cut sodium in 100 ml of liquid ammonia at −78°C; the blue color vanished immediately. Benzyl chloride (1.60 ml, 14.0 mmol) was added. After 30 min at −78 °C, the solvent was evaporated. From $CHCl_3$-methanol (1:1) came 273 mg of **43**. PLC (cyclohexane) of the mother liquor gave 191 mg (44% based on consumed **43**) of **47**; colorless crystals, mp 116-117 °C (methanol). – ^{1}H NMR ($CDCl_3$): δ 1.44-2.08 (m, br, 5 CH_2), 2.34-2.73 (m, br, 4 CH), 3.80 (s, 2 SCH_2), 7.21 (s, 2 C_6H_5). – ^{13}C NMR (C_6D_6): δ 27.8 (d, C-5, C-7), 33.8 (t, C-4, C-8, C-9, C-10), 34.1 (t, 2 SCH_2), 36.2 (d, C-1, C-3), 39.2 (t, C-6), 72.4 (s, C-2); 127.0, 128.6, 129.6 (3 d, 10 arom. CH), 138.6 (s, 2 arom. C_q). The sulfur functions deshield the α- and β-C, but shield the γ-C. In $CDCl_3$, the t of C-1/C-3 coincides with the t of the benzylic CH_2, but the coupling constants are different. – MS (20 eV, 100-110 °C); *m/z* (%): 380 (6) [M^+; ^{13}C 1.6/1.6; $^{34}S+^{13}C_2$ 0.75/0.68], 289 (9) [$M^+ - CH_2C_6H_5$; ^{13}C 1.7/1.7; $^{34}S + ^{13}C_2$ 0.96/0.93], 257 (100) [$M^+ - SCH_2C_6H_5$; ^{13}C 19/23; $^{34}S + ^{13}C_2$ 6.2/7.3], 166 (10) [$C_{10}H_{14}S^+$, **41**$^+$], 133 (2) [$C_{10}H_{13}^+$], 124 (3) [$C_7H_8S^+$], 91 (75) [$C_7H_7^+$, ^{13}C 5.9/5.6]. – Anal. Calcd for $C_{24}H_{28}S_2$: C 75.73, H 7.42, S 16.85. Found C 75.51, H 7.28, S 16.91.

(b) Correspondingly, 2.01 g (4.69 mmol) of pentathiepane (**44**) reacted with 560 mg (24.4 mg-atom) of sodium in 50 ml of liquid NH_3 at −78 °C, followed by 4.73 g (37.4 mmol) of benzyl chloride. Work-up as above led to 1.23 g (35%) of **47**, mp 116-117 °C.

Experiments with dispiro[adamantane-2,3'-(1,2,4)-trithiolane-5',2''-adamantane] (42). (a) 364 mg (1.0 mmol) of **42** [2] and 43.4 mg (0.33 mmol) of sodium thiophenoxide (**8**) in 4 ml of acetone were heated in the sealed tube to 60 °C for 12 h; no color change of the suspension was observed. After dilution with methanol, filtering afforded 342 mg (94%) of unchanged **42**, mp 191-192 °C (191-192 °C).[2] Tetrathiane (**43**) was not recognized by TLC in the mother liquor.

(b) 73.1 mg (0.20 mmol) of **42**, 6.5 mg of sulfur (0.20 mg-atom) and a catalytic amount of **8** in 5 ml of acetone were stirred under argon at rt for 8 h; the redbrown color of the oligothiolate anion faded slowly. After removal of the acetone, trituration with methanol gave 68 mg (93%) of unchanged **42**. According to TLC (cyclohexane), the mother liquor contained besides **42** some pentathiepane (**44**). There was no reaction of **42** with sulfur in refluxing benzene (without **8**).

ACKNOWLEDGMENTS

We express our thanks to the *Fonds der Chemischen Industrie* for supporting our research. Furthermore, special thanks are going to *Helmut Huber* for his help in the NMR

measurements, to *Reinhard Seidl* and *Dr. Werner Spahl* for the mass spectrometry, and to *Helmut Schulz* for the microanalyses.

REFERENCES

1. R. Huisgen and J. Rapp, *J. Am. Chem. Soc.*, 1987, **109**, 902.
2. R. Huisgen and J. Rapp, *Tetrahedron*, 1997, **53**, 939.
3. G. Mloston and H. Heimgartner, *Helv. Chim. Acta*, 1995, **78**, 1298.
4. K.-F. Wai and M. P. Sammes, *J. Chem. Soc., Perkin Trans. 1*, 1991, 183.
5. M. G. Voronkov, N. S. Vyazankin, E. N. Deryagina, A. S. Nakhmanovich, V. A.
a Usov, *'Reactions of Sulfur with Organic Compounds'*, ed. by J. S. Pizeh, Engl. Transl. by Consultants Bureau, New York, 1987, Chapter 5.
6. Preliminary communication: R. Huisgen, *Phosphorus, Sulfur, and Silicon*, 1989, **43**, 63.
7. Review: L. Fisera, R. Huisgen, I. Kalwinsch, E. Langhals, X. Li, G. Mloston, K. Polborn, J. Rapp, W. Sicking, R. Sustmann, *Pure Appl. Chem.*, 1996, **68**, 789.
8. W. Franek, *Sulfur Reports,* 1991, **10**, 193, 233.
9. P. Beak and J. Worley, *J. Am. Chem. Soc.*, 1970, **92**, 4142; 1972, **94**, 597.
10. Review: F. Duus, *'Organic Compounds of Sulphur, Selenium, and Tellurium'*, Vol. 3, ed. by D. H. Reid, The Chemical Society, London, 1975; pp 233-235.
11. A. P. Krapcho, D. R. Rao, M. P. Silvon, and B. Abegaz, *J. Org. Chem.*, 1971, **36**, 3885.
12. G. Mloston and R. Huisgen, *Tetrahedron Lett.*, 1989, **30**, 7045.
13. R. Sustmann, W. Sicking, and R. Huisgen, *J. Org. Chem.*, 1993, **58**, 82.
14. A. Fava, A. Iliceto, and E. Camera, *J. Am. Chem. Soc.*, 1957, **79**, 833. A. J. Parker and N. Kharasch, *Chem. Rev.* 1959, **59**, 583.
15. R. Singh and G. M. Whitesides, *J. Am. Chem. Soc.*, 1990, **112**, 1190, and preceding papers.
16. J. Rapp and R. Huisgen, *Tetrahedron*, 1997, **53**, 961.
17. K. Steliou, Y. Gareau, and D. N. Harpp, *J. Am. Chem. Soc.*, 1984, **106**, 799.
18. I. Kalwinsch, X. Li, J. Gottstein, and R. Huisgen, *J. Am. Chem. Soc.*, 1981, **103**, 7032.
19. E. Block, J. Z. Gillies, C. W. Gillies, A. A. Bazzi, D. Putnam, L. K. Revelle, D. Wang, and X. Zangh, *J. Am. Chem. Soc.*, 1996, **118**, 7492.
20. J. B. Baudin, M. G. Commenil, S. A. Julia, L. Toupet, and Y. Wang, *Synlett.*, 1993, 839. J. Hasserodt, H. Pritzkow, and W. Sundermeyer, *Liebigs Ann. Chem.*, 1995, 95.
21. K. G. Naik, *J. Chem. Soc.*, 1921, **119**, 379, 1231. K. G. Naik and M. D. Avasare, *J. Chem. Soc.*, 1922, **121**, 2592.

22. G. W. Kutney and I. W. J. Still, *Can. J. Chem.*, 1980, **58**, 1233.
23. R. W. Saalfrank and W. Rost, *Angew. Chem., Int. Ed. Engl.*, 1987, **24**, 855.
24. A. Elsässer and W. Sundermeyer, *Chem. Ber.*, 1985, **118**, 4553.
25. Y. Takikawa, T. Makabe, N. Hirose, T. Hiratsuka, R. Takoh, and K. Shimada, *Chem. Lett.*, 1988, 1517.
26. A. Senning, H. C. Hansen, M. F. Abdel Meged, W. Mazurkiewicz, and B. Jensen, *Tetrahedron*, 1986, **42**, 739.
27. C. Willgerodt, *Ber. Dtsch. Chem. Ges.*, 1887, **20**, 2492.
28. B. Magnusson, *Acta Chem. Scand.*, 1962, **16**, 772.
29. A. Fredga, *Acta Chem. Scand.*, 1958, **12**, 891.
30. B. Magnusson, *Acta Chem. Scand.*, 1959, **13**, 1031.
31. F. Asinger, M. Thiel, and G. Lipfert, *Liebigs Ann. Chem.*, 1959, **627**, 195.
32. F. O. Bobbio and P. A. Bobbio, *Chem. Ber.*, 1965, **98**, 998.
33. J. Houk and G. M. Whitesides, *J. Am. Chem. Soc.*, 1987, **109**, 6825.
34. K. Morita and S. Kobayashi, *Chem. Pharm. Bull. Jpn.*, 1967, **15**, 988.
35. D. Schumann, E. Frese, and A. Schönberg, *Chem. Ber.*, 1969, **102**, 3192.
36. M. M. Campbell, G. M. Anthony, and C. J. W. Brooks, *Org. Mass. Spectrom.*, 1971, **5**, 297.
37. D. Paquer, L. Morin, M. Vazeux, and C. G. Andrieu, *Rec. Trav. Chim. Pays-Bas*, 1981, **100**, 36, 52.
38. C. H. Bushweller, *J. Am. Chem. Soc.*, 1969, **91**, 6019.
39. C. H. Bushweller, J. Giolini, G. U. Rao, and J. W. O'Neil, *J. Am. Chem. Soc.*, 1970, **92**, 3055.
40. N. L. Allinger, M. J. Hickey, and J. Kao, *J. Am. Chem. Soc.*, 1976, **98**, 2741.
41. W. N. Hubbard, D. R. Douslin, J. P. McCullough, D. W. Scott, S. S. Todd, J. F. Messerly, I. A. Hosenlopp, A. George, and G. Waddington, *J. Am. Chem. Soc.*, 1958, **80**, 3547.
42. R. R. Fraser, G. Boussard, J. K. Saunders, J. B. Lambert, and C. E. Mixan, *J. Am. Chem. Soc.*, 1971, **93**, 2822.
43. J. D. Korp, I. Bernal, S. F. Watkins, and F. R. Fronczek, *Tetrahedron Lett.*, 1981, **22**, 4767.
44. R. Susilo, R. Gmelin, K. Roth, and H. Bauer, *Z. Naturforsch., Part B*, 1982, **37**, 234.
45. C. H. Bushweller, G. Bhat, L. J. Letendre, J. A. Brunelle, H. W. Bilofsky, H. Ruben, D. H. Templeton, and A. Zalkin, *J. Am. Chem. Soc.*, 1975, **97**, 65.
46. B. S. Pedersen, S. Scheibye, N. H. Nilsson, and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, 1965, **87**, 1353.
47. J. W. Greidanus, *Can. J. Chem.*, 1970, **48**, 3530.
48. W. Schlenk and E. Bergmann, *Liebigs Ann. Chem.*, 1928, **463**, 1.

Received, 27th November, 1996