

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 N₂ (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

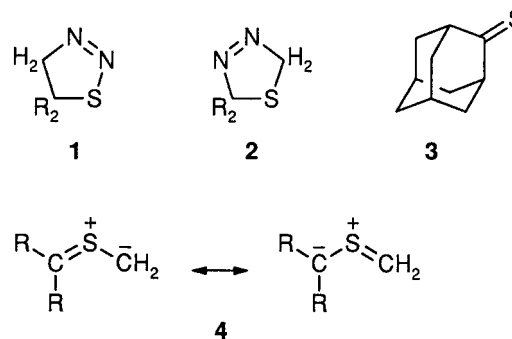
The 1,3-cycloadditions of thiocarbonyl ylides with C–C multiple bonds and hetero-double bonds offer a versatile route to five-membered S-heterocycles [1]. 2,5-Dihydro-1,3,4-thiadiazoles are formed by cycloaddition of diazoalkanes to thiocarbonyl com-

pounds, and thermal N₂ extrusion furnishes thioke-tone S-alkylides, which can be intercepted in situ.

Cycloadditions of diazomethane to dialkylthio-ketones 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.
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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 ¹H 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 LiAlH₄ 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

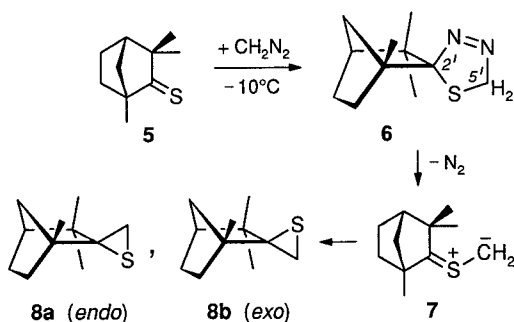
elimination of N₂ from **6** obeys the first-order law; the half-life in toluene amounts to 22.2 minutes at 46°C and to 16.5 minutes at 52°C. ¹H NMR analysis with weight standard indicated 63% of spirothiirane **8** and a diastereoisomer ratio of 60:40. We do not regard the small δ_H differences of the 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 N₂, the group C(2)-S-CH₂ 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.

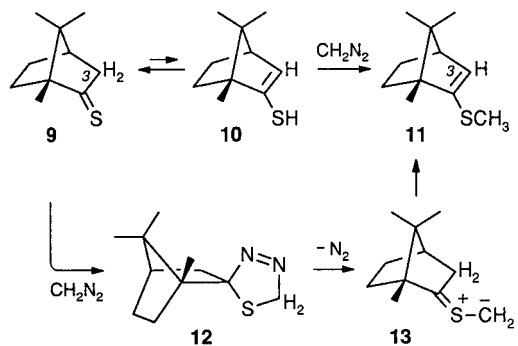
Thiocamphor (**9**) can tautomerize with a thioenol, in contrast to thiofenchone (**5**). A methylation of the acidic thioenol **10** by diazomethane appeared plausible, and indeed we obtained 2-(methylthio)-2-bornene (**11**) from the reaction at room temperature. However, when **9** and diazomethane reacted at -40°C and reached 10°C, the ¹H 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, ¹H NMR showed 82% of **11**, while the signals of **12** had disappeared (Scheme 3).

Compound **12** was confirmed by its ¹H NMR parameters. The observed AB spectrum at δ 5.45 and 5.89 with $J_{gem} = 16.8$ Hz is consistent with 5'-H₂ of **12**; the 5'-H₂ of **6** resonates at δ 5.55 (as A₂ 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 N₂ 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.

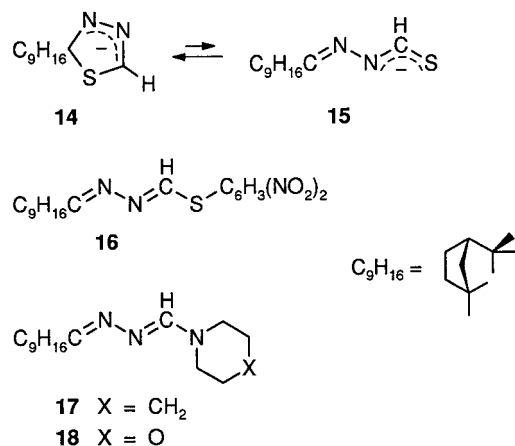
SPIROTHIADIAZOLINE 6 AS AN ACID

When **6** was treated with 1.0 equiv. of sodium methanolate in methanol, the lack of N₂ 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 N₂ 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 CH₃O singlet appears at δ 3.41 and that of CH₃S at 1.93. For analogy reasons, we suspect a structure incorporating *exo*-OCH₃ and *endo*-SCH₃. The initial step is probably protonation of **7** at the CH₂ termi-



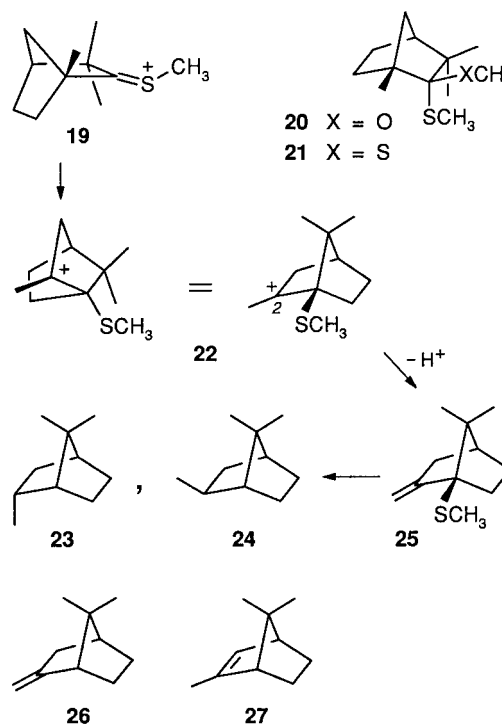
SCHEME 4

nus, 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 ¹H 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 CH₃S 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 ¹³C 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 5

tion of **25** does not completely take place via **26** as an intermediate. It is noteworthy that the hydrogenation of **26** with Pd/H₂ 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].

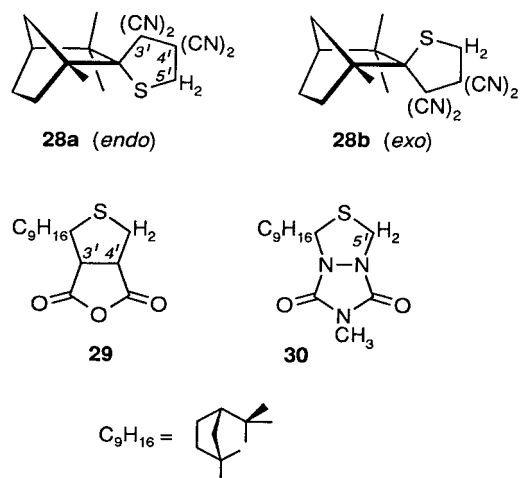
We briefly touch the problem of *endo/exo* assignment of **23** and **24**, even though it is not essential in our context. The hydroborations of bornene and apobornene proceed exclusively from the *endo* side. When the same procedure was applied to 2,7,7-trimethylnorbornene (**27**), it was concluded that the major product must be that of *endo*-hydroboration: 23/24 = 13:87 was found [19]. The connection with our ¹³C NMR parameters stems from the near identical ratios of 23/24 observed in catalytic hydrogenation, 27:73 for Pt/H₂ [19], and 29:71 for Pd/H₂ (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 N₂ 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 ¹³C 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



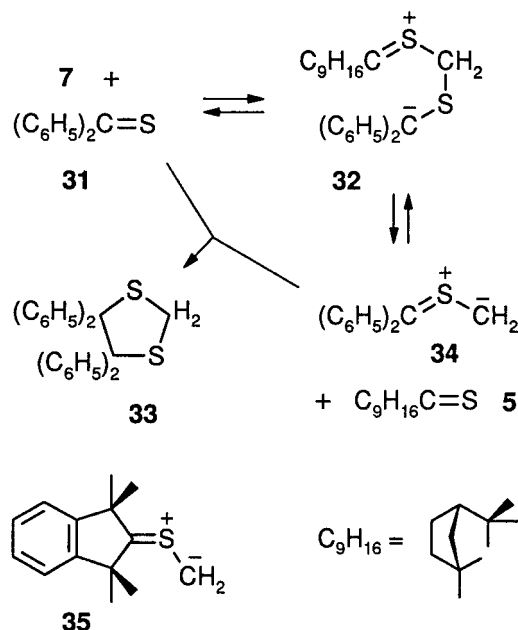
SCHEME 6

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 C₁₀H₁₆S⁺ (5⁺), accompanied by *m/z* 135 (40%) for C₁₀H₁₅⁺; [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 CH₂ 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 CH₂ 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].

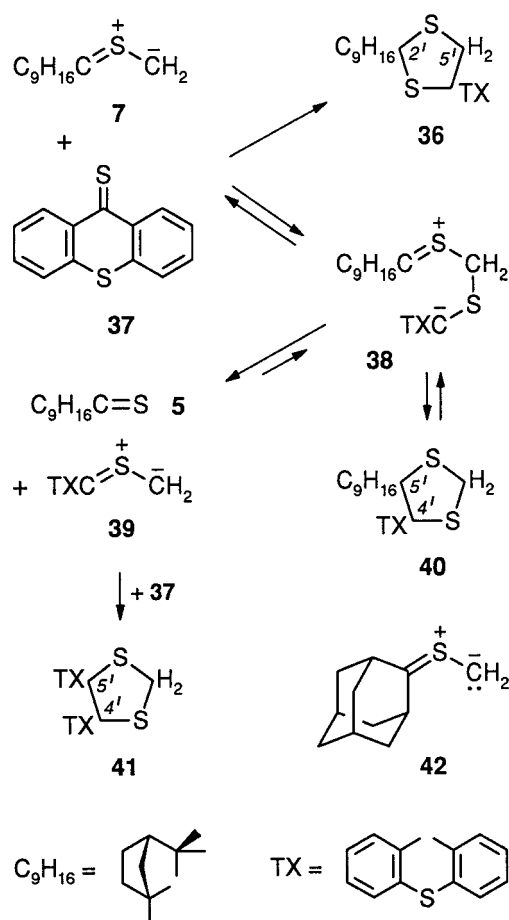
When the S-ylide **7** (2.00 mmol) interacted with thioxanthone (**37**) in THF at 40°C, 0.60 mmol of the 1,3-dithiolane **41** with two spiro-thioxanthene residues precipitated; the same compound was obtained



SCHEME 7

by Schönberg et al. from **37** and diazomethane [24] (Schönberg reaction [15]). ^1H 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 ^1H 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 $5'\text{-H}_2$ 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 ($\text{C}_{14}\text{H}_{10}\text{S}^+$), 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**) (1*R*,4*S*)-(–)-Thiofenchone (**5**) [28]. For purification on the 20 g scale, column chromatog-

raphy on silica gel (200 g) with pentane was suitable. ^1H 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 $0^\circ\text{C}/15$ mm and, finally, at $0^\circ\text{C}/0.01$ mm left a colorless oil; the ^1H NMR spectrum showed only the signals of thiadiazoline 6. The oil crystallized at -25°C , m.p. $66\text{--}67^\circ\text{C}$ (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. ^1H 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 $\text{C}_{11}\text{H}_{18}\text{N}_2\text{S}$ (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 $46 \pm 1^\circ\text{C}$. 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 $10^4 k_2 = 5.2 \text{ s}^{-1}$. The total N_2 volume (98%) was measured after cooling to room temperature. A second measurement at $52 \pm 1^\circ\text{C}$ (18 values with $r = 0.999$ up to 86% reaction) gave $10^4 k_2 = 7.0 \text{ s}^{-1}$.

Spiro[fenchane-2,2'-thiirane] (8)

The combined solutions of the kinetic experiments were freed of toluene in vacuo. The ^1H 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 $55\text{--}60^\circ\text{C}/10^{-3}$ 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 PF₂₅₄) with pentane, the isomer ratio was unchanged, and crystallization was not

achieved. ^1H 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 $\text{C}_{11}\text{H}_{18}\text{S}$ (182.32): C, 72.46; H, 9.95; S, 17.59; found: C, 72.35; H, 10.08; S, 17.53.

Fenchone $N\beta$ -(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 $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$, PLC (CH_2Cl_2), and recrystallization from isopropyl alcohol afforded 16 (420 mg, 56%) in golden-yellow needles, m.p. $72\text{--}73^\circ\text{C}$. IR (CHCl_3) ν 1346 vst, 1532 vst (NO_2); 1598 st, 1645 st ($\text{C}=\text{N}$). ^1H NMR (CDCl_3) δ 1.22, 1.25, 1.32 (3s, 3 CH_3), 1.4–2.0 (m, 7 H), 7.75 (s, $\text{HC}=\text{N}$), 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_5^+]. Anal. calcd for $\text{C}_{17}\text{H}_{20}\text{N}_4\text{O}_4\text{S}$ (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 $N\beta$ -(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 $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$. 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 ($\text{C}=\text{N}$). ^1H 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, $\text{CH}_2\text{-N}$), 7.64 (s, $\text{HC}=\text{N}$). ^{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, $\text{N}=\text{CH-N}$), 177.3 (s, C-2). MS (30°C); m/z (%) 261 (72) [M^+], 245 (9) [$\text{M}^+ - \text{CH}_3$], 233 (13) [$\text{M}^+ - \text{C}_2\text{H}_4$], 177 (30) [$\text{M}^+ - \text{NC}_5\text{H}_{10}$], 152 (45) [$\text{C}_9\text{H}_{16}\text{C} = \text{NH}_2^+$], 111 (37), 84 (100) [$\text{NC}_5\text{H}_{10}^+$], 83 (62), 81 (31). Anal. calcd for $\text{C}_{16}\text{H}_{27}\text{N}_3$ (261.40): C, 73.51; H, 10.41; N, 16.08; found: C, 73.57; H, 10.40; N, 15.78.

Fenchone $N\beta$ -(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) ν 869 st, 1116 vst (C-O), 1231 st, 1269 st, 1445 st, br.; 1605 vst, 1652 vst (C=N). ^1H NMR (CDCl_3) δ 0.9–2.13 (m, 7 H), superimposed by 1.23, 1.28, 1.32 (3s, 3 CH_3), AA'BB' at 3.19–3.45 (2 $\text{CH}_2\text{-N}$), 3.54–3.81 (m, 2 $\text{CH}_2\text{-O}$), 7.67 (s, $\text{CH}=\text{N}$). MS (30°C); m/z (%) 263 (92) [M^+], 248 (7) [$\text{M}^+ - \text{CH}_3$], 247 (11), 222 (8), 221 (6), 195 (7), 177 (100) [$\text{M}^+ - \text{NC}_4\text{H}_8\text{O}$], 152 (36) [$\text{C}_{10}\text{H}_{18}\text{N}^+$], 115 (29), 113 (42) [$\text{C}_5\text{H}_9\text{N}_2\text{O}^+$, probably $\text{OC}_4\text{H}_8\text{N-C}\equiv\text{NH}^+$], 91 (10) [C_7H_7^+], 86 (52) [$\text{OC}_4\text{H}_8\text{N}^+$], 81 (45) [C_6H_9^+]. Anal. calcd for $\text{C}_{15}\text{H}_{25}\text{N}_3\text{O}$ (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. ($\pm$)-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 ^1H NMR spectrum (CDCl_3). After 4 hours at room temperature, ^1H 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) ν 1562 m (C=C). ^1H 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 $\text{C}_{11}\text{H}_{18}\text{S}$ (182.32): C, 72.46; H, 9.95; S, 17.59; found: C, 72.89; H, 9.77; S, 17.27.

^1H 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 ($\pm$)-camphor 2,4-dinitrophenylhydrazone (140 mg, 83%), m.p. $156\text{--}158^\circ\text{C}$, 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 ^1H 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. $126\text{--}128^\circ\text{C}$. IR (KBr) ν 904 st, 926 st, 1069 vst, 1088 vst (C-O); 1473 st. ^1H 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) [$\text{M}^+ + 1$], 199 (15) [$\text{M}^+ - \text{CH}_3$], 183 (8) [$\text{M}^+ - \text{OCH}_3$], 167 (88) [$\text{M}^+ - \text{SCH}_3$], 152 (12) [$167 - \text{CH}_3$], 131 (13), 123 (9), 93 (10), 81 (100) [C_6H_9^+], 80 (13). Anal. calcd for $\text{C}_{12}\text{H}_{22}\text{OS}$ (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. $160\text{--}162^\circ\text{C}$, identified by mixed m.p. and ^1H NMR spectrum. ^1H 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, ^1H 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. $117\text{--}119^\circ\text{C}$. IR (KBr) ν 1105 m, 1346 m, 1386 m, 1459 st. ^1H 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) [$\text{M}^+ - \text{CH}_3$], 183 (87) [$\text{M}^+ - \text{SCH}_3$], 182 (100) [$183 - \text{H}$, $\text{C}_{11}\text{H}_{18}\text{S}^+$], 168 (33) [$\text{C}_{10}\text{H}_{16}\text{S}^+$, 5^+], 167 (73) [$182 - \text{CH}_3$], 139 (49), 135 (51) [$5^+ - \text{HS}$, $\text{C}_{10}\text{H}_{15}^+$], 127 (60), 119 (42), 93 (61) [C_7H_9^+], 91 (56) [C_7H_7^+], 81 (60) [C_6H_9^+]. Anal. calcd for $\text{C}_{12}\text{H}_{22}\text{S}_2$ (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. $159\text{--}162^\circ\text{C}$ (mixed m.p.).

1-(Methylthio)- α -fenchene (25). Colorless oil which solidifies at room temperature. ^1H 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, $\text{H}_2\text{C}=\text{C}$). Anal. calcd for $\text{C}_{11}\text{H}_{18}\text{S}$ (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 H₂O 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 ¹³C 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⁺ - CH₃], 109 (3) [123 - CH₂], 95 (7) [123 - 2 CH₂, C₇H₁₁⁺], 85 (6), 84 (93) [C₆H₁₂⁺], 83 (6), 69 (28) [C₅H₉⁺], 56 (100) [C₄H₈⁺].

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]). ¹³C NMR (CDCl₃, 20 MHz) δ 20.7, 21.7 (2q, 2 CH₃), 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, H₂C=), 156.3 (s, C-2). The hydrogenation of **26** with Raney nickel and boiling ethanol was carried out as described previously. The ¹³C 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 CH₃, 3 CH₂, 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 H₂ with Pd (10% on carbon). After uptake of 206 mL of H₂, workup as above furnished 995 mg (72%) with a ratio **23/24** = 29:71. The isomer separation by chromatography did not succeed. ¹H NMR (CDCl₃, 80 MHz) of CH₃ signals: δ 0.94, 1.00, 1.03 for **23** and 0.94, 1.07, 1.08 for **24**. ¹³C NMR CDCl₃, 20 MHz) of **23**: δ 17.8, 20.96, 21.9 (3q, 3 CH₃); 21.05, 29.8, 38.71 (3t, 3 CH₂); 31.9, 45.0, 49.1 (3d, 3 CH); 47.9 (s, C-7); **24**: 22.3, 22.93, 23.05 (3q, 3 CH₃); 28.0, 31.4, 39.4 (3t, 3 CH₂); 38.86, 45.0, 50.2 (3d, 3 CH); 46.3 (s, C-7). Anal. calcd for C₁₀H₁₈ (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 N₂). 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 N₂, 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 (CH₂Cl₂). 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 (CDCl₃) vs. trichloroethylene as standard: the s of CH₃ 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 (CDCl₃) δ 1.34, 1.64, 1.75 (3s, 3 CH₃), 1.3–2.4 (m, 7 H), 3.65, 3.75 (AB, *J* = 12.9 Hz, 5'-H₂). ¹³C NMR (CDCl₃) δ 21.2, 24.8, 31.1 (3q, 3 CH₃); 25.3, 30.8, 39.0, 47.0 (4t, 4 CH₂); 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) [C₁₀H₁₆S⁺, 5⁺], 123 (13) [C₉H₁₅⁺], 93 (6) [C₇H₉⁺], 91 (6) [C₇H₇⁺], 81 (100) [C₆H₅⁺]. Anal. calcd for C₁₇H₁₈N₄S (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 (CDCl₃) δ 1.30, 1.65, 1.83 (3s, 3 CH₃), 1.5–2.5 (m, 7 H), 3.75 (A₂, 5'-H₂); (C₆D₆): δ 0.94, 1.21, 1.43 (3s, 3 CH₃), 0.45–2.20 (m, 7 H), 2.44, 2.46 (AB, *J* = 13.6 Hz, 5'-H₂). ¹³C NMR (CDCl₃) δ 24.1, 24.6, 27.5 (3q, 3 CH₃); 22.9, 38.9, 41.5, 44.2 (4t, 4 CH₂); 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 C₁₇H₁₈N₄S (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 N₂, 98%). Colorless crystals of **29** (186 mg, 22%), m.p. 182–184°C, were obtained from ether/pentane (1:1) and recrystallized from CHCl₃/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 ¹H NMR analysis with *sym*-tetrachloroethane: 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. ¹H NMR (CDCl₃) δ 1.08, 1.20, 1.35 (3s, 3 CH₃), 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⁺-C₆H₁₁], 125 (41) [C₉H₁₇⁺], 123 (73) [C₉H₁₅⁺], 83 (22) [C₆H₁₁⁺], 81 (100) [C₆H₉⁺]. Anal. calcd for C₁₅H₂₀O₃S (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% N₂). After removal of the solvent, the residue in CH₂Cl₂ was extracted with 10% aqueous Na₂SO₃. The residue of the organic phase was separated by PLC (CH₂Cl₂): 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 ¹H NMR analysis (C₆D₆) was based on the AB spectra for 5'-H₂ of **30A** and **30B** and the s of trichloroethylene as weight standard, and indicated 54% of **30**; the s of NCH₃ (C₆D₆) showed A/B = 55:45.

Spiro[fenchane-2,2'-(1,3,4)-triazolidine]-3',4'-dicarbox(N-methylimide) (30). **Isomer 30A.** ¹H NMR (CDCl₃) δ 1.02, 1.28, 1.30 (3s, 3 CH₃), superimposed by 0.9–3.05 (several m, 7 H), 3.06 (s, NCH₃), 4.47, 4.60 (AB, *J* = 9.5 Hz, 5'-H₂); (C₆D₆): δ 0.89, 1.02, 1.40 (3s, 3 CH₃), 0.8–1.7 (m, 7 H), 2.69 (s, NCH₃), 3.12 (dq, *J* = 10.0, ~2 Hz, 1 H), 3.93, 4.04 (AB, *J* = 10.0 Hz, 5'-H₂). ¹³C NMR (20.2 MHz, C₆D₆): δ 17.5, 2 × 25.2, 26.6 (3q, 4 CH₃); 24.5, 37.6, 43.2 (3t, 3 CH₂), 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) [C₁₀H₁₆S⁺, 5⁺], 153 (13), 135 (41) [168 - SH, C₁₀H₁₅⁺], 125 (23), 113 (21), 112 (18), 91 (15) [C₇H₇⁺], 81 (66) [C₆H₉⁺]. Anal. calcd for

C₁₄H₂₁N₃O₂S (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. ¹H NMR (CDCl₃) δ 1.11, 1.33, 1.36 (3s, 3 CH₃); 1.40–2.20 (m, 7 H), 3.05 (s, NCH₃), 4.48, 4.84 (AB, *J* = 9.2 Hz, 5'-H₂); (C₆D₆): δ 0.98, 1.12, 1.38 (3s, 3 CH₃), 0.65–2.00 (m, 7 H), 2.56 (s, NCH₃), 3.99, 4.55 (AB, *J* = 10.4 Hz). ¹³C NMR (20.2 MHz, C₆D₆) δ 20.7, 24.1, 26.0, 29.0 (4q, 4 CH₃); 25.3, 32.2, 46.0, 50.0 (4t, 4 CH₂); 49.3, 52.4 (2s, C-1, C-3), 94.4 (s, C-2); 151.1, 155.9 (2s, 2 C=O); the ¹³C 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 N₂ was eliminated in 2.5 hours. Trituration of the crude product with ether left undissolved 853 mg (86%) of 4,4,5,5-tetra-phenyl-1,3-dithiolane (**33**), m.p. 205–208°C; after recrystallization from CHCl₃/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 ¹H NMR spectrum [**15**]. Anal. calcd for C₂₇H₂₂S₂ (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 N₂, 98%). Evaporation of THF and trituration with CDCl₃ 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'-H₂ at δ 3.3–4.0 indicated 49% of **36A** and **36B**. In the separation by PLC (petroleum ether/CH₂Cl₂ 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 CH₂Cl₂/ethanol still the broad m.p. 173–178°C, and consisted of **36**, A/B = 85:15 (¹³C 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). ¹H NMR (C₆D₆): δ 3.84 (s, 2-H₂), 6.20, 6.83, 7.16, 7.75 (4m, 16 arom. H); (CDCl₃): δ 4.48 (s, 2-H₂). Anal. calcd for C₂₇H₁₈S₄ (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.** ¹H NMR (CDCl₃) δ 1.12 (s, 2 CH₃), 1.25 (s, CH₃), 1.3–2.0 (m, 7 H), 3.53 and 3.84 (AB, *J* = 12.0 Hz, 5'-H₂), 7.0–7.5, 7.8–8.1 (2m, 6 + 2 arom. H). ¹³C NMR (CDCl₃, 20 MHz) δ

20.6, 26.6, 33.0 (3q, 3 CH₃), 26.0, 34.1, 43.4, 43.5 (4t, 4 CH₂), 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) [C₁₄H₁₀S₂⁺, M⁺ - 5; ¹³C₂ + ³⁴S calcd/found 0.22/0.19], 228 (0.5) [C₁₃H₈S₂⁺, 37⁺], 210 (100) [C₁₄H₁₀S⁺, 9-Methylene-thioxanthene⁺; ¹³C 16/15; ¹³C₂ + ³⁴S 0.22/0.19], 178 (4.2) [C₁₄H₁₀⁺, 210 - S, ¹³C 0.66/0.65; ¹³C₂ 0.05/0.05, S-free], 168 (0.7) [C₁₀H₁₆S⁺, 5⁺], 165 (8) [C₁₀H₁₃⁺, fluorenyl⁺], 152 (1.4) [C₁₂H₈⁺], 135 (0.5) [168 - SH], 123 (1.7) [C₉H₁₅⁺], 91 (1) [C₇H₇⁺], 81 (4) [C₆H₇⁺].

Adduct 36B. ¹³C NMR (CDCl₃) δ 19.0, 29.1, 29.9 (3q, 3 CH₃), 26.0, 33.2, 42.4, 44.8 (4t, 4 CH₂), 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 C₂₄H₂₆S₃ (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 H₂O, 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 (CDCl₃) δ 0.95 (s, 2 CH₃), 1.05 (s, CH₃), 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 (CDCl₃) δ 1.52 (d, *J* = 7.2 Hz, CH₃), 3.99 (q, *J* = 7.2 Hz, 1-H), 7.06 (s, 2 C₆H₅).

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