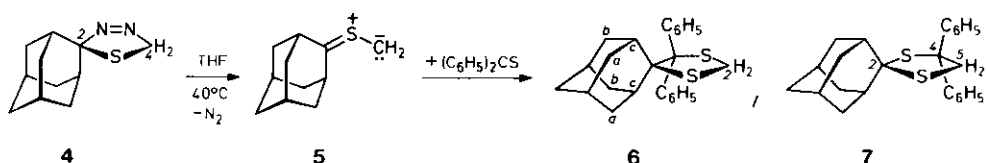


nucleophilic center of the thiocarbonyl ylide to the sulfur of the thione in the framework of the concerted process. It may be recalled that metalorganic reagents attack thiones at the sulfur or carbon function in competing pathways.⁸⁻¹⁰

The thermostability of *alkyl*-substituted 1,3,4-thiadiazolines exceeds that of the aryl-substituted ones. 1,3,4-Thiadiazoline-2-spiro-2'-adamantane (4), easily prepared from adamantanethione and diazomethane, can be stored; it loses N₂ with a half-life of 33 min at 45°C in xylene and the *S*-methylide (5) is intercepted by electron-deficient olefins, acetylenes, and carbonyl compounds.¹¹ The CH₂ group is more *nucleophilic* and more *basic* among the two termini of the 1,3-dipole 5.



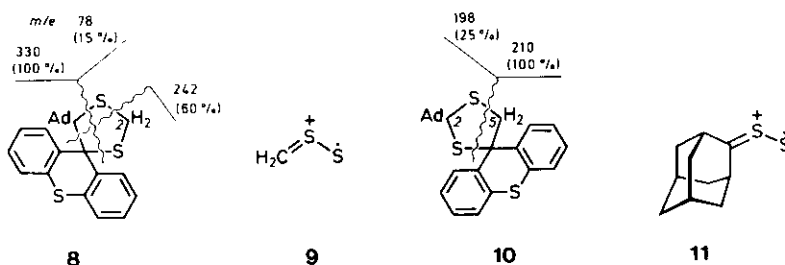
The thiocarbonyl ylide 5 served as an aliphatic model to study the *in situ* cycloadditions to thione compounds. In general, 2.0 mmoles of 4 in 4 ml THF reacted with 2.2 mmoles of thione for 8 h at 40°C. After evaporating the THF, the adduct yield was determined by quantitative ¹H NMR analysis in CDCl₃ in the presence of a weighed standard, usually 1,1,1,2-tetrachloroethane (δ 4.28). The isolated adducts were characterized by elemental analyses and spectra (Table 1).

Thiobenzophenone accepts 5 in both directions giving 50% 6 and 42% 7 which were separated by tlc. Probably the interaction of the voluminous substituents in 6 renders the second orientation - sterically less demanding - competitive. The independent synthesis from thiobenzophenone *S*-methylide (2) and adamantanethione at -45°C (63% 6)¹² constitutes infallible evidence for structure 6 with -S-CH₂-S-. The ¹H NMR spectra confirm the presence of a symmetry plane with singlets for 2-H₂ of 6 (δ 3.25) and for 5-H₂ of 7 (δ 3.90). Especially indicative are the ¹³C NMR spectra with one singlet, three doublets, and three triplets for the adamantyl group.

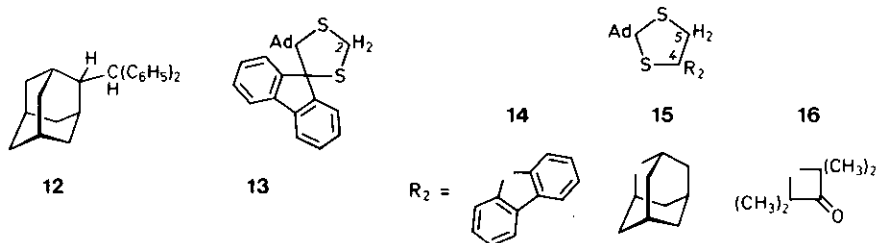
The thioxanthione adducts 8 and 10 are selected to illustrate the structural evidence achieved by the mass spectra. The main fragmentation leads to alkene (m/e = 330 for 8 and 210 for 10) and R₂CS₂ (m/e = 78 for 8 and 198 for 10); structures 9 and 11 are proposed for the latter. The hydrogenolysis of 8 by Raney nickel (W-2)¹³ in refluxing ethanol provided 2-benzhydryladamantane (12, 91%, mp 138-140°C).

Table 1. 1,3-Dithiolanes prepared by cycloaddition of adamantane-thione 5 to thiones

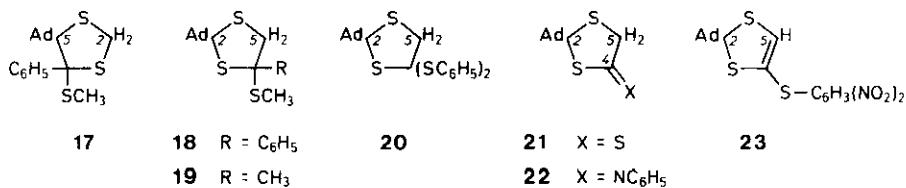
Dipolarophile	% yield	mp (°C)	For- mula	$\delta(^{13}\text{C})$ of CH_2
Thiobenzophenone	50	202-203	<u>6</u>	33.3
	+ 42	126-128	<u>7</u>	48.3
Thioxanthione	41	183-185	<u>8</u>	30.8
	+ 34	237-239	<u>10</u>	44.2
Thiofluorenone	60	172-177	<u>13</u>	29.6
	+ 18	not isol.	<u>14</u>	
Adamantanethione	86	165-166	<u>15</u>	45.5
2,2,4,4-Tetramethyl-cyclo- butane-1-one-3-thione	80	128-129	<u>16</u>	41.9
Methyl dithiobenzoate	51	166-168	<u>17</u>	28.1
	+ 45	109-111	<u>18</u>	47.3
Methyl dithioacetate	64	43-45	<u>19</u>	48.2
Diphenyl trithiocarbonate	85	122-124	<u>20</u>	45.9
Carbon disulfide (0.005 M <u>4</u>)	89	108-110	<u>21</u>	55.9
Carbon disulfide (0.2 M <u>4</u>)	41	108-110	<u>21</u>	55.9
	+ 40	230-231	<u>24</u>	48.2
Phenyl isothiocyanate	90	78-80	<u>22</u>	43.2



Thiofluorenone followed the same orientational pattern (13 major, 14 minor) as thiobenzophenone and thioxanthione. In the additions of 5 to two aliphatic thiones (adamantanethione, 2,2,4,4-tetramethylcyclobutanone-3-thione), however, only the sterically less hindered pathway (86% 15, 80% 16) was discernible. The mirror plane of 15 cuts the two adamantyl residues in halves, but these two residues have different environments; 13 of the expected 2 times 7 signals were observed in the ^{13}C NMR spectrum (CDCl_3). The other conceivable regioisomer of 15 possesses two C_2 planes and should give rise only to 7 δ_{C} values for the two vicinal adamantyl groups.



The occurrence of $m/e = 198$ (11) as the base peak in the MS is likewise in accordance with 15. The same fragment 198 (11) in the MS of 16 indicates that the two S-atoms are bonded to the adamantane part; base peak is 266 (M^+ - dimethylketene). The $\delta(^{13}\text{CH}_2)$ of the dithiolane ring turned out to be a valuable heuristic criterion. The C-5 of 15 occurs at δ 45.5 and appears in the range of 42 - 48 for all saturated 1,3-dithiolanes in which the adamantane provides the 2-position (Table 1, *type B*); the greater value of J_{CH} allows to distinguish the 5- CH_2 from those of the adamantane. When the CH_2 is flanked by two S-functions (*type A*), the triplet of $\delta(\text{C}-2)$ is found at δ 28 - 33. The parent 1,3-dithiolane shows $\delta_{\text{C}} = 34.4$ for C-2 and 38.1 for C-4/C-5, *i.e.*, a smaller difference in the same direction.¹⁴



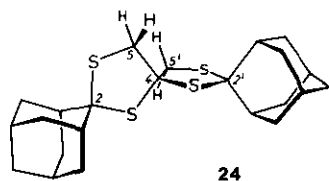
Unlike thiobenzophenone *s*-methylide (2) which furnished *type A* cycloadducts ($-\text{S}-\text{CH}_2-\text{S}-$) with dithiocarboxylic and trithiocarbonic esters,⁵ 5 combined with methyl dithiobenzoate to yield 51% 17 (*type A*) and 45% 18 (*type B*). The analogous additions to methyl dithioacetate and diphenyl trithiocarbonate produced only the *type B* products 19 and 20. The Ni-catalyzed hydrogenolysis converted adduct 17 into 2-benzyladamantane (84%, bp 135-136°C/0.7, benzylic CH_2 $\delta_{\text{H}} = 2.71$, d, $J = 7.5$ Hz) and the isomer 18 into adamantane (74%, mp 264-267°C). Likewise, the trithiocarbonate adduct 20 was hydrogenolyzed to give 62% adamantane.

Counting the $\delta(^{13}\text{C})$ of the adamantane C, CH and CH_2 reveals the lack of symmetry in 17-19: 10 signals. On the other hand, 7 signals (s, 3d, 3t) for 20 demonstrate the pairwise equivalence of the adamantane C-atoms due to a C_s plane. The ^1H NMR spectra allow the same conclusion: AB for 2- H_2 of 17 and for 5- H_2 of 18/19, but A_2 for

5-H₂ of 20. The structural assignments are supported by the mass spectra: The base peak of 17-19 is M⁺-SCH₃; M⁺-CH₂S₂ (90%) occurs in the MS of 17, whereas 18 and 19 display peaks at *m/e* = 198 (11) and 166 (adamantanethione⁺).

After 1 mmol of 4 in 200 ml carbon disulfide suffered N₂ extrusion at 40°C, quantitative ¹H NMR analysis indicated 89% of 21. The CS₂-adduct 21 (brick-red needles) displayed a symmetry plane in the ¹³C NMR spectrum (CDCl₃); the C=S was observed at δ 239.2. A strong argument in favor of the type B orientation was provided by treating 20 with 1 equiv NaOH and 2,4-dinitrochlorobenzene in ethanol: 83% thioenol ether 23 (yellow needles, mp 207-209°C, s δ 6.62 for 5-H). The type A regioisomer of 21 is incapable of forming a thioenolate anion. Moreover, the generation of adamantane with Ni/ethanol accords with structure 21.

The solution of the dithiolactone 21 in aniline was converted at 20°C to the cyclic thioimidic ester 22 (89%) and H₂S. The same colorless 22 resulted in 91% yield when thiadiazoline 4 was warmed in phenyl isothiocyanate as solvent at 40°C. The strong IR absorption of 22 at 1617 cm⁻¹ is assigned to C=N and C-4 was found at δ 172.6. No thiophilic reactions of carbon disulfide and isothiocyanates with nucleophiles are known. Neither carbon disulfide nor phenyl isothiocyanate reacted with thiobenzophenone *S*-methylide (2).



Like the dithiocarboxylic esters above, 21 is capable to add the thiocarbonyl ylide 5 when heated with 4 in cyclohexane for 8 h at 40°C; the colorless prisms of 24, mp 230-231°C, were obtained in 82% yield. The reaction of 1 mmol of 4 with 5 ml (83 mmol) CS₂ afforded 41% of the 1:1 adduct 21 and 40% of the 2:1 adduct 24; thus, the dipolarophilic activity of 21 exceeds that of CS₂ more than hundredfold.

The NMR spectra of 24 are picture-book tests of symmetry. Structure 24 possesses a C₂ axis which cuts the spiro center 4,4' under an angle of 45°. The two adamantane residues as well as the two dithiolane rings are equivalent, but due to chirality all ten C-atoms of the adamantyl are different and the 5-H₂ = 5'-H₂ are diastereotopic. Indeed, *one* AB spectrum is found for 5-H₂ + 5'-H₂ at δ 3.45 and 3.63 with *J*_{gem} = 12.0 Hz; the triplet at δ_C 48.2 confirms the identity of C-5 and C-5'. The

C-atoms 2 and 2' absorb as s at 78.7, and 4d and 5t were observed for the other 9 C-atoms of the two adamantane skeletons. The isolation of adamantane as product of hydrogenolysis of 24 as well as the mass spectrum with the molecular peak $m/e = 436$ (30%), 238 (100%) for $M^+ - C_{10}H_{14}S_2$, and 198 for $C_{10}H_{14}S_2$ (11, 35%) support 24.

Steric and electronic factors are probably intertwined in determining the addition direction of adamantanethione *S*-methylide (5) to CS double bonds. The 1,3-dipolar activity of 5 surpasses that of thiobenzophenone *S*-methylide (2).

ACKNOWLEDGMENT

We express our gratitude to the Fonds der Chemischen Industrie, Frankfurt, for support. G.M. thanks the Alexander von Humboldt Foundation for a fellowship.

REFERENCES AND NOTES

1. E. Bergmann, M. Magat, and D. Wagenberg, *Ber.Dtsch.Chem.Ges.*, 1930, 63, 2576.
2. A. Schönberg, D. Cernik, and W. Urban, *Ber.Dtsch.Chem.Ges.*, 1931, 64, 2577.
3. Review: A. Schönberg, B. König, and E. Singer, *Chem.Ber.*, 1967, 100, 767.
4. I. Kalwisch, Li X., J. Gottstein, and R. Huisgen, *J.Am.Chem.Soc.*, 1981, 103, 7032.
5. Li X. and R. Huisgen, *Tetrahedron Lett.*, 1983, 24, 4181.
6. R. Huisgen and Li X., *Tetrahedron Lett.*, 1983, 24, 4185.
7. Professor A. Schönberg, the pioneer of thione chemistry, died on January 10, 1985, in his 93rd year.
8. P. Beak and J.W. Worley, *J.Am.Chem.Soc.*, 1970, 92, 4142; 1972, 94, 597.
9. M. Dagonneau and J. Vialle, *Bull.Soc.Chim.France*, 1972, 2067; M. Dagonneau, D. Paquer, and J. Vialle, *ibid.*, 1973, 1699.
10. A. Ohno, K. Nakamura, M. Uohama, S. Oka, T. Yamabe, and S. Nagata, *Bull.Chem.Soc.Japan*, 1975, 48, 3718.
11. R. Huisgen and G. Mloston, *Tetrahedron Lett.*, 1985, 26, 1049.
12. Experiment by C. Fulka, Diploma Thesis, Univ. of München, 1982.
13. R. Mozingo, *Org. Syntheses*, Coll.Vol. 1955, 3, 181.
14. K. Pihlaja, M. Eskonmaa, R. Keskinen, A. Nikkilä, and T. Nurmi, *Org.Magn.Reson.*, 1981, 17, 246.

Received, 21st May, 1985