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REACTIONS OF α-DIAZOCAMPHOR WITH AROMATIC THIOKETONES

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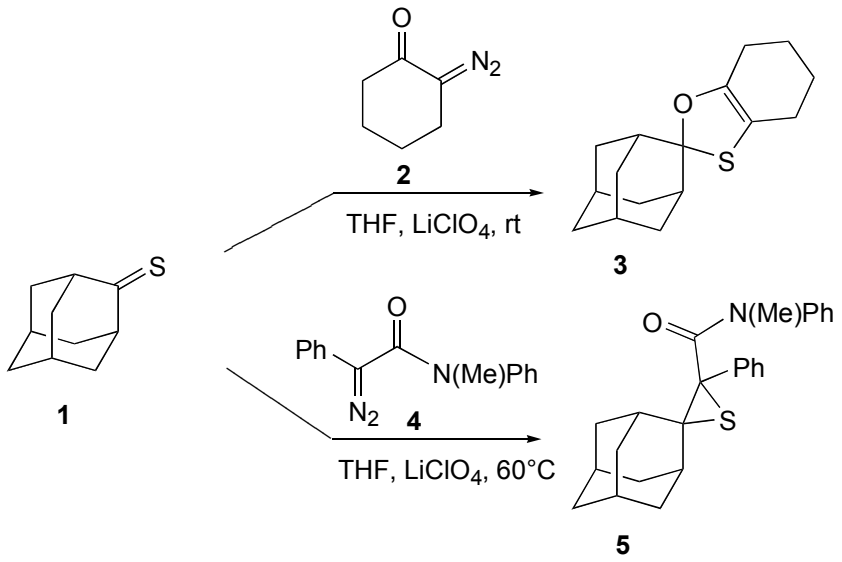
Abstract – The reactions of α-diazocamphor (**6**) with aromatic thioketones (**9a**-**d**) in dichloromethane at room temperature afforded mixtures of the stereoisomeric spirocyclic thiiranes (**10**) and (**11**). A reaction mechanism *via* [2+3] cycloaddition to give the spirocyclic 2,5-dihydro-1,3,4-thiadiazoles (**13**) and (**14**), subsequent elimination of nitrogen and 1,3-dipolar electrocyclization of the intermediate thiocarbonyl ylide (**15**) is proposed. The structure of the stereoisomers (**10a**) and (**11a**) has been established by X-Ray crystallography. Desulfurization of the mixtures (**10**/**11**) with triphenylphosphane in boiling THF yielded the alkylidene derivatives (**12**).

INTRODUCTION

In recent years, reactions of thiocarbonyl compounds with diazoalkanes have been studied extensively in our laboratories. It is now well established that these reactions proceed *via* a [2+3] cycloaddition to give 2,5-dihydro-1,3,4-thiadiazoles, which easily extrude nitrogen, and thiocarbonyl ylides are formed as reactive intermediates.[1-4] These 1,3-dipoles undergo either intramolecular reactions (e.g. electrocyclizations, 1,4-hydrogen shifts) or cycloadditions with electron-deficient dipolarophiles. Furthermore, 'superdipolarophilic' thiocarbonyl compounds,

especially aromatic thioketones, intercept these 1,3-dipoles efficiently to give 1,3-dithiolanes. Along with diazoalkanes, less reactive α-diazocarbonyl compounds, such as α-diazoesters, α-diazoamides, and α-diazoketones, were widely applied in non-catalyzed and catalyzed reactions.[5-8] In the absence of dipolarophiles, the thiocarbonyl ylides formed in these reactions were shown to undergo 1,5-dipolar electrocyclizations in competition with the 1,3-dipolar ring closure. The products of these processes are 1,3-oxathiols and thiiranes, respectively. For example, adamantanethione (**1**) reacts with diazocyclohexanone (**2**) in the presence of $LiClO_4$ to yield the 1,3-oxathiole (**3**)[8] (*Scheme 1*). Under comparable conditions, the reaction of **1** with the α-diazoamide (**4**) afforded thiirane (**5**) exclusively.[7]

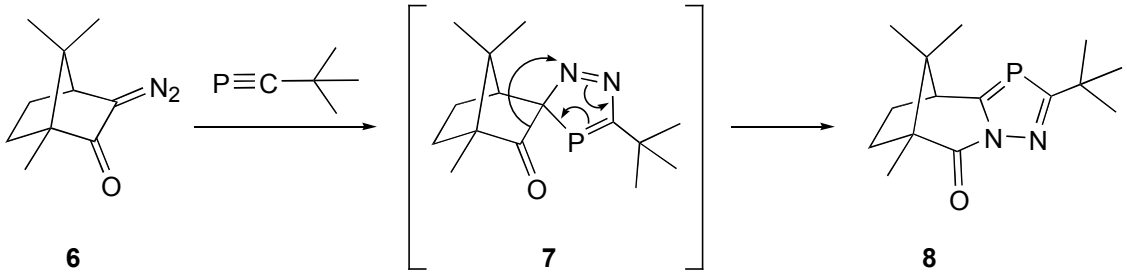
Scheme 1



Although α-diazocamphor (**6**) is a well known and easily available representative of α-diazoketones, its application as a 1,3-dipole is seldom reported. Two examples deserve a short comment. The firstly described [2+3] cycloadduct with 2,2-dimethylpropylidynephosphane,[9] structure (**7**), was finally established as the fused 1,3,4-phosphodiazole (**8**) with an enlarged camphor skeleton[10] (*Scheme 2*). An analogous ring enlargement was observed in the reaction of **6** with an electron-deficient acetylenic dipolarophile.[11]

To the best of our knowledge, no reactions of **6** with other typical dipolarophiles have been described. As thioketones are excellent dipolarophiles, we carried out a series of experiments with aromatic thioketones.

Scheme 2



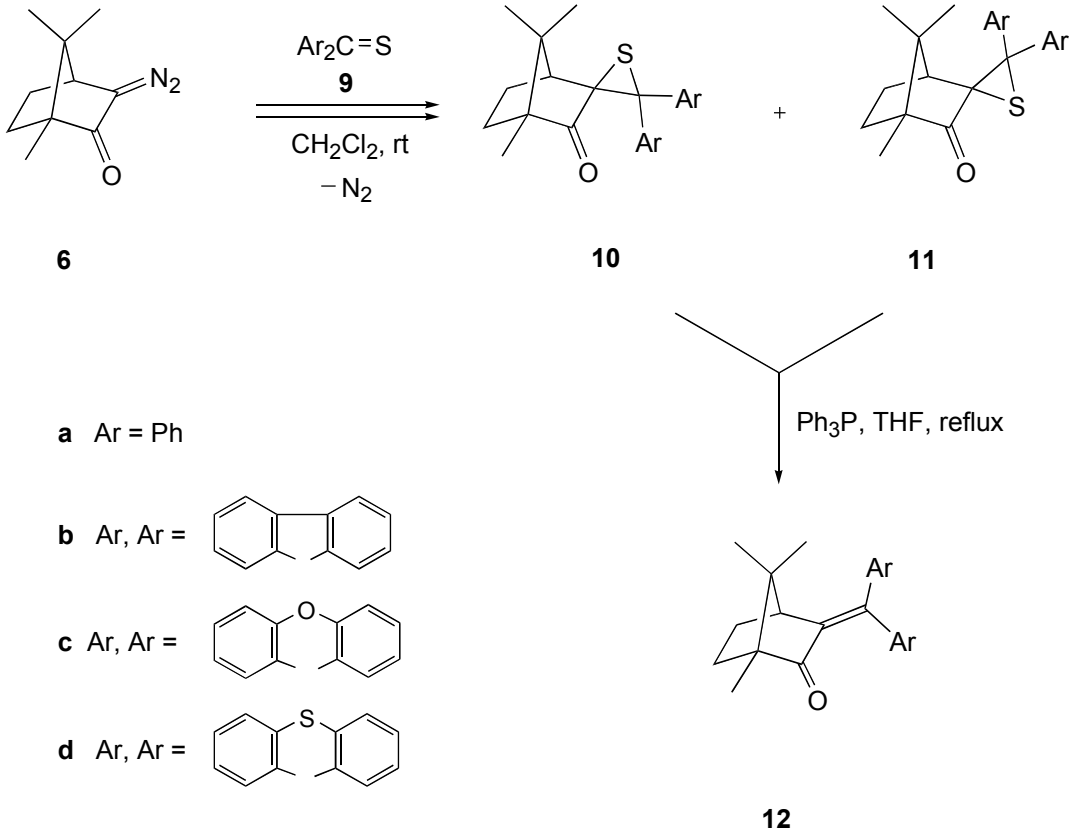
6 **7** **8**

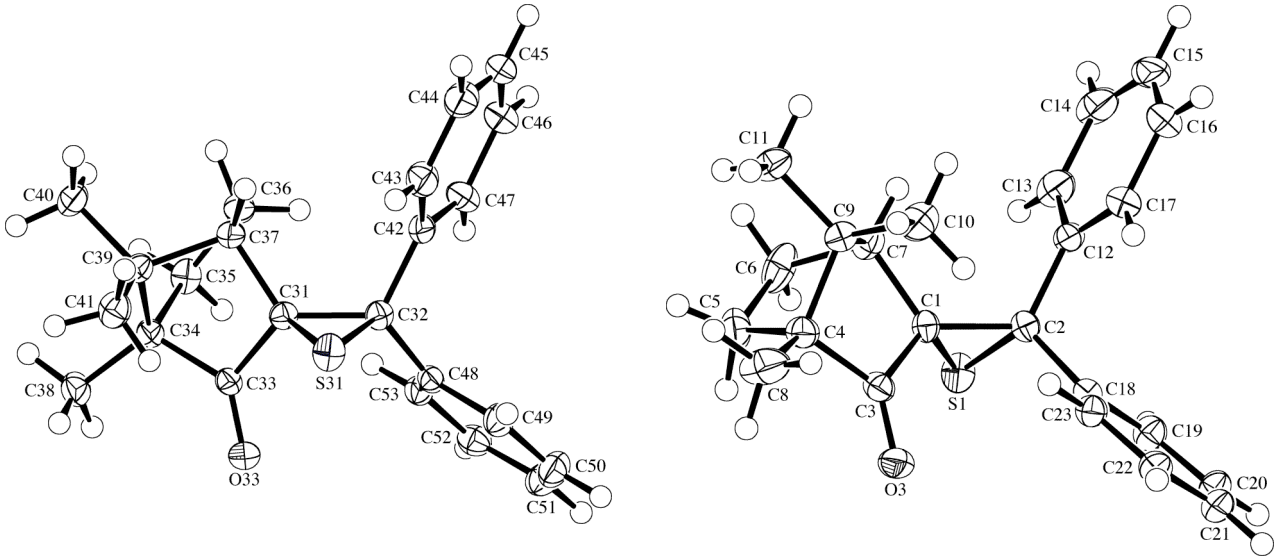
RESULTS AND DISCUSSION

A typical experiment with equimolar amounts of thiobenzophenone (**9a**) and **6** was carried out in dichloromethane at room temperature. Evolution of nitrogen ceased after 40 min and, after evaporation of the solvent, the solid residue was crystallized from methanol. The first fraction isolated after attempted crystallization from MeOH showed in the ^{1}H-NMR spectrum only signals in the aromatic region (7.1-7.7 ppm). In the ^{13}C-NMR spectrum, a characteristic signal for C_q appeared at 92.6 ppm. During the storage of the colorless solution at ambient temperature, the solution turned blue. The same color was observed during the determination of the melting point (120-122^{o}C). The appearance of this color indicates that thiobenzophenone (**9a**) is formed by thermal decomposition of the product. All these facts show that the isolated material is the known 3,3,5,5-tetraphenyl-1,2,4-trithiolane.[12] The second fraction formed a colorless solid, which melted in a broad range of 148-174^{o}C. Neither attempted chromatographic separation nor repeated crystallization led to a homogenous material. Both, ^{1}H- and ^{13}C-NMR spectroscopic data indicated the presence of two isomeric products in a ratio of *ca*. 1:1, which revealed aromatic as well as aliphatic signals. The ESI-MS (CH_2Cl_2/MeOH+NaI) showed the $[M+Na]^+$ peak at *m/z* 719. The collected data correspond to a 1:1 adduct of **6** and **9a** after elimination of nitrogen. Finally, an X-Ray crystal-structure determination showed that crystals containing a mixture of the two diaste-reoisomeric thiiranes (**10a**) and (**11a**) had been obtained from the solution (*Scheme 3, Figure 1).*

The asymmetric unit of **10a**/**11a** contains two symmetry-independent stereoisomeric molecules, one of which is the *exo*-isomer (1*S*,2*S*,4*R*) and the other is the *endo*-isomer (1*S*,2*R*,4*R*), so that the ratio of the stereoisomers in the crystal is necessarily 1:1. The absolute structure has been determined independently by the diffraction experiment and found to agree with the expected camphonate configuration.

Scheme 3





10a **11a**

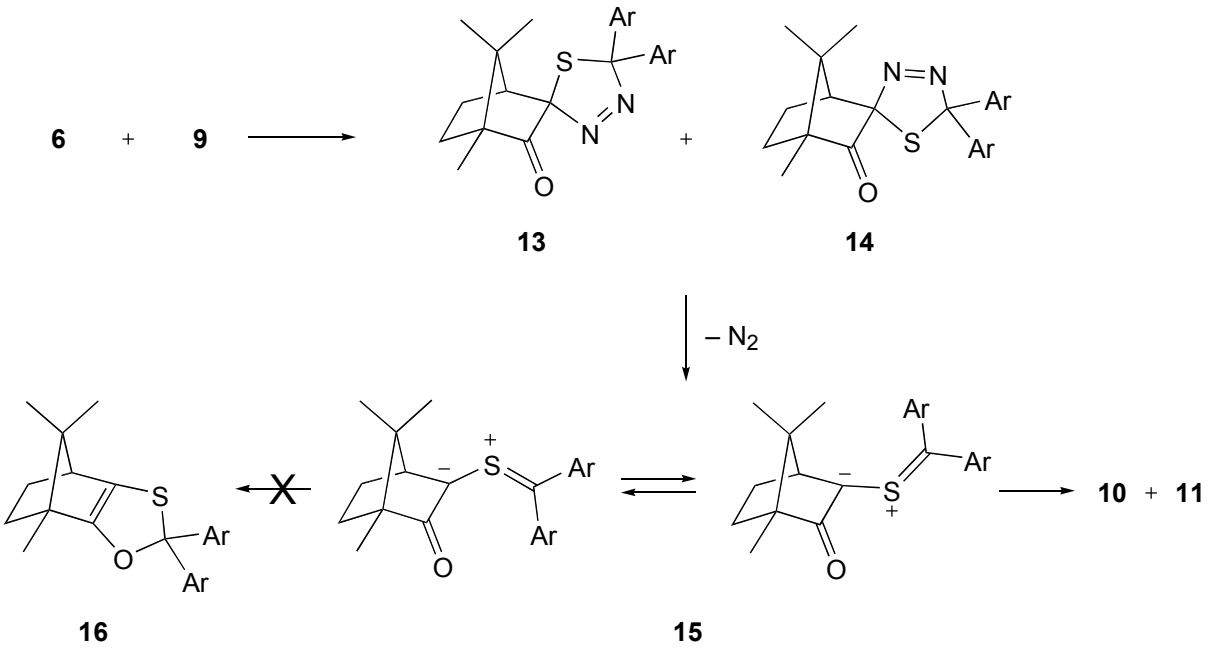
Figure 1. ORTEP plot[13] of the molecular structure of the two stereoisomeric thiiranes (**10a**) and (**11a**) (50% probability ellipsoids; arbitrary numbering of atoms).

The mixture (**10a**/**11a**) was treated with Ph_3P in boiling THF for 16 h. After treatment with methyl iodide and filtration through a short SiO_2 column, the solvent was evaporated and the semi-solid residue was crystallized from hexane to give colorless crystals (mp 114-116°C) of the documented 3-benzhydrylidenecamphor (**12a**)[14] (*Scheme 3*). The alternative desulfurization using $(Et_2N)_3P$ needed significantly shorter reaction times with an optimum at *ca*. 1.5 h.

In an analogous manner diazocamphor (**6**) was reacted with 9*H*-fluorene-9-thione (**9b**), 9*H*-xanthene-9-thione (**9c**), and 9*H*-thioxanthene-9-thione (**9d**). Whereas the reaction with **9b** at room temperature was complete after 20 min, the reactions with **9c** and **9d** were carried out at 45°C and needed several hours for completion. In all cases, non-separable mixtures of diasteroisomeric thiiranes (**10**) and (**11**) were obtained and subsequently desulfurized to give the corresponding 3-methylidene derivatives (**12**) (*Scheme 3*).

Recently, thiophthalide was also used as a fairly reactive dipolarophile in reactions with thiocarbonyl ylides.[3] However, no reaction occurred with **6,** either in boiling THF or in boiling toluene.

Scheme 4



A mechanistic interpretation of the reaction pathway leading to thiiranes (**10**) and (**11**) is outlined in *Scheme 4*. It is likely that the first step is a [2+3] cycloaddition of the diazo group with the C=S function to give the isomeric 1,3,4-thiadiazole derivatives (**13**) and (**14**). Similar

heterocycles, substituted with aromatic residues, are known to eliminate nitrogen easily, even below 0°C.[15] The resulting thiocarbonyl ylide (**15**) undergoes a rapid 1,3-dipolar electrocyclization to give **10** and **11**. The alternative 1,5-dipolar electrocyclization to **16** does not occur in this system. Inspection of *Dreiding*-models showed that the formation of the fused 1,3-oxathiole derivative would result in significant increase of ring strain.

In conclusion, the presented results show that α-diazocamphor is able to undergo [2+3] cycloadditions with the 'superdipolarophiles' (**9a**) and (**9b**) under mild conditions and with the less reactive thioketones (**9c**) and (**9d**) at a slightly elevated temperature, leading to thiiranes of type (**10** and **11**). The desulfurization of the latter with Ph_3P or $(Et_2N)_3P$ offers an alternative, efficient access to the synthetically useful 3-methylidene derivatives of camphor of type (**12**).[14,16,17]

EXPERIMENTAL

General remarks. Melting points were determined in a capillary using a MEL-TEMP II apparatus (*Aldrich*) and are uncorrected. IR spectra (KBr pellets) were recorded with a *Nexus* spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were registered in $CDCl_3$ on a *Tesla BS 687* instrument (^{1}H at 80 MHz, ^{13}C at 20 MHz, resp.) or a *Bruker AC-300* spectrometer (^{1}H at 300 and ^{13}C at 75 MHz, resp.) using TMS (δ = 0 ppm) as an internal standard. ^{13}C-NMR peak assignments were made on the basis of ATP experiments. MS (CI or ESI) were recorded on a *Finnigan-Mat-90* or *Finnigan-SSQ-700* spectrometer; *m/z* (rel. %). Elemental analyses were performed in the Analytical Laboratory of the University of Zürich or in the Laboratory of the Polish Academy of Sciences (CBMiM) in Lodz.

Starting materials. α-Diazocamphor (**6**) was prepared according to ref.[18] by oxidation of camphorquinone monohydrazone with yellow mercury oxide. Thiobenzophenone (**9a**),[19] 9*H*-fluorene-9-thione (**9b**),[20] 9*H*-xanthene-9-thione (**9c**),[19] and 9*H*-thioxanthene-9-thione (**9d**)[19] were synthesized by thionation of the corresponding ketones with *Lawesson*'s reagent in boiling toluene.

Reactions of α-diazocamphor (6) with thiobenzophenone (9a), 9*H*-fluorene-9-thione (9b), 9*H*-xanthene-9-thione (9c), and 9*H*-thioxanthene-9-thione (9d). General procedure. A solution containing 196 mg (1.1 mmol) of diazocamphor (**6**) in 1 mL of dry THF was stirred magnetically and 1 mmol of the corresponding thioketone (**9**) dissolved in 1 mL of dry THF was

added dropwise. In the experiments with **9a** and **9b**, the flask was cooled in a water/ice bath, and in the cases of **9c** and **9d**, the reactions were performed at rt. The reaction with **9b** was completed after 20 min, and in the case of **9a**, the cooling bath was removed after 20 min and stirring was continued for 40 min at rt until the blue color of the solution completely diappeared. In the reactions with **9c** and **9d**, the colored solutions were heated in an oil bath at 45°C. The evolution of nitrogen seased after 5 h and 6 h, respectively, indicating completion of the reaction. In all cases the solvent was evaporated and the oily residues were treated with methanol. Only in the mixture obtained with **9a** was a solid material filtered and identified as 3,3,5,5-tetraphenyl-1,2,4-trithiolane.[21] After removal of methanol, the oily residues were separated on preparative plates coated with silica gel (PLC) or by column chromatography. Analytically pure samples of mixtures of thiiranes (**10**) and (**11**) were obtained after crystallization. Yields refer to amounts isolated after chromatographic workup.

3,3,5,5-Tetraphenyl-1,3,4-trithiolane. Yield: 60 mg (28%). Colorless prisms (MeOH); mp 120-122°C (decomp, turns blue) (lit.,[21] mp 122-124°C). ^{13}C-NMR: 92.6 (2 C_q), 128.0, 128.3, 129.6 (20 arom. CH), 142.5 (4 arom. C_q).

*(1*S*,2*S*,4*R*)- and (1*S*,2*R*,4*R*)-4,7,7-Trimethyl-3,3'-diphenylspiro[norbornane-2,2'-thiiran]-3-one* (*ca*. 1:1 mixture of **10a** and **11a**); isolated by means of PLC (CH_2Cl_2/petroleum ether 1:1). Yield: 220 mg (63%). Colorless crystals (MeOH); mp 174-182°C. IR: 2964*m*, 1738*vs* (C=O), 1490*m*, 1445*s*, 754*m*, 702*vs*. ^{1}H-NMR: 0.95, 0.96, 1.00, 1.10, 1.25 (5*s* for 6 Me), 1.39-2.10 (*m*, 10 H), 7.16-7.35 (*m*, 12 arom. H), 7.43-7.50 (*m*, 8 arom. H). ^{13}C-NMR: 9.7, 10.0, 18.9, 20.1, 20.8, 21.1 (6 Me), 24.8, 28.6, 28.8, 31.3 (4 CH_2), 45.7, 46.6 (2 C_q), 49.5, 50.6 (2 CH), 59.3, 60.3, 60.8, 60.9 (4 C_q), 65.6, 68.2 (2 C_q), 127.1, 127.2, 127.3, 127.6, 127.7, 127.9, 129.1, 129.4, 129.5, 130.2 (10 arom. CH), 138.9, 139.4, 140.0, 140.6 (4 arom. C_q), 211.9, 213.6 (2 C=O). ESI-MS: 371 ([*M*+Na]$^+$). Anal. Calcd for $C_{23}H_{24}OS$: C, 79.27; H, 6.94; S, 9.20. Found: C, 79.35; H, 6.81; S, 9.14.

*(1"*S*,2"*S*,4"*R*)- and (1"*S*,2"*R*,4"*R*)-4",7",7"-Trimethyldispiro[9*H*-fluorene-9,2'-thiirane-3',2"-norbornan]-3"-one* (*ca*. 1:1 mixture of **10b** and **11b**); isolated by means of PLC (hexane/CH_2Cl_2 3:2). Yield: 230 mg (66%). Viscous oil; crystallized from hexane solution after storage in the refrigerator. Colorless crystals; mp 128-135°C. IR: 2959*s*, 1746*vs* (C=O), 1448*s*, 740*vs*. ^{1}H-NMR: 0.07, 0.80, 0.85, 0.93, 0.96, 1.19 (6*s*, 6 Me), 1.38-1.92, 2.04-2.14 (2*m*, *ca*. 8 H), 2.46 (*d*, *J* = 4.3 Hz, *ca*. 1 H), 2.56 (*d*, *J* = 4.4 Hz, *ca*. 1 H), 7.21-7.40, 7.63-7.72, 8.08-8.18 (3*m*, 16 arom.

H). ^{13}C-NMR: 9.6, 10.2, 18.7, 18.9, 20.7 (5 signals for 6 Me), 25.3, 26.4, 28.3, 32.1 (4 CH_2), 45.7, 46.3 (2 C_q), 51.0, 52.9 (2 CH), 58.4, 59.6, 59.7, 60.9, 63.1 (5 signals for 6 C_q), 119.3, 120.0, 124.0, 125.0, 126.2, 126.8, 127.2, 127.6, 128.3, 128.5 (10 signals for 16 arom. CH), 140.7, 140.8, 141.2, 141.3, 141.5, 142.0, 143.2, 143.5 (8 arom. C_q), 212.5, 213.8 (2 C=O). ESI-MS: 369 ([*M*+Na]$^+$), 337 ([*M*-S]$^+$). Anal. Calcd for $C_{23}H_{22}OS$: C, 79.73; H, 6.40; S, 9.25. Found: C, 79.85; H, 6.61; S, 9.03.

*(1*S*,2*S*,4*R*)- and (1*S*,2*R*,4*R*)-4,7,7-Trimethyldispiro[norbornane-2,2'-thiirane-3',9''-(9*H*-xanthen)]-3-one* (*ca*. 1:1 mixture of **10c** and **11c**); isolated by means of column chromatography (hexane with increasing amounts of CH_2Cl_2). Yield: 300 mg (83%). Colorless crystals; mp 154-176°C (MeOH/CH_2Cl_2). IR: 2964*s*, 1739*vs* (C=O), 1594*m*, 1471*vs*, 1458*vs*, 1445*vs*, 1295*s*, 1249*vs*, 1007*m*, 757*vs*. ^{1}H-NMR: 0.52, 0.75, 0.76, 0.81, 0.85, 1.07 (6*s*, 6 Me), 1.44-1.99 (*m*, 10 H), 7.07-7.55, 7.93-8.01 (2*m*, 16 arom. H). ^{13}C-NMR: 9.5, 10.0, 18.6, 19.0, 19.3, 20.7 (6 Me), 23.8, 26.5, 28.9, 31.8 (4 CH_2), 45.6, 46.0 (2 C_q), 49.8, 51.6 (2 CH), 57.4, 59.4, 60.2, 60.5, 66.0 (5 signals for 6 C_q), 115.6, 115.7, 116.2, 116.3, 122.6, 122.9, 129.3, 127.7, 128.5, 129.0, 129.1, 129.2, 129.3, 131.1, 131.7 (15 signals for 16 arom. CH), 118.9, 119.8, 121.5, 122.1, 154.0, 154.4, 155.1, 155.3 (8 arom. C_q), 211.6, 212.5 (2 C=O). ESI-MS: 385 ([*M*+Na]$^+$). Anal. Calcd for $C_{23}H_{22}O_2S$: C, 76.21; H, 6.12; S, 8.85. Found: C, 75.98; H, 6.19; S, 9.14.

*(1*S*,2*S*,4*R*)- and (1*S*,2*R*,4*R*)-4,7,7-Trimethyldispiro[norbornane-2,2'-thiirane-3',9''-(9*H*-thioxanthen)]-3-one* (*ca*. 1:1 mixture of **10d** and **11d**); isolated by means of column chromatography (hexane with increasing amounts of CH_2Cl_2). Yield: 298 mg (79%). Colorless crystals (hexane); mp 160-185°C. IR: 2960*s*, 1746*vs* (C=O), 1457*m*, 1437*m*, 777*m*, 742*s*. ^{1}H-NMR: 0.76, 0.77, 0.79, 0.86, 1.07 (5 signals for 6 Me), 1.25-1.40, 1.48-1.78, 1.88-1.97 (3*m*, 10 H), 7.19-7.45, 7.70-7.75, 7.97-8.02, 8.12-8.16 (4*m*, 16 arom. H). ^{13}C-NMR: 9.6, 10.0, 19.0, 19.5, 21.0, 22.2 (6 Me), 24.2, 28.3, 30.1, 31.3 (4 CH_2), 45.4, 46.2 (2 C_q), 49.5, 52.1 (2 CH), 59.0, 60.5, 60.8, 64.5, 66.9 (5 signals for 6 C_q), 125.0, 125.6, 126.0, 126.1, 126.4, 126.5, 127.6, 127.8, 131.8, 132.3 (10 signals for 16 arom. CH), 128.9, 129.7, 130.0, 131.9, 133.1, 133.2, 135.2, 136.6 (8 arom. C_q), 212.5, 212.8 (2 C=O). CI-MS (NH_3): 378 (6, [*M*+1-CH_3]$^+$), 347 (100, [*M*+1-S]$^+$), 213 (8). ESI-MS: 401 (100, [*M*+Na]$^+$). Anal. Calcd for $C_{23}H_{22}OS_2$: C, 72.97; H, 5.86; S, 16.94. Found: C, 72.80; H, 5.92; S, 16.81.

Desulfurization of thiiranes (10) and (11). General procedure. Triphenylphosphine (288 mg, 1.1 mmol) and 1 mmol of the corresponding mixture of **10** and **11** was dissolved in 3 mL of dry

THF and the clear solution was heated under reflux for 16 h under an atmosphere of nitrogen. After cooling to rt, the solvent was evaporated and the viscous residue was dissolved in 15 mL of petroleum ether. After addition of 1 mL of methyl iodide, the mixture was stirred magnetically for 2 h at rt and subsequently the solution was concentrated and filtered through a short chromatography column (*ca*. 10 cm) of silica gel. Pure products (**12**) were isolated using petroleum ether as an eluent. Crystallization from hexane afforded analytically pure samples. Reported yields refer to amounts of **12** obtained after chromatography. By using tris(diethylamino)phosphane instead of triphenylphosphane in boiling THF, the desulfurization was completed after 1.5 h.

3-Diphenylmethylidene-1,7,7-trimethylnorbornan-2-one (**12a**). Yield: 310 mg (98%). Pale yellow crystals (hexane); mp 114-116°C (lit.,[16] mp 113.5°C). IR: 2960*s*, 1718*vs* (C=O), 1626*s* (C=C), 1443*m, 1015m*, 769*m*, 701*s*. ^{1}H-NMR: 0.93, 0.95, 0.98 (3*s*, 3 Me), 1.49-1.56 (*m*, 1 H), 1.66-1.76 (*m*, 2 H), 2.06-2.15 (*m*, 1 H), 2.75 (*d*, *J* = 4.2 Hz, 1 H), 7.12-7.19 (*m*, 4 arom. H), 7.24-7.36 (*m*, 6 arom. H). ^{13}C-NMR: 9.6, 18.5, 20.7 (3 Me), 27.2, 30.4 (2 CH_2), 46.2, 58.9 (2 C_q), 51.5 (CH), 127.7, 127.75, 127.9, 128.1, 129.3, 129.4 (6 arom. CH), 139.8, 140.1, 141.7, 144.4 (2 arom. C_q + 2 olef. C_q), 207.0 (C=O). CI-MS (NH_3): 334 (11, $[M+NH_4]^+$), 317 (100, $[M+1]$).

*3-(9*H*-Fluoren-9-ylidene)-1,7,7-trimethylnorbornan-3-one* (**12b**). Yield: 289 mg (92%). Yellow crystals (hexane); mp 119-121°C (lit.,[17] mp 50-54°C). IR: 2961*vs*, 1713*vs* (C=O), 1586*vs* (C=C), 1446*vs*, 1323*m*, 1066*m*, 1013*vs*, 987*m*, 781*vs*, 729*vs*. ^{1}H-NMR: 0.87, 1.04, 1.10 (3*s*, 3 Me), 1.53-1.87 (*m*, 3 H), 2.23-2.34 (*m*, 1 H), 3.60 (*d*, *J* = 4.78 Hz, 1 H), 7.22-7.38 (*m*, 4 arom. H), 7.59-7.66 (*m*, 2 arom. H), 7.79 (*d*, *J* = 7.82 Hz, 1 arom. H), 9.20-9.23 (*m*, 1 arom. H). ^{13}C-NMR: 9.9, 18.8, 20.6 (3 Me), 25.6, 31.1 (2 CH_2), 46.5, 58.5 (2 C_q), 52.7 (CH), 119.0, 119.9, 126.4, 127.2, 128.2, 128.7, 129.6, 129.8 (8 arom. CH), 137.0, 139.0, 140.0, 140.6, 142.8, 143.2 (4 arom. C_q + 2 olef. C_q), 208.7 (C=O). CI-MS (NH_3): 332 (18, $[M+NH_4]^+$), 315 (100, $[M+1]^+$). Anal. Calcd for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 87.73; H, 6.76.

*1,7,7-Trimethyl-3-(9*H*-xanthen-9-ylidene)norbornan-2-one* (**12c**). Yield: 305 mg (92%). Yellow crystals (hexane); mp 164-166°C. IR: 2968*s*, 1718*vs* (C=O), 1599*vs* (C=C), 1447*vs*, 1255*s*, 1012*s*, 776*m*, 746*s*. ^{1}H-NMR: 0.69, 0.91, 0.94 (3*s*, 3 Me), 1.63-1.85 (*m*, 3 H), 2.20-2.29 (*m*, 1 H), 3.12 (*d*, *J* = 4.18 Hz, 1 H), 7.13-7.38 (m, 6 arom. H), 7.49-7.57 (*m*, 1 arom. H), 8.13-8.16 (*m*, 1 arom. H). ^{13}C-NMR: 9.6, 18.7, 20.3 (3 Me), 26.7, 30.5 (2 CH_2), 46.6, 58.2 (2 C_q), 52.1 (CH), 116.0, 116.5, 121.8, 122.7, 127.7, 129.4, 130.0, 130.3 (8 arom. CH), 121.4, 124.5, 130.8, 136.0,

153.2, 154.2 (4 arom. C_q + 2 olef. C_q), 206.3 (C=O). CI-MS (NH_3): 331 (100, $[M+1]^+$). Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.15; H, 6.47.

*1,7,7-Trimethyl-3-(9*H*-thioxanthen-9-ylidene)norbornan-2-one* (**12d**): Yield: 328 mg (95%). Yellow crystals (hexane); mp 107-109°C. IR: 2958*vs*, 1720*vs* (C=O),1606*s* (C=C), 1456*s*, 1438*s*, 1323*m*, 1070*m*, 1061*m*, 1013*vs*, 768*vs*, 742*vs*. ^{1}H-NMR: 0.65 (br *s*, 1 Me), 0.90, 0.91 (2*s*, 2 Me), 1.70-2.26 (*m*, 4 H), 2.81 (br. *s*, 1 H), 7.21-7.33 (*m*, 4 arom. H), 7.41-7.60 (*m*, 3 arom. H), 7.73-7.80 (*m*, 1 arom. H). ^{13}C-NMR: 9.5, 18.5, 20.4 (3 Me), 27.0, 30.3 (2 CH_2), 46.5 (br, C_q), 51.6 (br, CH), 58.5 (C_q), 124.9, 125.8, 126.5, 126.8, 127.4, 127.9, 128.0, 130.8 (8 arom. CH), 129.5, 133.3, 134.9, 135.7, 137.6, 138.2 (4 arom. C_q + 2 olef. C_q), 206. 2 (C=O). CI-MS (NH_3): 348 (26), 347 (100, $[M+1]^+$). Anal. Calcd for $C_{23}H_{22}OS$: C, 79.73; H, 6.39; S, 9.25 Found: C, 79.50; H, 6.49; S, 9.47.

X-Ray Crystal-Structure Determination of **10a**/**11a** (see *Table 1* and *Figure 1*).[22] All measurements were made on a *Nonius KappaCCD* diffractometer[23] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. The data collection and refinement parameters are given in *Table 1* and a view of the molecules is shown in *Figure 1*. Data reduction was performed with *HKL Denzo* and *Scalepack*.[24] The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method[25] was applied. The structure was solved by direct methods using SIR92,[26] which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the methyl groups). Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. Seven reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Refinement of the absolute structure parameter[27] yielded a value of –0.05(4), which confidently confirms that the refined coordinates represent the true absolute structure. Neutral atom scattering factors for non-hydrogen atoms were taken from ref.[28a], and the scattering factors for H-atoms were taken from ref.[29] Anomalous dispersion effects were included in F_c;[30] the values for *f '* and *f "* were those of ref.[28b] The values of the mass attenuation coefficients are those of ref.[28c] All calculations were performed using *SHELXL97*.[31]

Table 1. *Crystallographic Data of Compound* (**10a**/**11a**)

Crystallized from		$MeOH/CH_2Cl_2$
Empirical formula		$C_{23}H_{24}OS$
Formula weight [g mol^{-1}]		348.50
Crystal color, habit		colorless, prism
Crystal dimensions [mm]		0.22 × 0.22 × 0.32
Temperature [K]		160(1)
Crystal system		monoclinic
Space group		$P2_1$
Z		4
Reflections for cell determination		31727
2θ range for cell determination [°]		4 – 60
Unit cell parameters:	a [Å]	10.8709(2)
	b [Å]	13.3101(2)
	c [Å]	13.2127(2)
	β [°]	105.0013(9)
	V [$Å^3$]	1846.63(5)
D_X [g cm^{-3}]		1.253
μ(MoK_α) [mm^{-1}]		0.183
Scan type		ϕ and ω
2θ(max) [°]		60
Transmission factors (min, max)		0.891; 0.962
Total reflections measured		49352
Symmetry independent reflections		10784
Reflections with $I > 2\sigma(I)$		9225
Reflections used in refinement		10777
Parameters refined; restraints		457; 1
Final: $R(F)$ [$I > 2\sigma(I)$ reflections]		0.0411
$wR(F^2)$ (all data)		0.0965
Weights:	$w = [\sigma^2(F_o^2) + (0.0456P)^2 + 0.3504P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	
Goodness of fit		1.030
Final Δ_{max}/σ		0.001
$\Delta\rho$ (max; min) [e $Å^{-3}$]		0.21; -0.24

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