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Thiofenchone *S*-Methylide and Its Spiro-1,3,4-thiadiazoline Precursor

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ABSTRACT: *Spiro[fenchane-2,2'-(1,3,4)-thiadiazoline] (***6***), prepared from thiofenchone and diazomethane, extrudes* N_2 *(*$t_{1/2}$ *22 min, 46°C, toluene) and furnishes the S-methylide* **7** *which, in turn, closes the thiirane ring or else is intercepted by 1,3-cycloadditions to dipolarophiles (tetracyanoethylene, maleic anhydride, N-methyl-1,2,4-triazoline-3,5-dione, aromatic thioketones). When thiocarbonyl S-methylide* **7** *is set free in methanol, fenchone S,O-dimethylacetal is formed as an HX adduct. Catalysis by acetic acid converts* **7** *to 1-(methylthio)-α-fenchene (***25***) by way of a Wagner-Meerwein rearrangement. The addition of diazomethane to thiocampher leads, via thiadiazoline* **12**, *to thiocamphor S-methylide; the latter undergoes a 1,4-H shift, thus affording 2-methylthio-2-bornene (***11***).* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:136–145, 2001

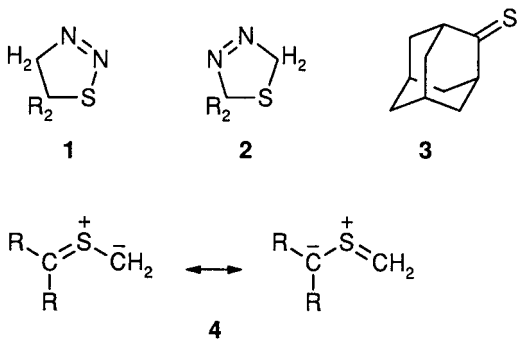
INTRODUCTION

The 1,3-cycloadditions of thiocarbonyl ylides with C–C multiple bonds and hetero-double bonds offer a versatile route to five-membered *S*-heterocycles [1]. 2,5-Dihydro-1,3,4-thiadiazoles are formed by cycloaddition of diazoalkanes to thiocarbonyl compounds, and thermal N_2 extrusion furnishes thioketone *S*-alkylides, which can be intercepted in situ.

Cycloadditions of diazomethane to dialkylthioketones afford the regioisomers **1** and **2** [2]. The higher the branching of the alkyl groups, the larger is the fraction of the 2,5-dihydro-1,3,4-thiadiazoles **2**, which suggests a steric effect. In this process, increasing solvent polarity favors **1**. Consideration of the dipole moments of thione and diazomethane supports a higher polarity of the transition state (TS) leading to **1**. This energetic disadvantage is mitigated by the use of polar solvents (Scheme 1).

The same interplay of forces is observed in diazomethane additions to cycloalkanethiones. Adamantanethione (**3**) afforded thiadiazolines of types **1** and **2** in a ratio of 9:91 in pentane, and 90:10 was observed in methanol, both at −30°C [3,4].

Ab initio calculations (RHF/6-21G*, CAS(6,5)//3-21G*) of the TS confirm the concerted pathway of



SCHEME 1

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Dedicated to Professor Richard Neidlein, Heidelberg, on the occasion of his 70th birthday.
1,3-Dipolar Cycloadditions, 120. For part 119 see Finke, J. A.; Huisgen, R., Temme, R. Helv Chim Acta, 2000, 83, 3333.

these diazomethane cycloadditions, as well as similar activation enthalpies for both directions of addition [5]. The low-lying LUs of thiones contribute weight to the HO(diazomethane)-LU(thione) interaction and promote our understanding of the superdipolarophilic character of thiones [6].

The cycloadditions of thiocarbonyl ylides **4** to *cis,trans*-isomeric dipolarophiles are usually stereospecific. However, strong steric hindrance at one terminus can change the mechanism from the concerted to a two-step pathway via a zwitterionic intermediate [7]. We report here on thiofenchone *S*-methylide (**7**) [8] in which the 1,3-dipolar system is more encumbered than in adamantanethione *S*-methylide (**42**).

SPIRO-1,3,4-THIADIAZOLINES OF FENCHANE AND CAMPHANE SERIES

The reaction of thiofenchone (**5**) with diazomethane at 0°C was described by Beiner et al. in 1973; Gas chromatography (GC) analysis of the oily product indicated 50% of the spirothiirane **8** with an *endo*/*exo* ratio of 65:35 [9]. The question of the reaction pathway was left open.

Our supposition that **5**, like other sterically hindered thiones, should add diazomethane to afford a type **2** thiadiazoline, turned out to be correct. The reaction in tetrahydrofuran (THF) at 0°C produced a sterically homogeneous spiro[fenchane-2,2′-(1,3,4)-thiadiazoline], as the ^{1}H NMR spectrum of the crude adduct revealed. On the other hand, assignment of the *endo*-structure **6** is merely based on the following analogy: The reduction of fenchone with $LiAlH_4$ produced α-fenchol (*endo*-OH) and β-fenchol (*exo*-OH) in a ratio of 97:3 [10,11]; as a consequence, we assume that diazomethane as well as the hydride ion enter from the *exo* side. The crystalline **6** can be stored at −25°C (Scheme 2).

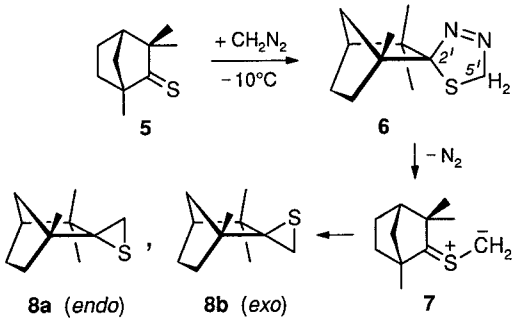
Kinetic measurements showed that the thermal elimination of N_2 from **6** obeys the first-order law; the half-life in toluene amounts to 22.2 minutes at 46°C and to 16.5 minutes at 52°C. ^{1}H NMR analysis with weight standard indicated 63% of spirothiirane **8** and a diastereoisomer ratio of 60:40. We do not regard the small δ_H differences of the methyl signals [9] as a reliable basis for an *endo*/*exo* assignment.

The generation of two diastereoisomers of **8** from one and the same thiadiazoline **6** would be inconsistent with a concerted formation of the new C–C bond. During the extrusion of N_2, the group C(2)–S–CH_2 swings into a quasi-plane: The thiofenchone *S*-methylide (**7**) occurs as an interceptible intermediate. Both *syn*- and *anti*-conformations are conceivable, and both can give rise to **8a** and **8b** by another set of conrotatory 90°C rotations about the C–S bonds.

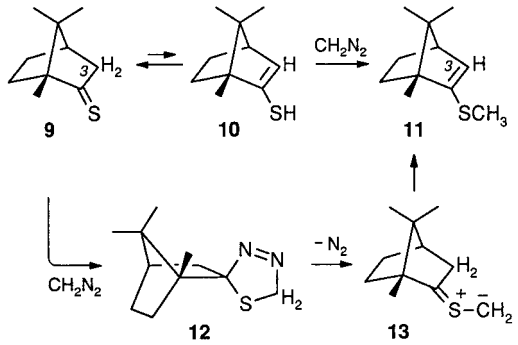
Thiocamphor (**9**) can tautomerize with a thioenol, in contrast to thiofenchone (**5**). A methylation of the acidic thioenol **10** by diazomethane appeared plausible, and indeed we obtained 2-(methylthio)-2-bornene (**11**) from the reaction at room temperature. However, when **9** and diazomethane reacted at −40°C and reached 10°C, the ^{1}H NMR spectrum showed the 1,3,4-thiadiazoline **12** and thioenol ether **11** side by side; the two sets of *C*-methyl singlets suggested a 1:1 ratio. After 4 hours at room temperature, ^{1}H NMR showed 82% of **11**, while the signals of **12** had disappeared (Scheme 3).

Compound **12** was confirmed by its ^{1}H NMR parameters. The observed AB spectrum at δ 5.45 and 5.89 with J_{gem} = 16.8 Hz is consistent with 5′-H_2 of **12**; the 5′-H_2 of **6** resonates at δ 5.55 (as A_2 spectrum). The properties of **11** agree with those described by Dagonneau et al. for the product from **9** and methyl magnesium bromide [12]. The vinylic 3-H appears as a doublet at δ 5.38.

Obviously, **12** extrudes N_2 at 20°C, and the thiocamphor *S*-methylide (**13**) favors a sigmatropic 1,4-H shift as a route to stabilization. This reaction type



SCHEME 2



SCHEME 3

is well documented [13,14] and is allowed to be concerted by orbital control. It is the counterpart of the 1,5-H shift of 1,3-dienes with adjacent C–H bond. The 1,4-H shift of *S*-methylide **13** via a five-membered TS supersedes thiirane formation; indeed, no thiirane was found.

SPIROTHIADIAZOLINE **6** *AS AN ACID*

When **6** was treated with 1.0 equiv. of sodium methanolate in methanol, the lack of N_2 evolution at 45°C signals complete conversion to the anion **14**. The latter shares the propensity for 1,5-electrocyclic ring opening with other thiadiazoline anions [15]. The thioformimidate **16**, obtained with 2,4-dinitrochlorobenzene, is derived from anion **15** (Scheme 4).

On the side, we mention the amidrazones **17** and **18** which were formed from **6** with piperidine or morpholine at room temperature in a multistep reaction: base-catalyzed equilibration of **6** with the open-chain tautomer (*N*-protonated **15**) and interaction of the latter with the sec-amine [16]. The structures **16–18** were confirmed by their spectra.

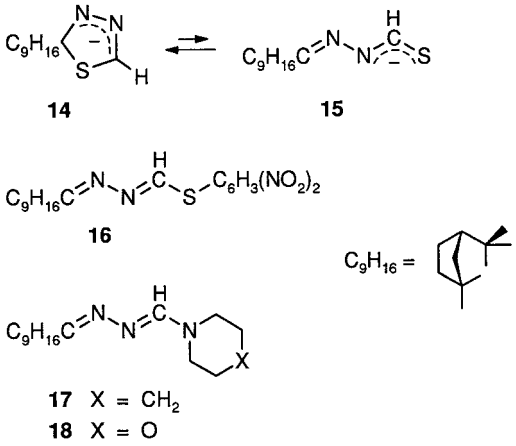
THIOFENCHONE S-METHYLIDE AND ACIDS

As heteroatom derivatives of allyl anions, thiocarbonyl ylides are bases. When the N_2 elimination from thiadiazoline **6** took place in methanol at 45°C, fenchone *O,S*-dimethylacetal (**20**) was formed in 96% yield. The conversion to fenchone 2,4-dinitrophenylhydrazone attested to the unchanged carbon framework. The homogeneity of **20** is remarkable; the CH_3O singlet appears at δ 3.41 and that of CH_3S at 1.93. For analogy reasons, we suspect a structure incorporating *exo*-OCH_3 and *endo*-SCH_3. The initial step is probably protonation of **7** at the CH_2 terminus, giving rise to the sulfonium ion **19** + methanolate, followed by ion recombination (Scheme 5).

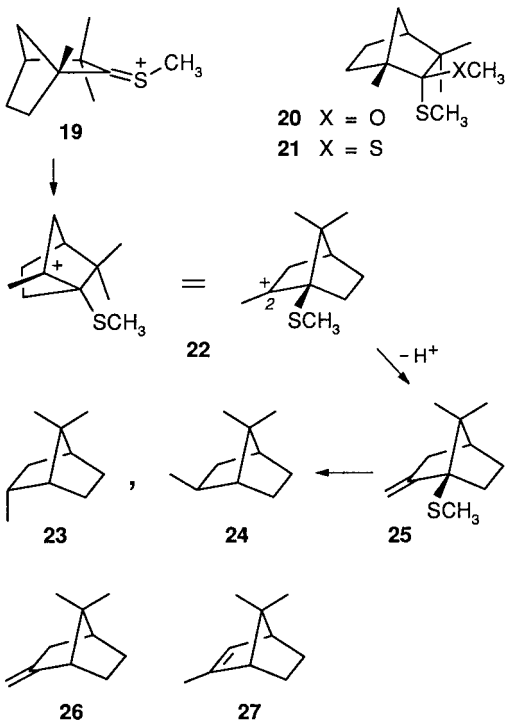
Liberation of the *S*-ylide **7** in the presence of 1 equiv. of acetic acid in THF (12 hours, 40°C) furnished 1-(methylthio)-α-fenchene (**25**), which is formed by a Wagner-Meerwein rearrangement [17] of the carbosulfonium ion **19**. The yield of **25** was 52% by ^{1}H NMR analysis and 44% by isolation. 2,2-Bis(methylthio)fenchane (**21**) appeared as a by-product (46%, based on 2 mol equiv. of **7**), but is of somewhat obscure provenance.

The vinyl protons of **25** appear at δ_H 4.83 and 5.12, whereas the CH_3S group resonates at 2.07. Chemical evidence came from the treatment of **25** with Raney nickel in refluxing ethanol. Beside the hydrogenolysis of the C–S bonds, a saturation of the C=C bond was observed. The products formed in this process were *endo*- and *exo*-2,7,7-trimethylnorbornane (**23** and **24**), in the literature also known as isobornylanes or α-fenchanes [18].

An authentic sample of α-fenchene (26) was subjected to the same hydrogenation with Raney nickel and ethanol. The *endo*/*exo* mixtures of **23** and **24** were identified by their ^{13}C signals (3q, 3t, 3d, 1s each), and a statistical analysis revealed the *endo*/*exo* ratios, **23**/**24**, namely 68:32 for the product from **25**, and 61:39 for the reduction of **26**. Since the deviation exceeds the error limit, we conclude that the reduc-



SCHEME 4



SCHEME 5

tion of **25** does not completely take place via **26** as an intermediate. It is noteworthy that the hydrogenation of **26** with Pd/H_2 in ethanol afforded **23** and **24** in the ratio of 29:71, that is, this time the exo-form predominates. Brown and Kawakami studied the reduction of α-fenchene and observed **23/24** = 14:86 for hydroboration/protonolysis and 27:73 for the Pt-catalyzed hydrogenation [19]. The reduction of α-fenchene, catalyzed by $Rh(PPh)_3Cl$, gave **23/24** = 63:37, according to Rousseau et al. [20].

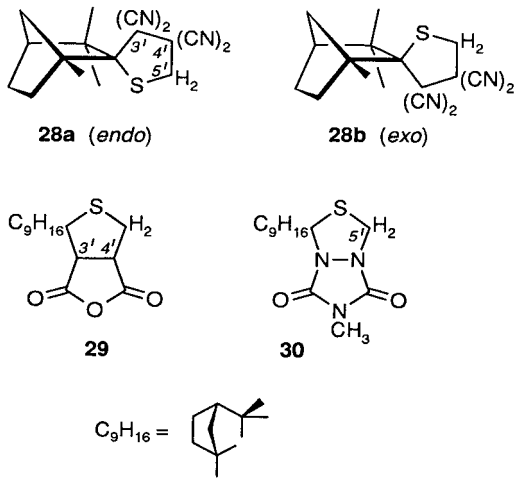
We briefly touch the problem of *endo*/*exo* assignment of **23** and **24**, even though it is not essential in our context. The hydroborations of bornene and apobornene proceed exclusively from the *endo* side. When the same procedure was applied to 2,7,7-trimethylnorbornene (**27**), it was concluded that the major product must be that of endo-hydroboration: **23/24** = 13:87 was found [19]. The connection with our ^{13}C NMR parameters stems from the near identical ratios of **23/24** observed in catalytic hydrogenation, 27:73 for Pt/H_2 [19], and 29:71 for Pd/H_2 (this work).

Why is the reaction of **7** with methanol not accompanied by the carbonium rearrangement to give **25** (an isomer of **7**), in contrast to the use of acetic acid as a catalyst? Methanolate recombines very rapidly with the carbosulfonium ion **19**, perhaps within a contact ion pair. The acetate anion is less nucleophilic and allows **19** a sufficient lifetime for the rearrangement. 2-Methylpropane-2-thiolate is a sterically hindered nucleophile. When **7** was set free from **6** in THF in the presence of 1.1 equiv. of *tert*-butyl mercaptan, ^1H NMR analysis established 59% of 1-(methylthio)-α-fenchene (**25**).

1,3-CYCLOADDITIONS OF THIOFENCHONE S-METHYLIDE (7)

Thiocarbonyl ylides are nucleophilic 1,3-dipoles, and electrophilic dipolarophiles are favored as cycloaddition partners. When N_2 was extruded from **6** in THF at 50°C in the presence of 1.2 equiv. of tetracyanoethylene, two crystalline cycloadducts were obtained and separated by preparative layer chromatography on silica gel (PLC). Quantitative ^1H NMR analysis indicated 59% and 29% of two stereoisomers **28a** and **28b**, the *endo*/*exo* assignment being unknown. The ^1H and ^{13}C NMR parameters fit structure **28** (Scheme 6).

The reaction with maleic anhydride (1.2 equiv.) provided a crystalline cycloadduct **29** (43%) and, in addition, 27% of **25**, the product of the Wagner-Meerwein rearrangement. Supposedly, a trace of maleic acid (hydrolysis of the anhydride) catalyzed the isomerization **7** → **25**. The presence of a second



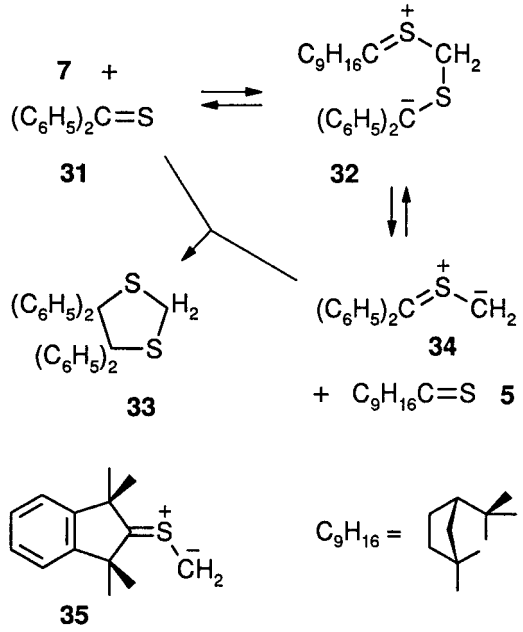
SCHEME 6

cycloadduct cannot be excluded. After the reaction of **7** with *N*-methyl-1,2,4-triazolinedione, ^1H NMR analysis established 54% of diastereoisomeric cycloadducts **30** in a ratio of 55:45. Partial separation was achieved by PLC, and moderate amounts of both isomers were obtained pure. Base peak in the MS of **30A** is *m/z* 168 for $C_{10}H_{16}S^+$ ($\mathbf{5}^+$), accompanied by *m/z* 135 (40%) for $C_{10}H_{15}^+$; $[M^+ - SH]$ is generally found as a fragment of the cation radicals of thioketones [21].

Surprisingly, the reaction of **6** (via **7**) with 2 equiv. of thiobenzophenone (**31**) did not give rise to the 1,3-dithiolane with spirofenchane group and two phenyl substituents, but rather to 4,4,5,5-tetraphenyl-1,3-dithiolane (**33**, 86% yield). The latter originates from addition of thiobenzophenone *S*-methylide (**34**) with **31** [15]. The transfer of a CH_2 group from **7** to **31**, producing **34** + **5**, and subsequent addition of **34** to a second molecule of **31** is a plausible pathway. Possibly, the transfer proceeds through **32**, which can be described as zwitterion or biradical (Scheme 7).

We encountered this CH_2 transfer in the reaction of **34** with adamantanethione (**3**); in addition to the expected cycloadduct, 8% of **33** was isolated [22]. The stronger the steric encumbrance of the thione *S*-methylide, the more the methylene transfer to thiobenzophenone becomes prevalent. For example, the reaction of *S*-ylide **35** with excess of **31** gave 96% of **33**, and tetramethylindane-2-thione was set free [23].

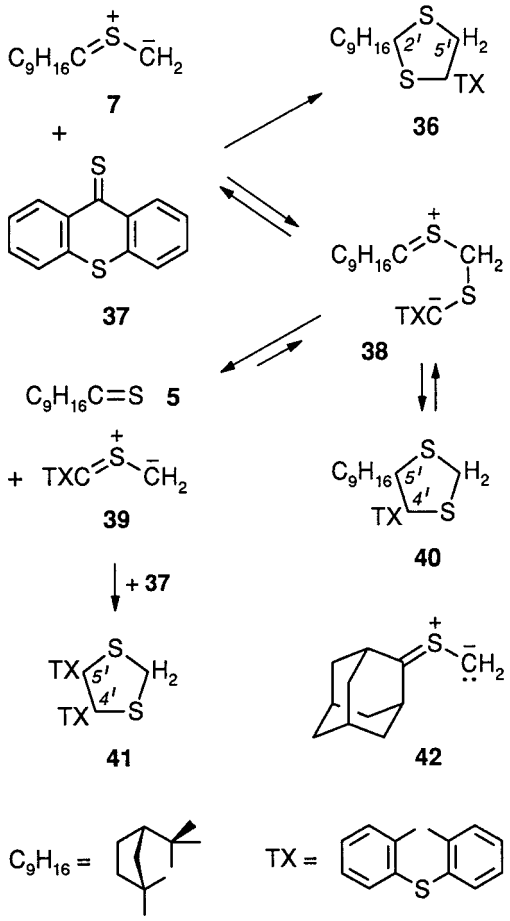
When the *S*-ylide **7** (2.00 mmol) interacted with thioxanthione (**37**) in THF at 40°C, 0.60 mmol of the 1,3-dithiolane **41** with two spiro-thioxanthene residues precipitated; the same compound was obtained



SCHEME 7

by Schönberg et al. from **37** and diazomethane [24] (Schönberg reaction [15]). ^{1}H NMR analysis of the soluble product showed 0.98 mmol of a mixture of two 1:1 cycloadducts. We did not succeed in separating them, but the similarity of the ^{1}H NMR spectra pointed to diastereoisomers of **36** with respect to the fenchylidene group; their ratio, 85:15, was determined from the intensities of ^{13}C signals. The AB spectrum of 5′-H_2 at δ 3.53 and 3.84 of the major cycloadduct did not distinguish between **36** and **40**. Clear evidence came from the C–S hydrogenolysis with nickel in ethanol: the occurrence of fenchane and 1,1-diphenylethane matched our expectation concerning **36**. The base peak in the MS is *m/z* 210 ($C_{14}H_{10}S^+$), which corresponds to [9-methylenexanthione]$^+$. This is a general fragmentation path of 1,3-dithiolanes [22,25] and accords with **36** (Scheme 8).

Since the 1,3-addition of adamantanethione *S*-methylide (**42**) to **37** produced two regioisomeric dithiolanes [25], our tentative reaction scheme displays both regioisomers as well, **36** and **40**. Due to the proximity of the voluminous groups in the 4′- and 5′-positions, **40** equilibrates with **38**, and stabilization is gained by formation of **41** via the splitting products **5** + **39** and renewed addition with **37**. The perpendicular arrangement of the thioxanthene residues in **41** probably generates less van der Waals pressure than the involvement of the fenchylidene group does in **40**. However, the mechanism of the addition of thione *S*-methylides to thiones (one-step or two-step) is not settled yet; the criterion of steric



SCHEME 8

course cannot be applied. The implications will be discussed elsewhere.

In conclusion: The cycloadditions of thiofenchone *S*-methylide (**7**) are hampered by severe steric hindrance which reduces the yields. In several experiments, substantial amounts of thiofenchone (**5**) point to side reactions. Adamantanethione *S*-methylide (**42**) and thiobenzophenone *S*-methylide (**34**) are certainly not free of steric screening of one of the terminal *C*-atoms; nevertheless, they still participate in the notoriously smooth course of 1,3-dipolar cycloadditions and furnish high adduct yields with electron-deficient dipolarophiles [26].

EXPERIMENTAL

General [27].

*2′,5′-Dihydrospiro[fenchane-2,2′-(1,3,4)-thiadiazole] (**6**) (1R,4S)-(−)-Thiofenchone (**5**) [28].* For purification on the 20 g scale, column chromatog-

raphy on silica gel (200 g) with pentane was suitable. ^{1}H NMR ($CDCl_3$) δ 1.12, 1.15, 1.28 (3s, 3 CH_3), 1.52, 1.72 (2m, 6H, 3 CH_2), 2.29 (m, 4-H).

Thiofenchone and Diazomethane. Compound **5** (840 mg, 5.00 mmol) was reacted with 20 mL of 0.475 M diazomethane (9.5 mmol, titrated content) in absolute THF for 2 hours. Evaporation at 0°C/15 mm and, finally, at 0°C/0.01 mm left a colorless oil; the ^{1}H NMR spectrum showed only the signals of thiadiazoline **6**. The oil crystallized at −25°C, m.p. 66–67°C (dec., N_2), and gave correct analyses without further purification (yield nearly quantitative). Dissolving in ether and cooling to −25°C afforded **6** as colorless rods. ^{1}H NMR ($CDCl_3$) δ 0.70 (s, CH_3), 0.94 (s, 2 CH_3), 1.53–1.82 (m, 3 CH_2), 2.69 (d, 4-H), 5.55 (s, 5′-H_2); (C_6D_6) δ 0.45, 0.65, 0.70 (3s, 3 CH_3), 1.00–1.68 (m, 3 CH_2), 2.49 (d, 4-H), 4.92 (s, 5′-H_2). Anal. calcd for $C_{11}H_{18}N_2S$ (210.34): C, 62.81; H, 8.63; N, 13.32; found: C, 62.64; H, 8.72; N, 12.84.

Even simpler is the passing of gaseous diazomethane, diluted by N_2, into the solution of 2.0 mmol of **5** in 30 mL of diethyl ether at −10°C, until the orange color turns light-yellow; this procedure requires some experience. Compound **6** crystallized from pentane at −78°C.

Kinetics of N_2 Extrusion from **6**. The magnetically stirred solution of 5.0 mmol of **6** in 10 mL of toluene was connected with a nitrometer (150 mL) and heated in a bath of 46 ± 1°C. After 6 minutes (22 mL of N_2), constancy of the temperature was assumed, and the N_2 volumes were monitored; the value after 180 minutes serving as V_∞. The plot of log ($V_\infty/V_\infty - V_t$) vs. time (20 values) was linear (r = 0.999) up to 90% reaction and provided $10^4\,k_2 = 5.2$ s^{-1}. The total N_2 volume (98%) was measured after cooling to room temperature. A second measurement at 52 ± 1°C (18 values with r = 0.999 up to 86% reaction) gave $10^4\,k_2 = 7.0$ s^{-1}.

Spiro[fenchane-2,2′-thiirane] (**8**)

The combined solutions of the kinetic experiments were freed of toluene in vacuo. The ^{1}H NMR analysis of the s at δ 2.36 with trichloroethylene (δ 6.70) as a weight standard indicated 63% of **8**, and an isomer ratio of 60:40 was determined from the integrals at δ 0.92 and 0.85. Bulb-to-bulb distillation at 55–60°C/10^{-3} mm furnished **8** (47%) as a colorless oil, which became glassy at 25°C and had a mintlike smell. After preparative layer chromatography (PLC) (2 mm silicagel, Merck PF_{254}) with pentane, the isomer ratio was unchanged, and crystallization was not achieved. ^{1}H NMR ($CDCl_3$, major/minor) δ 0.82/0.80 (s, CH_3), 0.92/0.85 (s, CH_3); both isomers: 1.01 (s, broadened, CH_3), 1.15–2.10 (m, 3 CH_2, 4-H), 2.36 (s, broad, 3′-CH_2). Anal. calcd for $C_{11}H_{18}S$ (182.32): C, 72.46; H, 9.95; S, 17.59; found: C, 72.35; H, 10.08; S, 17.53.

Fenchone Nβ-[(2,4-Dinitrophenylthio)-methylene]hydrazone (**16**)

Compound **6** (420 mg, 2.00 mmol) in 20 mL of absolute methanol was reacted with sodium methanolate (2.00 mmol); no N_2 evolution was observed at 45°C. 2,4-Dinitrochlorobenzene (405 mg, 2.00 mmol) was slowly added, and the solution heated to 45°C for 30 minutes. Workup with H_2O/CH_2Cl_2, PLC (CH_2Cl_2), and recrystallization from isopropyl alcohol afforded **16** (420 mg, 56%) in golden-yellow needles, m.p. 72–73°C. IR ($CHCl_3$) ν 1346 vst, 1532 vst (NO_2); 1598 st, 1645 st (C=N). ^{1}H NMR ($CDCl_3$) δ 1.22, 1.25, 1.32 (3s, 3 CH_3, 1.4–2.0 (m, 7 H), 7.75 (s, HC=N), 7.80 (d, J = 8.6 Hz, 6′-H), 8.55 (dd, J = 8.6, 2.0 Hz, 5′-H), 8.82 (d, J = 2.0 Hz, 3′-H). MS (90°C); *m/z* (%) 376 (11) [M^+], 81 (100) [$C_6H_9^+$]. Anal. calcd for $C_{17}H_{20}N_4O_4S$ (376.43): C, 54.24; H, 5.36; N, 14.89; S, 8.52; found: C, 54.27; H, 5.37; N, 14.74; S, 8.82.

Fenchone Nβ-(Piperidinomethylene)hydrazone (**17**)

Compound **6** (2.00 mmol) in 10 mL of piperidine was kept for 3 hours at room temperature and worked up with H_2O/CH_2Cl_2. PLC (CH_2Cl_2/ethanol 9:1) provided **17** (250 mg, 48%) as a colorless oil. IR (neat) ν 1105 m, 1209 st, 1258 st, 1453 st; 1609 vst, 1652 vst (C=N). ^{1}H NMR ($CDCl_3$) δ 0.90–1.87 (m, 15 H), superimposed by 1.17, 1.22, 1.28 (3s, 3 CH_3), 3.04–3.38 (m, CH_2-N), 7.64 (s, HC=N). ^{13}C NMR ($CDCl_3$) δ 17.6, 23.3, 24.0 (3q, 3 CH_3), 24.8, 25.5 (2t, 2 CH_2), 25.6 (t, 2 CH_2), 34.4 (t, broadened, CH_2), 43.2 (t, CH_2), 47.2 (t, 2 N-CH_2), 44.9, 50.3 (2s, C-1, C-3), 48.8 (d, C-4), 157.7 (d, N=CH–N), 177.3 (s, C-2). MS (30°C); *m/z* (%) 261 (72) [M^+], 245 (9) [M^+-CH_3], 233 (13) [$M^+ - C_2H_4$], 177 (30) [$M^+ - NC_5H_{10}$], 152 (45) [$C_9H_{16}C = NH_2^+$], 111 (37), 84 (100) [$NC_5H_{10}^+$], 83 (62), 81 (31). Anal. calcd for $C_{16}H_{27}N_3$ (261.40): C, 73.51; H, 10.41; N, 16.08; found: C, 73.57; H, 10.40; N, 15.78.

Fenchone Nβ-(Morpholinomethylene)hydrazone (**18**)

The same procedure with 2.00 mmol of **6** and 10 mL of morpholine furnished 220 mg (42%) of 18 as a

colorless oil. IR (neat) *v* 869 st, 1116 vst (C-O), 1231 st, 1269 st, 1445 st, br.; 1605 vst, 1652 vst (C=N). ^{1}H NMR ($CDCl_3$) δ 0.9–2.13 (m, 7 H), superimposed by 1.23, 1.28, 1.32 (3s, 3 CH_2), AA′BB′ at 3.19–3.45 (2 CH_2-N), 3.54–3.81 (m, 2 CH_2-O), 7.67 (s, CH=N). MS (30°C); *m/z* (%) 263 (92) [M^+], 248 (7) [M^+-CH_3], 247 (11), 222 (8), 221 (6), 195 (7), 177 (100) [M^+-NC_4H_8O], 152 (36) [$C_{10}H_{18}N^+$], 115 (29), 113 (42) [$C_5H_9N_2O^+$, probably OC_4H_8N-C≡NH^+], 91 (10) [$C_7H_7^+$], 86 (52) [$OC_4H_8N^+$], 81 (45) [$C_6H_9^+$]. Anal. calcd for $C_{15}H_{25}N_3O$ (263.37): C, 68.40; H, 9.57; N, 15.96; found: C, 68.21; H, 9.54; N, 15.76.

*2′,5′-Dihydrospiro[camphane-2,2′-(1.3.4)-thiadiazole] (**12**)*

*Thiocamphor (**9**) and Diazomethane.* (±)-9 [29], (500 mg, 2.97 mmol) was added to ~12 mmol of diazomethane in 30 mL of ether at −40°C. After the solution reached 10°C in 2 hours, thin-layer chromatography (TLC) showed that **9** was consumed. Ether and diazomethane were removed in vacuo at 0°C. The remaining colorless oil contained **11** and **12** in nearly 1:1 ratio, according to the six C–CH_3 singlets in the ^{1}H NMR spectrum ($CDCl_3$). After 4 hours at room temperature, ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as weight standard (s at δ 3.70, 6.05) indicated 82% of **11** (d at δ 5.38).

*2-(Methylthio)-2-bornene (**11**).* IR (neat) *v* 1562 m (C=C). ^{1}H NMR ($CDCl_3$) δ 0.78, 0.83, 1.00 (3s, 3 CH_3), 1.0–2.1 (m, 2 CH_2), 2.17 (s, SCH_3), 2.34 (t, J = 3.5 Hz, 4-H), 5.38 (d, J = 3.5 Hz). Anal. calcd for $C_{11}H_{18}S$ (182.32): C, 72.46; H, 9.95; S, 17.59; found: C, 72.89; H, 9.77; S, 17.27.

^{1}H NMR of Thiadiazoline **12** ($CDCl_3$, subtraction of signals of **11**) δ 0.67, 0.93, 1.04 (3s, 3 CH_3), 0.8–2.5 (m, 6H), 5.45, 5.89 (AB, J = 16.8 Hz, 5′-H_2).

Acid Cleavage of **11**. Enol ether **11** (0.50 mmol) was briefly refluxed with 2,4-DNPH in aqueous ethanolic H_2SO_4. The orange crystals of (±)-camphor 2,4-dinitrophenylhydrazone (140 mg, 83%), m.p. 156–158°C, were identified by mixed m.p. with an authentic sample (164°C) [30].

*Thiofenchone S-Methylide (**7**) and Acids*

Methanol. Compound **6** (210 mg, 1.00 mmol, freshly recryst.) was heated in 10 mL of methanol in a 45°C bath for 8 hours. After removal of methanol at the rotary evaporator, the ^{1}H NMR analysis ($CDCl_3$), based on the integrals of s at δ 3.41 (OCH_3) and that of *as*-tetrachloroethane (δ 4.28), indicated 96% of **20**. PLC (petroleum ether/CH_2Cl_2 9:1) and crystallization from methanol at −78°C gave *exo*-2-methoxy-*endo*-2-(methylthio)fenchane (**20**, 130 mg, 61%), m.p. 126–128°C. IR (KBr) *v* 904 st, 926 st, 1069 vst, 1088 vst (C–O); 1473 st. ^{1}H NMR ($CDCl_3$) δ 0.70–2.22 (m, 7 H), superimposed by 1.10, 1.13, 1.15 (3s, 3 CH_3), 1.93 (s, SCH_3), 3.41 (s, OCH_3). MS (30°C); *m/z* (%) 215 (3) [M^+ + 1], 199 (15) [M^+ − CH_3], 183 (8) [M^+ − OCH_3], 167 (88) [M^+ − SCH_3], 152 (12) [167 − CH_3], 131 (13), 123 (9), 93 (10), 81 (100) [$C_6H_9^+$], 80 (13). Anal. calcd for $C_{12}H_{22}OS$ (214.36): C, 67.23; H, 10.26; S, 14.96; found: C, 66.92; H, 10.23; S, 15.05.

Compound **20** (107 mg, 0.50 mmol) was reacted with 2,4-DNPH in ethanolic H_2SO_4. After 2 days at room temp., 145 mg (87%) of (−)-fenchone 2,4-dinitrophenylhydrazone was filtered, m.p. 160–162°C, identified by mixed m.p. and ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$) δ 1.32, 1.37, 1.45 (3s, 3 CH_3), 1.2–2.1 (m, 7H), 7.82 (d, J = 9.6 Hz, 6′-H), 8.20 (dd, J = 9.6, 2.4 Hz, 5′-H), 9.00 (d, J = 2.4 Hz, 3′-H).

Acetic Acid. Compound **6** (841 mg, 4.00 mmol) in 12 mL of abs. THF and 240 mg (4.00 mmol) of acetic acid was heated at 40°C for 12 hours (96% N_2). After evaporation of the solvent, ^{1}H NMR analysis ($CDCl_3$) with trichloroethylene showed 2.08 mmol (52%) of **25** (s at δ 4.83). PLC (petroleum ether/CH_2Cl_2 9:1) furnished 210 mg, 0.91 mmol of **21** (46%, based on 2 equiv. of **6**) as the first fraction, followed by **25** (320 mg, 44%). A second PLC procedure was required to obtain **25** analytically pure.

*2,2-Bis(methylthio)fenchane (**21**).* Compound **21** was recrystallized from methanol at −78°C, m.p. 117–119°C. IR (KBr) *v* 1105 m, 1346 m, 1386 m, 1459 st. ^{1}H NMR ($CDCl_3$) δ 0.80–2.45 (m, 7 H), superimposed by 1.21 (s, 3-*endo*-CH_3), 1.27 (s, 1-CH_3, 3-*exo*-CH_3), 2.05 (s, *endo*-SCH_3), 2.11 (s, *exo*-SCH_3). MS (30°C); *m/z* (%) 230 (6) [M^+], 215 (32) [M^+ − CH_3], 183 (87) [M^+ − SCH_3], 182 (100) [183 − H, $C_{11}H_{18}S^+$], 168 (33) [$C_{10}H_{16}S^+$, **5**$^+$], 167 (73) [182 − CH_3], 139 (49), 135 (51) [**5**$^+$ − HS, $C_{10}H_{15}^+$], 127 (60), 119 (42), 93 (61) [$C_7H_9^+$], 91 (56) [$C_7H_7^+$], 81 (60) [$C_6H_9^+$]. Anal. calcd for $C_{12}H_{22}S_2$ (230.43): C, 62.54; H, 9.62; S, 27.83; found: C, 62.99; H, 9.46; S, 27.87. The reaction with 2,4-DNPH in ethanolic H_2SO_4 (5 minutes on steam bath) gave rise to (−)-fenchone 2,4-dinitrophenylhydrazone (87%) as orange needles, m.p. 159–162°C (mixed m.p.).

*1-(Methylthio)-α-fenchene (**25**).* Colorless oil which solidifies at room temperature. ^{1}H NMR ($CDCl_3$) δ 0.78, 1.05 (2s, 2 CH_3), 1.07–2.0 (m, 6 H), 2.07 (s, SCH_3), 2.28–2.70 (m, 1 H), 4.83, 5.12 (2t, $J \approx$ 2 Hz, H_2C=). Anal. calcd for $C_{11}H_{18}S$ (182.32): C, 72.46; H, 9.95; S, 17.59; found: C, 72.42; H, 9.81; S, 17.54.

Conversion of **25** *to 2,7,7-Trimethylbicyclo[2.2.1]-heptane (***23,24***).* Compound **25** (550 mg, 3.02 mmol) in 50 mL of absolute ethanol and ca. 15 g Raney nickel (freshly prepared W2 [31]) were refluxed for 20 hours, hot filtered, and washed with 3 × 20 mL of hot ethanol. After adding H_2O and 40 mL of pentane, the phase separation required 2 days. The pentane was slowly distilled (Vigreux column) from a 40°C bath; then distillation at 165°C (bath) gave 245 mg of isobornylane as a 68:32 mixture of *endo*-2-methyl (**23**) and *exo*-2-methyl (**24**) form. The ^{13}C NMR spectrum showed 19 signals (20 expected; coincidence: d at 45.0); **23** and **24** were identified with the hydrogenation product of α-fenchene (see below). MS (20°C); *m/z* (%) 138 (1.8) [M^+], 123 (1.2) [$M^+ - CH_3$], 109 (3) [123 − CH_2], 95 (7) [123 − 2 CH_2, $C_7H_{11}^+$], 85 (6), 84 (93) [$C_6H_{12}^+$], 83 (6), 69 (28) [$C_5H_9^+$], 56 (100) [$C_4H_8^+$].

*Hydrogenation of (1S,4R)-(+)-α-Fenchene (***26***).* (+)-α-Fenchol was converted to the tosylate, m.p. 96–98°C, and the elimination of TsOH followed the procedure (KF in diglycol) given by Hanack [32]. Spinning-band column distillation afforded **26**, b.p. 155.8–156.4°C (156–157°C [32]). ^{13}C NMR ($CDCl_3$, 20 MHz) δ 20.7, 21.7 (2q, 2 CH_3), 28.6, 28.8 (2t, C-5, C-6), 37.5 (t, C-3), 45.0 (d, C-4), 46.0 (s, C-7), 53.8 (d, C-1), 103.0 (t, $H_2C=$), 156.3 (s, C-2). The hydrogenation of **26** with Raney nickel and boiling ethanol was carried out as described previously. The ^{13}C NMR spectrum of the product showed the same signals as the sample which originated from **25**, but in the ratio **23/24** = 61:39. The comparison of H-decoupled and off-resonance spectrum provided the multiplicities. The expectation that within each group (3 CH_3, 3 CH_2, 3 CH, 1 C_q) integrals would be similar for **23** on one side and for **24** on the other, was fulfilled. The integrals clearly fell into two groups of 9 + 9 + coincidence signal; isomer ratios resulted from a statistical analysis. Note that ^1H NMR spectra (100 MHz) were useless for the analysis here.

In a further experiment, α-fenchene (**26**, 1.36 g, 10 mmol) in ethanol was shaken under H_2 with Pd (10% on carbon). After uptake of 206 mL of H_2, workup as above furnished 995 mg (72%) with a ratio **23/24** = 29:71. The isomer separation by chromatography did not succeed. ^1H NMR ($CDCl_3$, 80 MHz) of CH_3 signals: δ 0.94, 1.00, 1.03 for **23** and 0.94, 1.07, 1.08 for **24**. ^{13}C NMR $CDCl_3$, 20 MHz) of **23**: δ 17.8, 20.96, 21.9 (3q, 3 CH_3); 21.05, 29.8, 38.71 (3t, 3 CH_2); 31.9, 45.0, 49.1 (3d, 3 CH); 47.9 (s, C-7); **24**: 22.3, 22.93, 23.05 (3q, 3 CH_3); 28.0, 31.4, 39.4 (3t, 3 CH_2); 38.86, 45.0, 50.2 (3d, 3 CH); 46.3 (s, C-7). Anal. calcd for $C_{10}H_{18}$ (138.24): C, 86.88; H, 13.12; found: C, 86.58; H, 13.00.

2-Methylpropane-2-thiol. Thiadiazoline **6** (2.00 mmol) and 2.20 mmol of the thiol in 4 mL of absolute THF were heated to 40°C for 8 hours (49 mL of N_2). After removal of the solvent, the ^1H NMR integral of the s at δ 4.83 (vinyl-H), compared with that of weighed trichloroethylene, indicated 59% of 1-(methylthio)-α-fenchene (**25**).

*Cycloadditions of Thiofenchone S-Methylide (***7***)*

Tetracyanoethylene (TCNE). Compound **6** (1.00 g, 5.94 mmol) and TCNE (900 mg, 7.03 mmol) in 5 mL of THF were reacted at 50°C for 2.5 hours (146 mL of N_2, 98%). After evaporation, the minor cycloadduct **28B** (155 mg, 8%) crystallized from ether/pentane (1:5), m.p. 163–165°C (dec.). The excess of TCNE was removed by aqueous sodium sulfite, and the residue of the mother liquor was subjected to PLC (CH_2Cl_2). The main zone furnished the major isomer **28A** (445 mg, 24%), m.p. 163–164°C, from methanol. In separate experiments in absolute THF (or benzene), the crude product was ^1H NMR-analyzed ($CDCl_3$) vs. trichloroethylene as standard: the s of CH_3 at δ 1.34 and 1.30 indicated 59% (62%) of **28A** and 29% (27%) of **28B**, corresponding to adduct yields of 88% (89%).

*3′,3′,4′,4′-Tetracyanospiro-[fenchane-2,2′-thiolane] (***28***). Isomer* **A**. Colorless needles, m.p. 166–167°C (dec.) from methanol at −25°C. ^1H NMR ($CDCl_3$) δ 1.34, 1.64, 1.75 (3s, 3 CH_3), 1.3–2.4 (m, 7 H), 3.65, 3.75 (AB, J = 12.9 Hz, 5′-H_2). ^{13}C NMR ($CDCl_3$) δ 21.2, 24.8, 31.1 (3q, 3 CH_3); 25.3, 30.8, 39.0, 47.0 (4t, 4 CH_2); 49.3 (d, C-4); 50.4, 53.9, 55.6, 57.1 (4s, C-1, C-3, C-3′, C-4′); 78.5 (s, C-2), 111.1, 111.55, 111.60, 111.9 (4s, 4 CN). MS (90°C); *m/z* (%): 310 (7) [M^+], 257 (3), 232 (6), 228 (5), 199 (5), 168 (7) [$C_{10}H_{16}S^+$, **5**$^+$], 123 (13) [$C_9H_{15}^+$], 93 (6) [$C_7H_9^+$], 91 (6) [$C_7H_7^+$], 81 (100) [$C_6H_9^+$]. Anal. calcd for $C_{17}H_{18}N_4S$ (310.41): C, 65.77; H, 5.85; N, 18.05; S, 10.33; found: C, 65.61; H, 5.80; N, 18.15; S, 10.41.

Isomer **B**. Colorless needles from methanol, m.p. 165–166°C (dec., mixed m.p. with **A** depressed). ^1H NMR ($CDCl_3$) δ 1.30, 1.65, 1.83 (3s, 3 CH_3), 1.5–2.5 (m, 7 H), 3.75 (A_2, 5′-H_2); (C_6D_6): δ 0.94, 1.21, 1.43 (3s, 3 CH_3), 0.45–2.20 (m, 7 H), 2.44, 2.46 (AB, J = 13.6 Hz, 5′-H_2). ^{13}C NMR ($CDCl_3$) δ 24.1, 24.6, 27.5 (3q, 3 CH_3); 22.9, 38.9, 41.5, 44.2 (4t, 4 CH_2); 51.1 (d, C-4); 49.7, 50.7, 55.2, 55.7 (4s, C-1, C-3, C-3′, C-4′); 81.8 (s, C-2); 2 × 111.4, 112.8, 113.0 (4s, 4 CN). Anal. calcd for $C_{17}H_{18}N_4S$ (310.41): C, 65.77; H, 5.85; N, 18.05; S, 10.33; found: C, 65.60; H, 5.77; N, 17.78; S, 10.31.

Maleic Anhydride. Compound **6** (2.97 mmol) and maleic anhydride (freshly sublimated, 350 mg, 3.57 mmol) in 6 mL of THF were stirred in a 45°C bath for 2.5 hours (73 mL of N_2, 98%). Colorless crystals of **29** (186 mg, 22%), m.p. 182–184°C, were obtained from ether/pentane (1:1) and recrystallized from $CHCl_3$/ether. Bulb-to-bulb distillation of the mother liquor at 60–65°C/1 mm gave **25** (203 mg, 38%) as a colorless liquid which glass-like solidified. The product of a second experiment was subjected to ^{1}H NMR analysis with *sym*-tetraychloroethane: the broad s of vinyl-H at δ 4.83 indicated 27% of **25**, and the m at 3.6–4.0 showed 43% of **29**.

*Spiro[fenchane-2,2′-thiolane]-3′,4′-dicarboxylic anhydride (**29**).* m.p. 185–186°C. ^{1}H NMR ($CDCl_3$) δ 1.08, 1.20, 1.35 (3s, 3 CH_3), 1.5–2.5 (m, 7H), 2.95–3.50 (m, 2H), 3.58–4.00 (m, 2H). MS (80°C); *m/z* (%): 280 (21) [M^+], 237 (12), 207 (9), 197 (35) [M^+-C_6H_{11}], 125 (41) [$C_9H_{17}^+$], 123 (73) [$C_9H_{15}^+$], 83 (22) [$C_6H_{11}^+$], 81 (100) [$C_6H_9^+$]. Anal. calcd for $C_{15}H_{20}O_3S$ (280.38): C, 64.25; H, 7.19; S, 11.44; found: C, 64.44; H, 7.17; S, 11.42.

4-Methyl-1,2,4-triazoline-3,5-dione. Compound **6** (7.36 mmol) and 1.00 g (8.83 mmol) of the cyclic azo compound in 12 mL of THF were reacted at 50°C for 3 hours (100% N_2). After removal of the solvent, the residue in CH_2Cl_2 was extracted with 10% aqueous Na_2SO_3. The residue of the organic phase was separated by PLC (CH_2Cl_2): fenchone (347 mg, 30%), **30B** (90 mg, 4%) as a pale-yellow oil, and **30A** (224 mg, 10%), was eluted with ethyl acetate and crystallized from benzene/methanol, m.p. 162–165°C (dec., red). In a second experiment, the ^{1}H NMR analysis (C_6D_6) was based on the AB spectra for 5′-H_2 of **30A** and **30B** and the s of trichloroethylene as weight standard, and indicated 54% of **30**; the s of NCH_3 (C_6D_6) showed **A/B** = 55:45.

*Spiro[fenchane-2,2′-(1,3,4)-triazolidine]-3′,4′-dicarbox(N-methylimide) (**30**). Isomer **30A**.* ^{1}H NMR ($CDCl_3$) δ 1.02, 1.28, 1.30 (3s, 3 CH_3), superimposed by 0.9–3.05 (several m, 7 H), 3.06 (s, NCH_3), 4.47, 4.60 (AB, J = 9.5 Hz, 5′-H_2); (C_6D_6): δ 0.89, 1.02, 1.40 (3s, 3 CH_3), 0.8–1.7 (m, 7 H), 2.69 (s, NCH_3), 3.12 (dq, J = 10.0, ~2 Hz, 1 H), 3.93, 4.04 (AB, J = 10.0 Hz, 5′-H_2). ^{13}C NMR (20.2 MHz, C_6D_6); δ 17.5, 2 × 25.2, 26.6 (3q, 4 CH_3); 24.5, 37.6, 43.2 (3t, 3 CH_2), 41.1 (dd, probably C-5′), 49.6 (d, C-4), 51.3, 51.6 (2s, C-1, C-3), 91.7 (s, C-2), 146.2, 149.9 (2s, 2 C=O). MS (80°C), *m/z* (%): 295 (30) [M^+], 240 (3), 212 (10), 210 (16), 182 (15), 168 (100) [$C_{10}H_{16}S^+$, **5**$^+$], 153 (13), 135 (41) [168 - SH, $C_{10}H_{15}^+$], 125 (23), 113 (21), 112 (18), 91 (15) [$C_7H_7^+$], 81 (66) [$C_6H_9^+$]. Anal. calcd for $C_{14}H_{21}N_3O_2S$ (295.40): C, 56.92; H, 7.17; N, 14.23; S, 10.86; found: C, 57.09; H, 7.30; N, 13.98; S, 10.83.

*Isomer **30B**.* ^{1}H NMR ($CDCl_3$) δ 1.11, 1.33, 1.36 (3s, 3 CH_3); 1.40–2.20 (m, 7 H), 3.05 (s, NCH_3), 4.48, 4.84 (AB, J = 9.2 Hz, 5′-H_2); (C_6D_6): δ 0.98, 1.12, 1.38 (3s, 3 CH_3), 0.65–2.00 (m, 7 H), 2.56 (s, NCH_3), 3.99, 4.55 (AB, J = 10.4 Hz). ^{13}C NMR (20.2 MHz, C_6D_6) δ 20.7, 24.1, 26.0, 29.0 (4q, 4 CH_3); 25.3, 32.2, 46.0, 50.0 (4t, 4 CH_2); 49.3, 52.4 (2s, C-1, C-3), 94.4 (S, C-2); 151.1, 155.9 (2s, 2 C=O); the ^{13}C signal intensities point to **A/B** = 60:40.

Thiobenzophenone. From **6** (511 mg, 2.43 mmol) and **31** (963 mg, 4.86 mmol, freshly distilled) in 8 mL of THF at 50°C, 98% of N_2 was eliminated in 2.5 hours. Trituration of the crude product with ether left undissolved 853 mg (86%) of *4,4,5,5-tetraphenyl-1,3-dithiolane* (**33**), m.p. 205–208°C; after recrystallization from $CHCl_3$/pentane, the colorless **33** showed m.p. 206–208°C (dec., blue; 199–200°C [33], 205–207°C [15]), and was identified by its ^{1}H NMR spectrum [15]. Anal. calcd for $C_{27}H_{22}S_2$ (410.58): C, 78.98; H, 5.40; S, 15.62; found: C, 78.83; H, 5.40; S 15.60.

*Thioxanthione (**37**).* Compounds **6** (420 mg, 2.00 mmol) and **37** (502 mg, 2.20 mmol) in 6 mL of THF at 40°C were stirred for 8 hours (49 mL of N_2, 98%). Evaporation of THF and trituration with $CDCl_3$ at 0°C left **41** (280 mg, 30%) undissolved, m.p. 170–172°C (168–170°C [24]). After addition of a weighed amount of *sym*-tetrachloroethane, the AB systems of 5′-H_2 at δ 3.3–4.0 indicated 49% of **36A** and **36B**. In the separation by PLC (petroleum ether/CH_2Cl_2 7:3), thiofenchone (**5**) moved as the first fraction and was identified by its R_F. The second fraction (280 mg, 34%), colorless crystals, m.p. 168–175°C, showed after recrystallization from CH_2Cl_2/ethanol still the broad m.p. 173–178°C, and consisted of **36, A/B** = 85:15 (^{13}C NMR integrals). Our attempts of separating the *exo, endo* isomers by chromatography or fractional crystallization failed.

*Dispiro[1,3-dithiolane-4,9′;5,9″-bis(thioxanthene)] (**41**).* ^{1}H NMR (C_6D_6): δ 3.84 (s, 2-H_2), 6.20, 6.83, 7.16, 7.75 (4m, 16 arom. H); ($CDCl_3$): δ 4.48 (s, 2-H_2). Anal. calcd for $C_{27}H_{18}S_4$ (470.68): C, 68.90; H, 3.85; S, 27.25; found: C, 69.25; H, 3.95; S, 27.24.

*Dispiro[fenchane-2,5′-(1,3)-dithiolane-4′,9″-thioxanthene] (**36**). Adduct **36A**.* ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 2 CH_3), 1.25 (s, CH_3), 1.3–2.0 (m, 7 H), 3.53 and 3.84 (AB, J = 12.0 Hz, 5′-H_2), 7.0–7.5, 7.8–8.1 (2m, 6 + 2 arom. H). ^{13}C NMR ($CDCl_3$, 20 MHz) δ

20.6, 26.6, 33.0 (3q, 3 CH_3), 26.0, 34.1, 43.4, 43.5 (4t, 4 CH_2), 49.6 (d, C-4), 126.0, 126.1, 126.5, 126.8, 127.5 (5d, 8 arom. CH), 48.5, 56.2, 71.1, 87.2 (4s, 4 aliph. C_q), 134.2, 134.3, 138.5, 139.0 (4s, 4 arom. C_q). MS (90°C); *m/z* (%) 410 (0.1) [M^+], 242 (2.2) [$C_{14}H_{10}S_2^+$, $M^+ - \mathbf{5}$; $^{13}C_2 + {}^{34}S$ calcd/found 0.22/0.19], 228 (0.5) [$C_{13}H_8S_2^+$, $\mathbf{37}^+$], 210 (100) [$C_{14}H_{10}S^+$, 9-Methylenethioxanthene$^+$; ^{13}C 16/15; $^{13}C_2 + {}^{34}S$ 0.22/0.19], 178 (4.2) [$C_{14}H_{10}^+$, 210 − S, ^{13}C 0.66/0.65; $^{13}C_2$ 0.05/0.05, S-free], 168 (0.7) [$C_{10}H_{16}S^+$, $\mathbf{5}^+$], 165 (8) [$C_{10}H_{13}^+$, fluorenyl$^+$], 152 (1.4) [$C_{12}H_8^+$], 135 (0.5) [168 − SH], 123 (1.7) [$C_9H_{15}^+$], 91 (1) [$C_7H_7^+$], 81 (4) [$C_6H_7^+$].

Adduct **36B**. ^{13}C NMR ($CDCl_3$) δ 19.0, 29.1, 29.9 (3q, 3 CH_3), 26.0, 33.2, 42.4, 44.8 (4t, 4 CH_2), 49.8 (d, C-4), 47.2, 57.4, 70.9, 85.9 (4s, 4 aliph. C_q), 125.5, 127.0, 127.1, 127.3 (4d, 8 arom. CH), 128.8 (s, only 1 arom. C_q visible). Anal. calcd for $C_{24}H_{26}S_3$ (410.65, 85:15 mixture): C, 70.19; H, 6.38; S, 23.43; found: C, 69.92; H, 6.18; S, 23.39.

Hydrogenolysis of **36**. 615 mg (1.50 mmol) and ~ 5 g Raney nickel [31] in 20 mL of ethanol were refluxed for 10 hours, filtered, washed with hot ethanol, diluted with 50 mL of H_2O, and extracted with 3 × 30 mL of pentane. After distillation of pentane over a column, *fenchane* (125 mg, 60%) distilled at 60–80°C (bath)/10 mm as a colorless oil; ^1H NMR ($CDCl_3$) δ 0.95 (s, 2 CH_3), 1.05 (s, CH_3), 1.05–1.8 (m, 9H). The residue in the microflask consisted of *1,1-diphenylethane* (215 mg), ^1H NMR-identified with an authentic sample; ^1H NMR ($CDCl_3$) δ 1.52 (d, J = 7.2 Hz, CH_3), 3.99 (q, J = 7.2 Hz, 1-H), 7.06 (s, 2 C_6H_5).

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