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3-*exo*,3'-*exo*-(1*R*,1'*R*)-Bithiocamphor – a Versatile Source for Functionally Different 3,3'-Bibornane Derivatives – I. Ring-Closure Reactions and Prototropic Rearrangements☆

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Abstract: The title compound **3**, derived from (+)-camphor, allows preparatively useful conversions to be carried out at the 3,3'-bibornane skeleton. The reactions are characterized by steric factors. Despite the increasing steric strain in the bicyclic units, ring-closure reactions of **3** to born-2-ene anellated sulfur-heterocycles are possible, including the formation of the 1,2-dithiine (**6**), thiophene (**11**), and 1,2,3-trithiepine system (**13**), respectively. Compound **6** is distinguished by several unusual properties. In contrast to the normal behaviour of aliphatic thioketones, **3** cannot exist as enthiol. The latter and related intermediates are immediately stabilized by 1,5-prototropic rearrangements leading to bornylidene units e.g. in **16** and consecutive products.

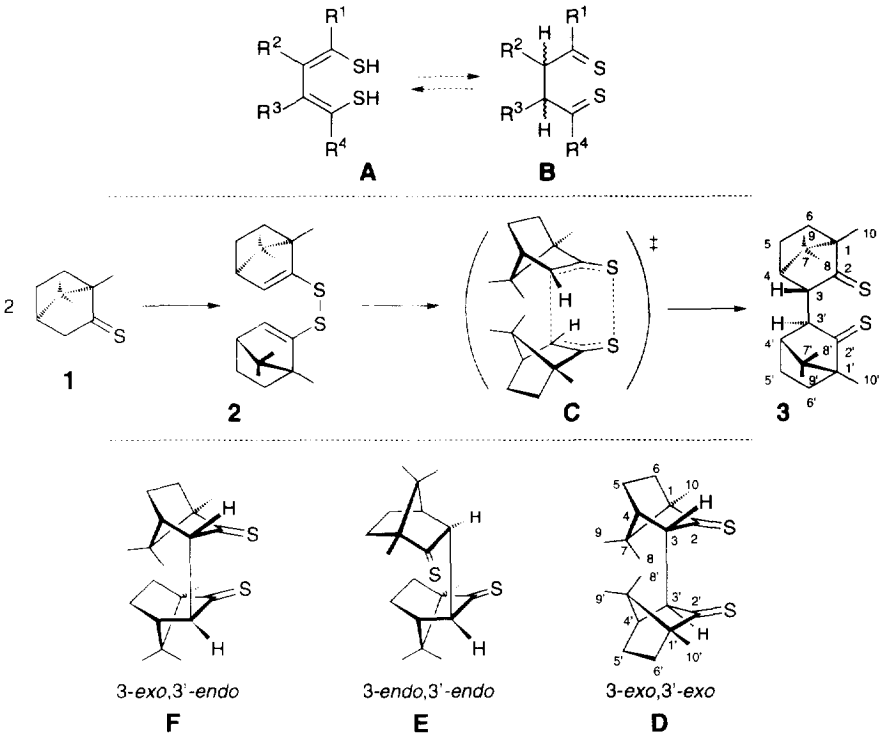
Introduction

It is well established that thioxo groups undergo prototropic isomerization to a greater extent than oxo groups due to the different extent of overlapping of the p_z-orbitals of the heteroatom with that of the adjacent carbon atom. Thus, butadiene-1,4-dithiols **A** exist as the favoured tautomers rather than the butane-1,4-dithiones **B** (*Scheme 1*) whilst the 1,4-diketone structure is preferred in the corresponding oxa analogues.[1] Exceptions arise from conjugation of the thioxo groups in **B** with π-donor substituents (R^1, R^4)[2] or as a result of unfavourable steric factors in **A** caused by particular anellations (R^1–R^2, R^3–R^4). The latter is exhibited by the title compound **3** ≡ **D** where the strain of the C-C-double bonds in the bornene in **A** leads to the preference for the structure **B**.

In the course of our work on enthiols, especially those of type **A** and the related disulfides (1,2-dithiines),[1,3] the title compound **3** attracted our attention as an „artificially" stabilized 1,4-dithione from which some unusual behaviour might be expected. In addition, the structure of **3** suggested to us that it could be an interesting precursor for various 1,4-difunctional chiral derivatives. Although **3** was first described almost 60 years ago by *Sen* [4], with the exception of its condensation reactions with hydroxylamine and hydrazine, and its reduction with sodium amalgam, no further reactions of **3** have been reported. A preliminary account of the work described herein has been published.[3d]

3-*exo*,3'-*exo*-(1*R*,1'*R*)-Bithiocamphor (**3** ≡ **D**) was first prepared from (1*R*)-thiocamphor **1** [derived from (1*R*)-(+)-camphor] with sodium hydride in benzene and subsequent oxidation with iodine in the same solvent.[4a] In this one-pot approach the intermediate disulfide **2** undergoes a spontaneous Cope rearrangement, thermodynamically favoured as a result steric strain in the bornene units of **2** as noted above. Later *Campbell* and *D. M. Evgenios* [5] were able to isolate **2** by reaction of **1** with chloramine T and to rearrange it in a separate step by heating or on prolonged storage to a product which could be assigned as the 3-*exo*,3'-*exo* -linked isomer rather than the alternative structures **E** and **F** from ^{1}H NMR (singlet at 2.51 ppm for H 3 and H-3'). Finally the structure of **3** ≡ **D** was unequivocally established by X-ray diffraction.[3d] The thiocamphor units are only slightly twisted towards each other with a C4-C3-C3'-C4' torsion angle of only 0.7° and with an optimal

distance of both sulfur atoms of about 4.05 Å. The stereospecific formation of **3** ≡ **D** is evidently explained by the involvement of a chair-like transition state as shown in **C**.



Scheme 1

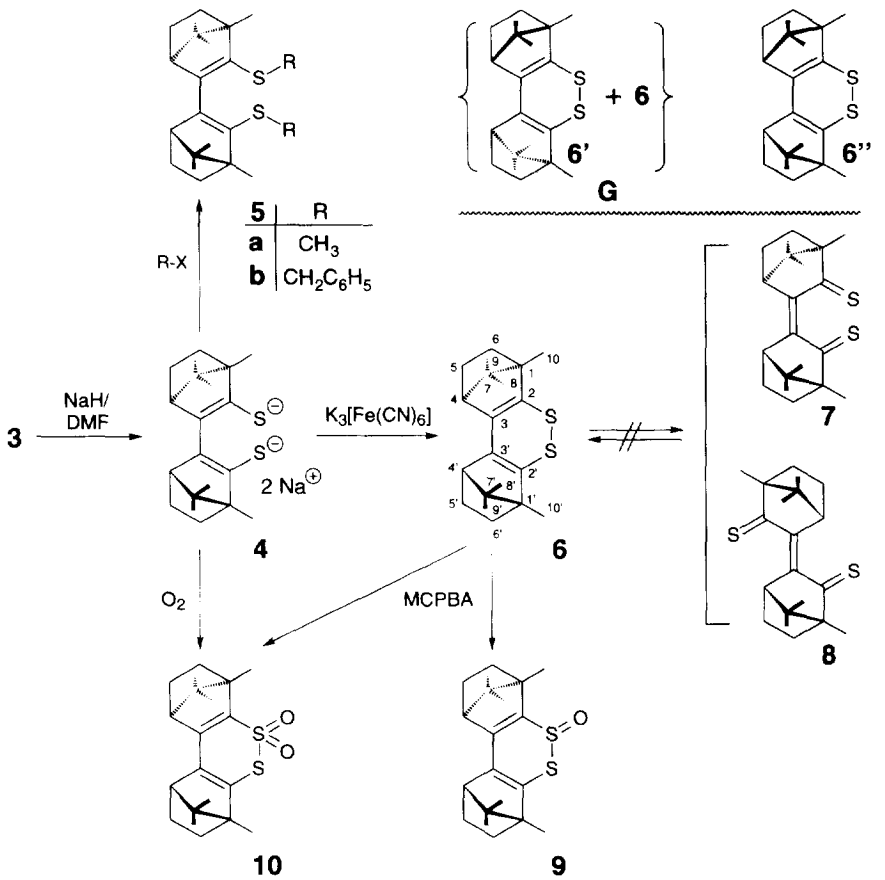
Results and Discussion

1. Reactions Forming Bornene Units; Ring-Closure Reactions

Due to the steric shielding of the hydrogen atoms at C-3 and C-3' (cf. X-ray elucidation)[3d] attempts to deprotonate **3** by means of LDA in tetrahydrofuran or with chloramine T (as used for the access to **2**) failed. However, the complete deprotonation of **3** proceeds smoothly in the presence of less bulky bases, e.g. sodium hydride in DMF, and leads initially to the sodium bis-enthiolate **4** (red-violet solution)[6] which can be subsequently quenched with methyl iodide and benzyl chloride with the formation of the biborn-2-ene derivatives **5a,b** (*Scheme 2*)

From in-situ oxidation of **4** with potassium hexacyanoferrate(III), the diborneno-1,2-dithiine **6** is produced in excellent yield. This compound was isolated as deep red needles and in solution has an absorption maximum at 490 nm in common with other spectral properties of other 1,2-dithiines.[1a,c,d,3b,c] The X-ray analysis, as reported in our preliminary communication,[3d] indicates a twisted cyclic disulfide structure with a C-S-S-C torsion angle of 47° with a twist of both bornene units around 24° and with a normal S-S-bond length of 2.065 Å. The presence of the alternative thioxo valence isomers **7** and **8**, respectively, can be excluded even although they should be expected as a result of the preference of semicyclic over intracyclic double bonds in the bornane skeleton, as emphasized at the beginning and as shown in the ready formation of **3** from **2**.[7] In solution ($CDCl_3$) there is no indication of any equilibrium of **6** with **7** or **8**, respectively, as evidenced by means of

^{13}C NMR spectroscopy (absence of signals in the C=S range). An equilibrium between different conformers cannot be observed up to -95°C in solution (no doubling or broadening of the ^{1}H signals of the CH_3 groups).



Scheme 2

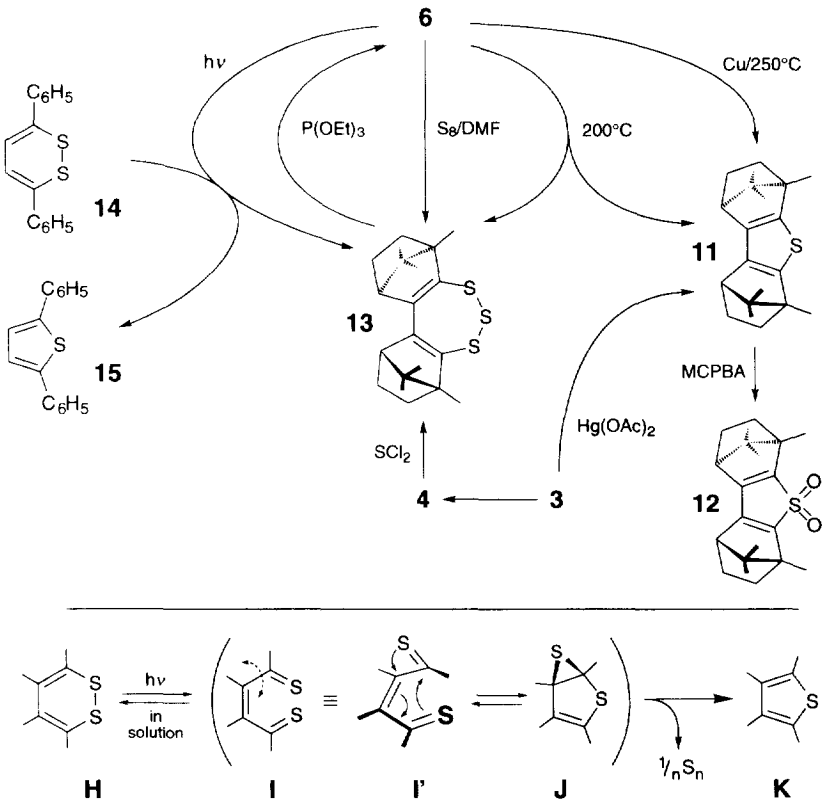
Thus, **6** may be regarded as the simplest example of a strained and „artificial" stabilized bibornenedithiol derivative, playing a key role in consecutive transformations. Furthermore, **6** represents a member of the class of 1,2-dithiines which are distinguished by a number of unusual properties[1a,c,d,3a-g,8] (colour, spontaneous sulfur extrusion, occurrence as plant constituents with a promising biological activity). However, by contrast **6** exhibits some unusual properties due to some unusual steric factors (see below).

Using *racemic* thiocamphor the analogous sequence leads to a racemic mixture **G** composed by the (1*R*, 1'*R*)-diborneno-1,2-dithiine **6** and the enantiomeric (1*S*,1'*S*)-diborneno-1,2-dithiine **6'** but no meso-diastereomeric (1*R*,1'*S*)-diborneno-1,2-dithiine **6''** (cf. the preparation of "dl-bis-thiocamphor" in ref.[4a]). Product mixture **G** exists as deeply red needles melting at 70-73°C (cf. m.p. 123°C for **6**) and is identical with that separately produced from **6** and **6'** [the latter was obtained from (1*S*)-thiocamphor]. Thus, the dithiine formation may be regarded also as a test for the stereoselection which should occur in an earlier step i.e. in the transformation from **1** to **2**.

Oxidation of **6** with one mole *m*-CPBA at 0°C smoothly leads to the sulfoxide **9** which is remarkably stable in contrast with the usual characteristics of compounds of the 1,2-dithiine series.[1a,c,d] At this time no further

details of its steric structure can be disclosed. By means of dynamic ^1H NMR investigations a ring inversion can be ascertained resulting in an activation barrier of $\Delta G^{\neq} \approx 45$ kJ·mol^{-1} [based on the singlets $\delta = 0.73$ and 0.75 ppm ($CDCl_3$) of the methyl groups and successive doubling of these singlets on cooling below -60°C; coalescence temperature T_C = -66.5°C]. With excess *m*-CPBA at elevated temperature **6** is oxidized to the sulfone **10** which may also be obtained directly from **3** via **4** by the rapid passage of air through a DMF solution. Attempted transformation of **6** to **10** by an analogous treatment with oxygen failed (SET assistance due to the deep red colour of the solution of **4** in DMF ?).[6]

Whilst 3,6-disubstituted 1,2-dithiines undergo facile sulfur extrusion, e.g. in solution by exposure to normal daylight at ambient temperature,[1c,d] **6** is extremely stable despite the fact that it has the same electronic characteristics as 1,2-dithiines. In addition its mass spectrum (70 eV) contains no peak attributable to the loss of sulfur. Above 200°C in the presence of copper bronze, **6** is transformed to the thiophene **11** (*Scheme 3*). The latter can also be obtained instantly (but in lower yield) from **3** by treatment with mercuric(II) acetate. Oxidation of **11** by *m*-CPBA furnishes the stable thiophene sulfone **12**.



Scheme 3

The lack of any tendency of **6** to extrude sulfur in contrast to the behaviour of the non-anellated 1,2-dithiines requires some explanation. In accord with the well known valence isomerization in the heterocyclohexa-1,3-diene series[9] the photo-induced process should commence with electrocyclic ring opening of **H** to the dithione **I**, followed by an intramolecular [π4 + π2]-cycloaddition in the twisted form **I'** to the episulfide **J** which ultimately produces the thiophene **K** by extrusion of sulfur. The torsion around the C1-C2 bond of **I** for the intramolecular cycloaddition to **I'** should be completely hindered in **6** and should be generally the lim-

iting factor in the sulfur extrusion from dianellated 1,2-dithiines. The nature and the fate of the extruded sulfur are presently being investigated.

In total contrast, **6** shows a marked tendency for the insertion of one sulfur atom with the formation of the diborneno-1,2,3-trithiepine **13** (deep yellow crystals). The difference between **6** and the 3,6-disubstituted 1,2-dithiines is emphatically demonstrated by its reaction with 3,6-diphenyl-1,2-dithiine **14**[1c] in normal daylight at room temperature. In this reaction **6** accepts one sulfur atom from **14** and changes completely to **13** with loss of colour to the thiophene **15**. It is unclear if sulfur transfer takes place directly from **14** to **6** or via a primary extrusion of sulfur which is accepted by **6** in a second step. Elemental sulfur reacts with **6** in DMF solution at room temperature to produce **13** in quantitative yield. When heated at 200°C a disproportion reaction is observed in which one molecule acts formally as a sulfur donor and the other as a sulfur acceptor with the formation of **11** and **13**. Compounds **13** is also accessible by the in-situ reaction of **4** with sulfur dichloride. One sulfur atom in **13** can be easily removed with regeneration of **6**, by treatment with triethyl phosphite. The high formation tendency of **13** may be considered as an effect of steric compulsion by the rigid bornene units.

The structure of **13** has been elucidated by X-ray crystallography (*Figure 1*).[10a,11a] Whilst both bornene units are only slightly twisted towards each other, the central S2-atom strongly stands out within the C-S_3-C-moiety producing an envelope type shape. The temperature dependence of ^{1}H NMR spectrum characterizes a dynamic process in terms of a reversible inversion of the seven membered ring. From the coalescence temperature at -30.5°C (related to the methyl proton signals) an activation barrier of $\Delta G^{\neq} = 54.3$ kJ·mol^{-1} could be determined.[12]

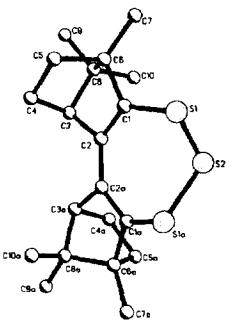


Figure 1. X-ray crystal structure[10a,11a] of (1*R*,1'*R*)-diborn-2-eno[2,3-*d*;3',2'-*f*][1,2,3]trithiepine (**13**).
Selected data – bond lengths: S1-S2 = 2.037(8) Å, S2-S1a = 2.096(36) Å; torsion angles: S1-S2-S1a-C1a = -74.79°, C1-C2-C2a-C1a = 1.22°.

2. Reactions Forming New Bornylidene Units; Prototropic Rearrangements

Reaction of **6** with sodium borohydride results in the formation of the blue-violet mercapto-(*Z*)-enthione **16a** and not the isomeric bi-bornenethiol **L**, X = H (*Scheme 4*). Accordingly the C=S group is characterized by a ^{13}C NMR signal at 249.2 ppm and the SH group by a ^{1}H NMR signal at 3.73 ppm. The assignment of the (*Z*)-configuration as well as the *endo*-SH position agrees with findings of 2D-NOE measurements (NOESY; NOE between H-4 and H-4'; see experimental part). The structure of **16a** was conclusively established by X-ray crystallography (*Figure 2*).[10b,11b]

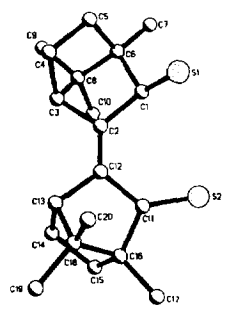


Figure 2. X-ray crystal structure[10b,11b] of 2-(*endo*-mercapto)-2'-thioxo-(1*R*,1'*R*)-(*Z*)-3,3'-bibornanylidene (**16a**).
Selected data – bond lengths: C1-S1 = 1.838(7) Å, C11-S2 = 1.657(7) Å; torsion angles: C1-C2-C12-C11 = 6.52°, C12-C2-C1-S1 = 68.59°, C2-C12-C11-S2 = 0.99°.

The formation of **16a** can be explained by a suprafacial 1,5-H shift according to **L'** (X may be BH_2 in the primary step). This principle of stabilization (*path i*) demonstrates the thermodynamical disadvantage of the intracyclic double bonds in the bornene units and is generally obeyed (see the following). Analogously, the deep blue alkylthio-enthiones **16b,c** are obtained by reaction of **6** with alkyllithium; the structure assignment is based on NMR spectroscopy and especially on the excellent accordance of the UV/Vis spectra with that of **16a**. The latter can be transformed back to **6** (via enthiolization and oxidation) by the action of sodium ethanolate and oxygen. Furthermore, **16a** is completely methylated with Me_2SO_4 in basic medium to **5a**; the same product is also obtained by successive in-situ treatment of **6** with MeLi (via **16b**) and MeI.

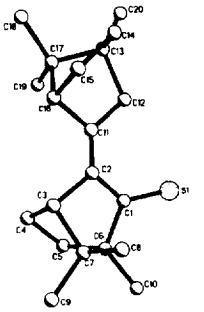
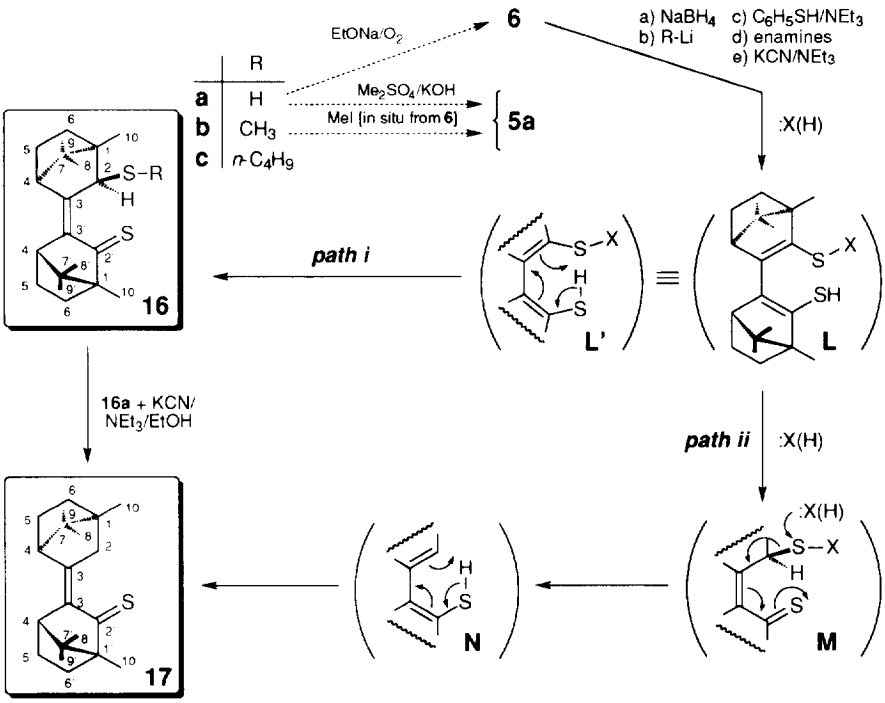


Figure 3. X-ray crystal structure[13,14] of 2'-thioxo-(1*R*,1'*R*)-(*Z*)-3,3'-bibornanylidene (**17**).
Selected data – bond lengths: C1-S1 = 1.65(2)Å; bond angles: C2-C1-S1 = 130.1°; C6-C1-S1 = 123.3°.

An alternative reaction (*path ii*) involves the elimination of one thiol group with the formation of the red-violet enthione **17** whose structure once more was established by X-ray crystallography (*Figure 3*).[13,14] The preservation of the (*Z*)-configuration supports the proposed reaction path. Thus, the primary intermediate **L** undergoes nucleophilic attack again (X = nucleophile residue) via **M** to yield **N** which in turn undergoes a 1,5-H shift with the formation of **17**. For example, reaction of **6** with benzenethiol leads to **17** along with diphenyl disulfide as coproduct. Compound **17** is also formed by the reaction of **6** with enamines or with potassium cyanide (in the former case no coproduct was detected, but in the second case rhodanide was observed). Potassium cyanide also causes dethiolization of **16a** with the formation of **17**.



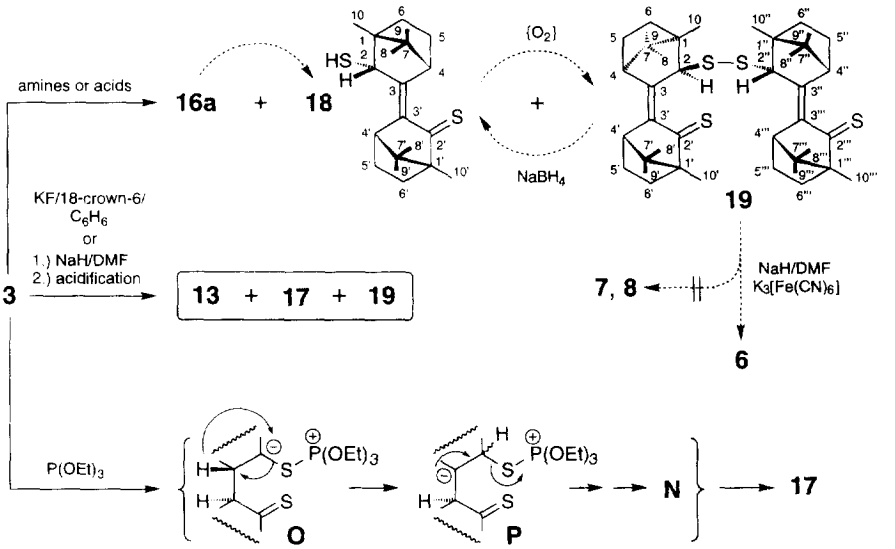
Scheme 4

The reactions of **6** noted above underline some of the features of the reaction behaviour of the dithione **3**: As already indicated by the preferred formation of the mercapto-(*Z*)-enthione **16a** from **6** via a 1,5-H-shift, all attempts are precluded to obtain the bi-bornenethiol **5**, R = H, due to the steric strain and by stabilization via prototropy and by subsequent processes.

Thus, treatment of **3** with acids (HCl) or secondary amines (piperidine, morpholine) at elevated temperature affords product mixtures consisting of **16a** (minor product) with larger amounts of the (*E*)-isomer **18**. In addition **19**, **13** and **17** are also produced (*Scheme 5*).

The (*E*)-configurated **18** is characterized by absorption at shorter wavelengths in the visible region compared with that of **16a** (red-violet instead of blue-violet crystals). Its structure is clearly deduced from ^{1}H

NMR studies: A strong NOE between H-4' and H-2 is consistent with the (*E*)-configuration in contrast with the strong NOE between H-4 and H-4' arising from the (*Z*)-configurated **16a**. The isomerization of **16a** to **18** indicates that the latter is the thermodynamically more stable one, and therefore the primary formation of **16a** from **L/L'** via 1,5-H shift (cf. *Scheme 4*) as a kinetically controlled process.



Scheme 5

The (*Z*)/(*E*)-disulfide **19** (deep blue crystals) is formed from **16a** and **18**. Its structure is established by mass spectrometry and by ^{1}H and ^{13}C NMR spectroscopy where four different sets of signals corresponding to four bornane units and the assignments for H-4, H-4', H-4'' and H-4''' are of immense diagnostic use. In the case of the C_2-symmetrical (*Z*)/(*Z*)- and (*E*)/(*E*)-combinations, respectively, only the half of signal sets would be expected. The crucial points being the NOE between H-4 and H-4' [(*Z*)-configuration of one half of the molecule analogous to **16a**] and the presence of two ^{13}C-signals for both C=S groups. Moreover the ^{1}H NMR spectrum shows no change at temperature increasing (observed up to 65°). Reductive cleavage of **19** by means of $NaBH_4$ furnishes a 1:1-mixture of **16a** and **18**. By successive treatment of **19** with sodium hydride in DMF and potassium cyanoferrate(III), the 1,2-dithiine **6** results rather than the valence isomers **7** or **8**, respectively.

Treatment of **3** with potassium fluoride in the presence of 18-crown-6 in boiling benzene yields a mixture of the trithiepine **13**, the enthione **17** and the disulfide **19**. (The latter arising via the initially produced **16a** followed by a series of consecutive reactions.) When **3** is heated with triethyl phosphite at elevated temperature, desulfurization takes place with the formation of **17**, which may be rationalized by attack at the thioxo-sulfur to **O**, followed by rearrangement to **P** and then via intermediate **N** (see to this *Scheme 4*).

Conclusions

The title compound **3**, a sterically stabilized 1,4-dithione (versus a butadiene-1,4-dithiol), permits simple access to other chiral compounds. Its stereoselective synthesis is a result of a Cope rearrangement of the disulfide precursor **2** [derived from (+)-camphor]. — Two types of behaviour are evident. *1.)* The formation of born-2-ene units despite increasing ring strain, especially in ring closure reactions at the sulfur atoms, for example. Transformation of **3** to the deeply coloured diborneno-1,2-dithiine **6** by subsequent deprotonation

and oxidation as well as to the diborneno-1,2,3-trithiepine **13** by reaction with elemental sulfur. The influence of steric strain is manifested by several pecularities such as the failure to extrude sulfur under mild conditions and rearrangements of the primarily formed disulfide fission products. — *2.)* The double bond displacement from intracyclic to semicyclic positions in order to minimize or avoid ring strain by the born-2-ene units is one of the fundamentals of the reactivity. This is demonstrated by the non-existence of the enthiols **L** (including X = H), stabilization by 1,5-H-shifts forming semicyclic double bond systems, e.g. in the mercapto-enthiones **16.** This primary process is repeatedly followed by various consecutive reactions.

Experimental Part

NMR spectra:Varian Unity 500 (^{1}H: 499.84 MHz, ^{13}C: 125.71 MHz), Bruker WP 200 (^{1}H: 200.13 MHz, ^{13}C: 50.3327 MHz), Bruker AC 80 (^{1}H: 80.13 MHz, ^{13}C: 20.149 MHz). ^{1}H and ^{13}C NMR spectra were recorded with TMS as internal standard. – MS: Varian MAT CH6, AMD Intectra 402 (70 eV). – IR: Carl Zeiss Jena Specord 71 and 75. – UV: Beckman DK-2A. – Column chromatography (CC): silica gel [60 mesh (Merck)]. – Optical rotations: Polarimeter 241 (Perkin Elmer), Polartronic (Schmidt & Haensch). – HPLC: Merck Hitachi L-4000 (UV detector). – Melting points: Heating stage microscope (Boetius M; all temperatures quoted are not corrected). – X-ray analyses: Diffractometer STADI4 (Stoe, MoK$_\alpha$ radiation, $3 < 2\Theta < 54°$). – Elemental analyses: Carlo Erba (automatic apparatus).

(1*R*,1'*R*)-3-*exo*,3'-*exo*-Bithiocamphor (**3**): Preparation according to ref.[5] from (+)-camphor; orange cuboids; m.p. 180°C. – UV/Vis (MeCN): λ_{max} (lg ε): 247 nm (4.11), 278 (3.53, sh.), 4.85 (2.22). – X-ray analysis in ref.[3d]. – ^{1}H NMR ($CDCl_3$)[15]: δ = 0.66 (H-8, H-8'; 2 CH_3), 0.98 (H-9, H-9'; 2 CH_3), 1.06 (H-10, H-10'; 2 CH_3), 1.32 (H-5$_{endo}$, H-5'$_{endo}$), 1.52 (H-6$_{endo}$, H-6'$_{endo}$), 1.71 (H-6$_{exo}$, H-6'$_{exo}$), 2.03 (H-5$_{exo}$, H-5'$_{exo}$), 2.33 (H-4, H-4'), 2.49 (H-3$_{endo}$, H-3'$_{endo}$); $^3J_{4,5exo}$ ($^3J_{4',5'exo}$) = 3.6 Hz. – ^{13}C NMR[15] ($CDCl_3$): δ = 13.9 (C-10, C-10'; 2 CH_3), 20.5 (C-9, C-9'; 2 CH_3), 21.0 (C-8, C-8'; 2 CH_3), 29.1 (C-5, C-5'), 31.8 (C-6, C-6'), 48.8 (C-7, C-7'), 49.2 (C-4, C-4'), 67.7 (C-1, C-1'), 69.9 (C-3, C-3'), 274.4 (C-2, C-2'; 2 C=S). – MS (70 eV), *m/z* (%): 334 (61) [M$^+$], 319 (12) [M$^+$ – CH_3], 301 (100) [M$^+$ – SH], 273 (20) [M$^+$ – C_2H_4 – SH], 167 (30) [M$^+$/2], 133 (9) [M$^+$/2 – H_2S].

2,2'-Di(methylthio)-(1*R*,1'*R*)-3,3'-biborn-2-ene (**5a**). – A solution of 334 mg (1 mmol) **3** [derived from (1*R*)-(+)-camphor] in 20 ml abs. THF is added to a suspension of 150 mg (6.25 mmol) NaH in 10 ml abs. THF at -30°C with stirring under an argon atmosphere. The resulting violet mixture is treated with an excess of MeI (2.3 g) which causes the reaction mixture to become pink in colour. After stirring (16 h) at ambient temperature the solvent is removed at reduced pressure and the residue partitioned between water and CH_2Cl_2. The organic phase is washed with water and concentrated. The resulting oil is dissolved in MeOH and cooled to -40°C to initiate crystallization. Colourless needles crystals; yield: 250 mg (70%); m.p. 36-37°C. – ^{1}H NMR ($CDCl_3$): δ = 0.78-1.93 (m, 26 H, aliphat.), including 0.78, 0.80 (2 s, 6 H, C[CH_3]$_2$), 1.12 (s, 6 H, 2 CH_3), 2.10 (s, 6 H, 2 CH_3S), 2.52 (d, 3.6 Hz, 2 H, H-4/H-4'). – MS (70 eV), *m/z* (%): 362 (71) [M$^+$], 347 (100) [M$^+$ - CH_3], 319 (34) [M$^+$ - C_3H_7]. – $C_{22}H_{34}S_2$ (362.6): calcd. C 72.89, H 9.47, S 17.64; found C 72.81, H 9.46, S 17.75.

2,2'-Di(benzylthio)-(1*R*,1'*R*)-3,3'-biborn-2-ene (**5b**). – A solution of 334 mg (1 mmol) **3** in 40 ml abs. DMF, prepared at 50-60°C, is added to a suspension of 100 mg NaH (approx. 80% suspension in paraffin oil) under stirring under an argon atmosphere at 0°C. After the addition stirring is continued for a further hour and then a solution of 380 mg (3 mmol) benzyl chloride is added (colour changes to yellow). The mixture is then treated with water (50 ml) and the mixture extracted with diethyl ether (2 x 30 ml). The concentrated extracts are purified by CC [*n*-hexane/C_6H_6 (4:1)]. Pale yellow leaflets (on prolonged standing); yield: 184 mg (36%); m.p. 91°C. – ^{1}H NMR ($CDCl_3$): δ = 0.81-1.90 (m, 24 H, aliphat.), including 0.81 (s broad, 12 H, 2 C[CH_3]$_2$), 1.24 (s, 6 H, 2 CH_3), 2.45 (d, J = 4.0 Hz, 2 H, H-4/H-4'), 3.80 (s broad, 4 H, 2 $PhCH_2$), 7.22-7.34 (m, 10 H, aromat.). – ^{13}C NMR ($CDCl_3$): δ = 13.3, 19.9, 26.5, 27.2, 33.5, 39.3, 54.5, 57.0, 59.7 (8 C, aliphat.), 127.9, 128.6, 129.4, 133.7 (4 C, including 133.7: *ipso*-C), 139.2, 148.9 (2 C, olefin.). – MS (70 eV), *m/z* (%): 514

(50) [M+], 423 (68) [M+ - C_7H_7], 332 (100) [M+ - 2 C_7H_7],. – $C_{34}H_{42}S_2$ (514.8): calcd. C79.75, H 7.81, S 12.44; found C 78.99, H 7.98, S 12.78.

(1*R*,1'*R*)-Diborn-2-eno[2,3-*c*;3',2'-*e*][1,2]dithiine (**6**): To a solution of 334 mg (1 mmol) **3** and NaH described as above for **5b** is added an aqueous solution of 2.5 g $K_3[Fe(CN_6)]$ (20 ml, 7.6 mmol) which causes the product to precipitate immediately. Alternatively, 2.2 g solid $K_3[Fe(CN_6)]$ can be used but in this instance stirring at ambient temperature for 4 h is required. The product is filtered off by suction and recrystallized from EtOH/H_2O (5:2). – Dark red needles; yield: 319 mg (96%); m.p. 122-123°C {analogously prepared **(±)-Diborn-2-eno[2,3-*c*;3',2'-*e*][1,2]dithiine** (**G**) derived from (±)-camphor: yield 90%; m.p. 72-73°C}.– UV/Vis (MeCN): λ_{max} (lg ε): 287 nm (3.29), 380 (4.36), 490 (4.45). – $[\alpha]_D^{20}$ = -147.4° ($CHCl_3$, c = 0.5, d = 1 dm). – X-ray analysis in ref.[3d]; ^1H NMR ($CDCl_3$): δ = 0.77 (H-9, H-9'; 2 CH_3), 0.80 (H-8, H-8'; 2 CH_3), 0.98 (H-10, H-10', 2 CH_3), 1.12 (H-5*endo*, H-5'*endo*), 1.43 (H-6*endo*, H-6'*endo*), 1.63 (H-6*exo*, H-6'*exo*), 2.38 (H-4, H-4'). – ^{13}C NMR ($CDCl_3$): δ = 11.3 (C-10, C-10'; 2 CH_3), 19.0 (C-9, C-9', 2 CH_3), 19.6 (C-8, C-8'); 2 CH_3), 25.9 (C-5, C-5'), 33.0 (C-6, C-6'), 52.8 (C-4, C-4'), 56.3, 57.5 (C-1, C-7, C-1', C-7'), 130.6 (C-3, C-3'), 144.1 (C-2, C-2'; 2 C-S). – MS (70 eV), *m/z* (%): 332 (100) [M+], 317 (5) [M+ – CH_3], 304 (43) [M+ – C_2H_4], 289 (24) [M+ – C_3H_7], 271 (20) [M+ – C_2H_4 – SH], 261 (15) [M+ – C_2H_4 – C_3H_7]. – $C_{20}H_{28}S_2$ (332.6): calcd. C 72.23, H 8.48, S 19.28; found C 72.27, H 8.70, S 19.33.

(1*R*, 1'*R*)-Diborn-2-eno[2,3-*c*;3',2'-*e*][1,2]dithiine-S-oxide (**9**): A solution of 332 mg (1 mmol) **6** in 15 ml CH_2Cl_2 is treated dropwise with a solution of 300 mg (≈ 1 mmol) *m*-CPBA in 15 ml CH_2Cl_2. A deep yellow colour is developed. After stirring for a further hour the reaction mixture is purified by CC. Elution of the first yellow band affords the title compound, which is then crystallized from EtOH/H_2O (3:1). – Lemon yellow needles; yield: 247 mg (71%); m.p. 141-143°C. – IR (KBr): $\tilde{\nu}$ = 1580 cm^{-1} (m, C=C), 1070 (s, S=O). – UV (MeCN): λ_{max} (lg ε): 221 nm (3.68), 290 (3.26). – $[\alpha]_D^{20}$ = +150° ($CHCl_3$, c = 0.5, d = 1 dm). – ^1H NMR ($CDCl_3$): δ = 0.73, 075, (2 s, 6 H, 2 CH_3), 0.90 (s-broad, 6 H, 2 CH_3), 1.16, 1.34 (2 s, 6 H, 2 CH_3), 1.08-2.11 (m, 8 H, CH_2), 2.79, 2.83 (2 d, J = 3, 6 Hz, 2 H, H-1/H-10) {low-temperature measurements in CD_2Cl_2: commencement of doubling of the CH_3-signal δ = 1.29 at -66.5°C (completed at -83°C)}. – ^{13}C NMR ($CDCl_3$): δ = 11.6, 11.7, 19.0, 19.4, 19.8, 24.8, 26.0, 32.0, 34.4, 52.8, 53.1, 53.8, 56.4, 57.2, 57.5, 58,7 (16 C, saturd.), 134.2, 135.0, 136.0, 143.8 (4 C, olef.). – MS (70 eV), *m/z* (%): 348 (2) [M+], 332 (5) [M+ – O], 300 (78) [M+ – SO], 285 (18) [M+ – SO – CH_3], 257 (100) [M+ – SO – C_3H_7]. – $C_{20}H_{28}OS_2$ (348.5): calcd. C 68.96, H 8.05, S 18.39; found C 68.39, H 8.21, S 18.55.

(1*R*, 1'*R*)-Diborn-2-eno[2,3-*c*;3',2'-*e*][1,2]dithiine-S-dioxide (**10**).

*a) From **3** via **4***: A solution of 334 mg (1 mmol) **3** and NaH in DMF described as above for **5b** is treated with a rapid current of air until the colour of the solution becomes pale yellow (about 30 min). After the addition of 50 ml H_2O, the mixture is extracted with diethyl ether (2 x 30 ml). The resulting oil is purified by CC [*n*-hexane/C_6H_6 (1:1)]. – Yellow needles; yield: 240 mg (66%); m.p. 184-185°C (after recrystallization from EtOH). – IR (KBr): $\tilde{\nu}$ = 1530 cm^{-1} (m, C=C), 1300, 1120 (s, SO_2). – UV (MeCN): λ_{max} (lg ε): 287 nm (3.21), 350 (3.26). – $[\alpha]_D^{20}$ = +65° ($CHCl_3$, c = 1, d = 1 dm). – ^1H NMR ($CDCl_3$): δ = 0.84-2.10 (m, 26 H, aliphat.), including 0.84, 0.85, 0.87, 0.88, 1.08, 1.39 (6 s, 18 H, 6 CH_3), 2.65, 2.75 (2 d, J = 4.0 Hz, 2 H, H-1/H-10). – ^{13}C NMR ($CDCl_3$): δ = 11.1, 12.0, 18.5, 18.7, 19.1, 19.3, 19.9, 24.7, 25.8, 31.9, 33.7, 52.7, 53.7, 57.2, 58.6, 59.0 (16 C, saturd.), 133.2, 135.7, 143.4, 150.0 (4 C, olef.). – MS (70 eV), *m/z* (%): 364 (86) [M+], 336 (100) [M+ – C_2H_4], 321 (25) [M+ – C_3H_7], 300 (27) [M+ – SO_2]. – $C_{20}H_{28}O_2S_2$ (364.5): calcd. C 65.89, H 7.74, S 17.59; found C 65.50, H 7.83, S 17.07.

*b) From **6***: The reaction is carried out as described for **9** employing twice the amount of *m*-CPBA at ambient temperature followed by 15 min reflux. – Yield: 266 mg (73%).

(1*R*, 1'*R*)-Diborn-2-eno[2,3-*b*;3',2'-*d*]thiophene (**11**).

*a) From **6***: An intimate mixture of 332 mg (1 mmol) **6** and 400 mg (excess) copper bronze is heated for 45 min at 250°C (bath temperature). The cooled mixture is extracted with diethyl ether (3 x 30 ml), concentrated and the resulting solid recrystallized from EtOH/H_2O (7:1). – Colourless needles; yield: 192 mg (64%); m.p. 97-98°C. – $[\alpha]_D^{20}$ = +208.1 ($CHCl_3$, c = 1.05 g/100 ml, d = 1 dm). – ^1H NMR ($CDCl_3$): δ = 0.69-1.98 (m, 26

H, aliph.), including 0.76 (s, 6 H, 2 CH_3), 0.88 (s, 6 H, 2 CH_3), 1.21 (s, 6 H, 2 CH_3), 2.75 (d, J = 4.0 Hz, 2 H, H-1/H-9). – ^{13}C NMR (C_6D_6): δ = 12.9, 20.4, 28.0, 30.2, 34.6, 51.3, 55.0, 60.5 (8 C, saturd.), 143.7, 149.3 (2 C, olefin.). – MS (70 eV), *m/z* (%): 300 (82) [M^+], 285 (50) [$M^+ - CH_3$], 257 (100) [$M^+ - C_3H_7$]. – $C_{20}H_{28}S$ (300.5): calcd. C 79.90, H 8.72, S 10.67; found. C 79.51, H 9.01, S 10.47.

b) From 3: A mixture of 111 mg (0.3 mmol) **3**, 0.5 g (1.5 mmol) $Hg(OAc)_2$, 30 ml CH_2Cl_2 and 10 ml AcOH is heated under reflux for 2 h during which time the colour of **3** is discharged. After removal of the solids, the organic phase is washed with water (2 x 30 ml), dried (Na_2SO_4) and concentrated at reduced pressure. The resulting oil is decolourized (active carbon) and crystallized from EtOH/H_2O (7:1). Yield: 31 mg (35%).

(1*R*, 1'*R*)-Diborn-2-eno[2,3-*b*;3',2'-*d*]thiophene-S-dioxide (12). – To a solution of 300 mg (1 mmol) **11** in 50 ml CH_2Cl_2 is added 2.5 g (50-60 perc.) *m*-CPBA. After heating under reflux for 45 min, the solvent is removed at reduced pressure and the residue purified by CC on silica gel using CH_2Cl_2 as eluant. – Colourless needles; yield: 166 mg (50%); m.p. 250-251°C [from EtOH/H_2O (1:1)]. – IR (KBr): $\tilde{\nu}$ = 1650 cm^{-1} (m, C=C), 1280, 1100 (s, SO_2). – $[\alpha]_D^{20}$ = +19.79° ($CHCl_3$, c = 0.96 g/100 ml, d = 1 dm). – ^1H NMR ($CDCl_3$): δ = 0.81-2.09 (m, 28 H, aliph.), including 0.81 (s, 6 H, 2 CH_3), 0.86 (s, 6 H, 2 CH_3), 1.25 (s, 6 H, 2 CH_3), 2.60 (d, J = 4.1 Hz, 2 H, H-1/H-9). – ^{13}C NMR ($CDCl_3$): δ = 11.1, 18.5, 19.2, 25.6, 31.8, 51.6, 57.1, 59.3 (8 C, saturd.), 148.5, 150.1 (2 C, olefin.). MS (70 eV), *m/z* (%): 332 (91) [M^+], 316 (7) [M^+ –O], 304 (18) [$M^+ - C_2H_4$], 289 (100) [$M^+ - C_3H_7$]. – $C_{20}H_{28}O_2S$ (332.5): calcd. C 72.29, H 8.43, S 9.64; found C 71.88, H 8.60, S 8.98.

(1*R*, 1'*R*)-Diborn-2-eno[2,3-*d*;3',2'-*f*][1,2,3]trithiepine (13).

a) From 3 via 4: A solution prepared from 334 mg (1 mmol) **3** and NaH in DMF as described for **5b** is treated with 0.1 ml (1,3 mmol) of freshly distilled SCl_2 with stirring over a 1 hour period during which time the colour of the mixture changes from black-violet to yellow-orange. The title compound (in addition to some **6**) is isolated by CC [*n*-hexane/C_6H_6 (4:1)] and recrystallized from EtOH/H_2O (6:1). Deep yellow needles; yield: 222 mg (61%); m.p. 143°C. – UV/Vis (MeCN): λ_{max} (lg ε): 255 nm (3.43), 318 (3.43), 390 (3.20). – X-ray analysis in Figure 1[10a,11a] – $[\alpha]_D^{20}$ = +200.97° ($CHCl_3$, c = 1.03 g/100 ml, d = 1 dm). – ^1H NMR ($CDCl_3$)[15]: δ = 0.76, 0.82, 1.09 (6 CH_3), 1.19 (H-5_{endo}, H-5'$_{endo}$), 1.23 (H-6_{endo}, H-6'$_{endo}$), 1.66 (H-6_{exo}, H-6'$_{exo}$), 1.95 (H-5_{exo}, H-5'$_{exo}$), 2.75 (H-4, H-4'); $^3J_{4,5exo}$ = 3.6 Hz. – ^{13}C NMR ($CDCl_3$):[15] δ = 12.4, 19.4, 19.6 (6 CH_3), 25.5 (C-5, C-5'), 55.1 (C-7, C-7'), 32.0 (C-6, C-6'), 57.4 (C-4, C-4'), 60.0 (C-1, C-1'), 148.5 (C-2, C-2'). – MS (70 eV), *m/z* (%): 364 (100) [M^+], 332 (51) [M^+– S], 304 (23) [M^+– S – C_2H_4], 300 (31) [M^+– 2S], 272 (50) [M^+– 2S – C_2H_4], 257 (58) [M^+– 2S – C_2H_4 – CH_3]. – $C_{20}H_{28}S_3$ (364.6): calcd. C 65.82, H 7.68, S 26.33; found C 65.51, H 7.60, S 25.81.

b) From 6: To a solution of 332 mg (1 mmol) **6** in 30 ml abs. DMF at ambient temperature is added an excess (320 mg, 10 mmol) of finely powdered elemental sulfur which causes the colour of the solution to change from deep red to brown red. The solvent is removed at reduced pressure and the product obtained by crystallization from 70-perc. EtOH or by chromatography as described above, respectively. – Yield: 360 mg (99%).

Thermolysis of 6 to 11 and 13: Compound **6** (498 mg, 1.5 mmol) is heated alone or in decalin solution at 190-210°C for 5-10 min (colour change from deep red to pale yellow). The crude reaction mixture is purified by CC [60 cm length; *n*-hexane/C_6H_6 (4:1)] and all mixed fractions are rechromatographed to afford **11** (first zone): 129 mg (43%); **13** (second zone): 142 mg (39%).

Light induced reaction between 6 and 3,6-diphenyl-1,2-dithiine (14) to 13 and 2,5-diphenylthiophene (15): A solution of 332 mg (1 mmol) **6** and 537 mg (2 mmol) **14**[1b] in 30 ml dry solvent (MeCN, C_6H_6 or CH_2Cl_2) is exposed to sunlight or to a 500-W lamp, respectively, until the red colour is discharged (maximum 2 h). Compound **13** is obtained in quantitative yield by CC [*n*-hexane/C_6H_6 (4:1), first fraction]. Subsequent elution affords **15** (m.p. 153°C) also in quantitative yield and sulfur.

Reaction of 13 with triethyl phosphite to 6: A solution of 728 mg (2 mmol) **13** in 20 ml dry toluene is treated with 0.34 ml (2.2 mmol) $P(OEt)_3$. An orange colour is developed immediately. The reaction is

completed by heating the solution at 60-70°C for 30 min. The solvent is removed at reduced pressure and the residue is recrystallized from EtOH/H_2O (3:1). 478 mg (72%) **6**, red needles, m.p. 122-123°C.

2-(*endo*-Mercapto)-2'-thioxo-(1*R*,1'*R*)-(*Z*)-3,3'-bibornanylidene (16a).

a) From 6 by reaction with $NaBH_4$: A solution of 332 mg (1 mmol) **6** dissolved in a mixture of 10 ml benzene, 20 ml EtOH and 2 ml water is treated with stirring and under an argon atmosphere with 380 mg (10 mmol) $NaBH_4$. After stirring at room temperature for 1 h, during which time the colour changes from red to blue-violet, the mixture is acidified by the addition of 10 ml 2N H_2SO_4. The mixture is then treated with 20 ml benzene, the organic phase separated, dried (Na_2SO_4) and concentrated at reduced pressure. The residue is purified by CC (petroleum ether; blue-violet zone) and subsequent recrystallization from EtOH/H_2O (7:1) yields 183 mg (55%) of **16a**. Blue-violet leaflets; m.p. 132-133°C. – UV/Vis (MeCN): λ_{max} (lg ε): 259 nm (3.25), 342 (3.75), 558 (1.35), 586 (1.32, sh.). – X-ray analysis in Figure 2[10b,11b]. – $[\alpha]_D^{20}$ = -21.43° ($CHCl_3$, c = 1.05 g/100 ml, d = 1 dm). – ^{1}H NMR ($CDCl_3$)[15]: δ = 0.68 (H-8), 0.73 (H-8'), 0.95 (H-9'), 0.96 (H-10), 0.98 (H-9), 1.11 (H-10'), 1.22 (H-6'$_{endo}$), 1.28 (H-5'$_{endo}$), 1.51 (H-5$_{endo}$), 1.52 (H-6$_{endo}$, exchangeable with H-6$_{exo}$), 1.71 (H-6'$_{exo}$), 1.86 (H-6$_{exo}$, exchangeable with H-6$_{endo}$), 1.94 (H-5$_{exo}$), 2.00 (H-5'$_{exo}$), 2.41 ($^3J_{4,5exo}$ =4.9 Hz, H-4), 2.70 ($^3J_{4',5'exo}$ = 3.7 Hz, H-4'), 3.73 (SH), 4.07 ($^3J_{2,SH}$ = 5.9 Hz, H-2). – ^{13}C NMR ($CDCl_3$)[15,16]: δ = 13.4 (C-10), 13.8 (C-10'), 18.9 (C-9), 19.0 (C-8), 19.4 (C-9'), 19.9 (C-8'), 25.0 (C-5), 26.0 (C-5'), 30.9 (C-6), 34.8 (C-6'), 48.6 (C-7, exchangeable with C-7'), 49.0 (C-7', exchangeable with C-7), 49.3 (C-2), 50.6 (C-1), 52.5 (C-4'), 55.0 (C-4), 70.2 (C1'), 143.1 (C-3), 162.6 (C-3'), 249.2 (C-2'). – 2D-NOE [NOESY] measurements: strong NOE between H-4 and H-4' [distance between H-4 and H-4': 2.2 Å (molecular modelling, Alchemy)]: (*Z*)-configuration; NOE from H-2 to SH and H-10 (3.1 Å) and H-8 (3.0 Å), no NOE to H-6$_{endo}$: *exo*-position of H-2. – MS (70 eV), *m/z* (%): 334 (60) [M^+], 302 (11) [M^+ – S], 273 (33) [M^+ – SH – C_2H_4]. – $C_{20}H_{30}S_2$ (334.7): calcd. C 71.85, H 9.00, S 19.20; found C 71.35, 9.40, S 18.86.

b) From 6 by reaction with thiophenol: A solution of 332 mg (1 mmol) **6**, 330 mg (3 mmol) thiophenole and 202 mg triethylamine in 10 ml DMF is stirred for 10 min. The solvents are removed at reduced pressure and the residue purified by CC [*n*-hexane/C_6H_6 (3:1)] to afford 180 mg (55%) diphenyl disulfide (first fraction) and then 230 mg (69%) **16a** (second fraction). **Transformation of 16a to 5a**: A mixture of 500 mg (1.5 mmol) **16a**, 500 mg (4 mmol) Me_2SO_4, 1 g anhydrous K_2CO_3, 200 mg triturated KOH and 30 mg 18-crown-6 in 20 ml abs. benzene is heated under reflux for 8 h under an argon atmosphere. The mixture is then treated with 500 mg MeI and reflux continued for a further 8 h. The product (400 mg) is isolated by CC (middle fraction) and crystallized from MeOH at low temperature. Yield of **5a**: 200 mg (37%). – **Transformation of 16a to 6**: Compound **16a** (334 mg, 1 mmol) is dissolved in an ethanolic solution of sodium ethanolate [prepared from 115 mg (5 mmol) Na and 25 ml of anhydrous EtOH]. Air is passed into the solution for 1 h during which the solution becomes dark red. After addition of 30 ml H_2O the product is extracted twice by means of 30 ml diethyl ether. CC [*n*-hexane/C_6H_6 (4:1)] yields 163 mg (49%) **6**.

2-(*endo*-Methylthio)-2'-thioxo-(1*R*,1'*R*)-(*Z*)-3,3'-bibornanylidene (16b): A solution of 332 mg (1 mmol) **6** in 20 ml abs. THF is treated at -30°C with 1 ml of a solution of MeLi (1.6 N) with stirring under an argon atmosphere. After stirring at this temperature for 1 h and then at room temperature for 2 h, the mixture is hydrolyzed by the addition of 10 ml water. The resulting dark blue mixture is partitioned between 30 ml diethyl ether and 50 ml water, the organic layer separated, dried (Na_2SO_4) and concentrated. Recrystallization from EtOH/H_2O (8:1) affords intense blue needles or prisms, 220 mg (63%); m.p. 107-108°C. – UV/Vis (MeCN): λ_{max} (lg ε): 330 nm (4.09), 585 (2.39). – $[\alpha]_D^{20}$ = -483.87° ($CHCl_3$, c = 0.93 g/100 ml, d = 1 dm). – ^{1}H NMR (C_6D_6): δ = 0.61-2.28 (m, 30 H, aliphat.), including 0.60, 0.83, 0.86, 0.87, 0.89, 1.02, (6 s, 18 H, 6 CH_3), 2.22 (s, 3H, CH_3S), 2.27 (d, J = 4.0 Hz, H-4'), 2.57 (d, J = 4.0 Hz, 1 H, H-4), 3.70 (s [broad], 1 H, H-2). – ^{13}C NMR ($CDCl_3$): δ = 13.6, 14.7, 19.0, 19.2, 19.4, 19.8, 20.1, 24.6, 25.5, 25.9, 30.6, 30.7. 35.6, 48.8, 52.6, 52.9, 54.8, 70.1 (18 C, saturd.), 143.7, 157.8 (2 C, olefin.), 247.7 (C=S). – MS (70 eV), *m/z* (%): 348 (18) [M^+], 301 (100) [M^+ – SCH_3], 285 (16) [M^+ – 2S – H], 273 (5) [M^+ – SCH_3 – C_2H_4]. – $C_{21}H_{32}S_2$ (348.6): calcd. C 72.41, H 9.19, S 18.40; found C 71.99, H 9.43, S 18.52. – **in situ Transformation of 16b to 5a**: Under an argon atmosphere and with stirring, 1 ml (1.6 mmol) of MeLi in 4 ml diethyl ether is added at -30°C to 300 mg (0.9 mmol) of **6** in 5 ml dry diethyl ether. An excess of MeI (1 ml) is then added and the

mixture stirred at room temperature for 3 h. The addition of 10 ml water followed by separation yields an oil, which is crystallized from MeOH to yield 320 mg **5a** (98%).

2-(*endo*-*n*-Butylthio)-2'-thioxo-(1*R*,1'*R*)-(*Z*)-3,3'-bibornanylidene (16c): A similar procedure to that used for **16b** was used employing an equivalent of BuLi and isolating the product by CC (petroleum ether). Blue oil; yield: 156 mg (40%). – UV/Vis (MeCN): λ_{max} (lg ε): 330 nm (3.92), 586 (2.83). – $[\alpha]_D^{20}$ = -377° ($CHCl_3$, c = 1, d = 1 dm). – ^{1}H NMR ($CDCl_3$): δ = 0.69-2.91 (m, 36 H, aliphat.), including 0.69, 0.90, 0.94, 0.95, 1.11, 1.23 (6 s, 18 H, 6 CH_3), 2.30 (d, J = 4.0 Hz, 1 H, H-4'), 2.64 (d, J = 4.1 Hz, 1 H, H-4), 3.86 (s, 1 H, H-2). – ^{13}C NMR ($CDCl_3$): δ = 13.6, 13.8, 14.7, 19.0, 19.4, 20.1, 22.5, 24.5, 25.9, 28.7, 30.8, 31.8, 35.6, 36.4, 48.7, 52.3, 52.9, 54.8, 59.6, 69.9, 73.4 (21 C, saturd.), 143.5, 157.9 (2 C, olefin.), 247.0 (C=S). – MS (70 eV), *m/z* (%): 390 (27) [M^+], 333 (7) [$M^+ - C_4H_9$], 301 (100) [$M^+ - SC_4H_9$], 258 (22) [$M^+ - SC_4H_9 - C_3H_7$]. – $C_{24}H_{37}S_2$ (389.7): calcd. C 74.10, H 9.59, S 16.31; found C 73.38, H 9.84, S 16.66.

2'-Thioxo-(1*R*,1'*R*)-(*Z*)-3,3'-bibornanylidene (17).

*a) From **3** and P(OEt)$_3$*: A mixture of 334 mg (1 mmol) **3** and 1.66 g (10 mmol) $P(OEt)_3$ is heated for 3 h at 200°C. The excess reagent is removed at reduced pressure. The highly coloured oil is purified by CC [*n*-hexane/C_6H_6 (3:1)] and recrystallized from EtOH/H_2O (6:1); 202 mg (67%) **17**. – Red-violet needles; m.p. 119-120°C – UV/Vis (MeCN): λ_{max} (lg ε): 325 nm (4.21), 545 (2.28). – X-ray analysis in Figure 3[13,14]. – $[\alpha]_D^{20}$ = +37.25° ($CHCl_3$, c = 1.02 g/100 ml, d = 1 dm). – ^{1}H NMR (C_6H_6): δ = 0.65, 0.72, 0.73, 0.79, 0.81, 1.26 (6 s, 18 H, 6 CH_3), 1.28-1.95 (m, 10 H, 5 CH_2), 2.19 (d, J = 4.0 Hz, 1 H, H-4'), 2.52 (d, J = 4.2 Hz, 1 H, H-4). – ^{13}C NMR (C_6D_6): δ = 13.9, 15.2, 18.0, 18.2, 19.5, 19.7, 20.2, 25.5, 27.1, 33.6, 35.1, 46.1, 47.8, 49.1, 52.1, 55.1, 69.1 (17 C, saturd.), 142.2, 157.7 (2 C, olefin.), 250.0 (C=S). – MS (70 eV), *m/z* (%): 302 (100) [M^+], 287 (62) [$M^+ - CH_3$], 274 (51) [$M^+ - C_2H_4$], 259 (98) [$M^+ - C_3H_7$]. – $C_{20}H_{30}S$ (302.5): calcd. C 79.47, H 9.93, S 10.60; found C 78.94, H 9.63, S 10.75.

*b) From **6** and 1-pyrrolidino-1-cyclopentene*: A mixture of 332 mg **6** and 1.37 g (10 mmol) 1-pyrrolidino-1-cyclopentene is heated for 30 min at 100-120°C. Isolation by CC [*n*-hexane/C_6H_6 (3:1)] yields 275 mg **17** (91%; first fraction). An analogous procedure using 1-morpholino-1-cyclohexene produces 70% **17**.

*c) From **6** and KCN*: A mixture of 332 mg **6**, 325 mg (5 mmol) KCN, 202 mg (2 mmol) NEt_3 and 20 ml EtOH is heated under reflux for 5 min. The solvent is removed at reduced pressure and the residue purified by chromatography (see above) to give 202 mg **17** (67%).

*d) From **16a** and KCN*: Using the same conditions as in *(c)*, **17** is isolated in 69% yield.

Transformations of 3.

A) By influence of amines: For example, a solution of 500 mg (1.5 mmol) **3** and 1 g (11.5 mmol) morpholine in 30 ml anhydrous toluene is heated under reflux for 3 h. The product is isolated by CC [*n*-hexane/C_6H_6 (5:1)]. The first fraction (blue, 300 mg) is recrystallized from EtOH to yield **18** (contaminated with 20% **16a** by NMR), 130 mg (26%). The second fraction (blue) is recrystallized from C_6H_6/EtOH (1:2) to afford **19**, 30 mg (6%). The product ratio depends upon the amine employed (piperidine, dicyclohexylethylamine, *n*-hexylamine), the additional formation of **13** and **17** is also observed and prolonged reaction times lead to increasing amounts of **19** (e.g. up to 50% after 5 h reflux). – **2-(*endo*-Mercapto)-2'-thioxo-(1*R*,1'*R*)-(*E*)-3,3'-bibornanylidene (18)** : Blue-violet plates; m.p. 171-173°C (1:1 mixed m.p. with **16a**: 115°C). – UV/Vis (MeCN): λ_{max} (lg ε): 259 nm (3.15), 341 (3.72), 562 (1.73). – ^{1}H NMR ($CDCl_3$)[15] δ = 0.70 (H-8), 0.71 (H-8'), 0.90 (H-10), 0.93 (H-9), 0.98 (H-9'),1.08 (H-10'), 1.22 (H-6$_{endo}$), 1.22 (H-6'$_{endo}$), 1.42 (H-5$_{endo}$), 1.49 (SH), 1.55 (H-5'$_{endo}$), 1.69 (H-6'$_{exo}$), 1.90 (H-6$_{exo}$), 1.95 (H-5$_{exo}$), 2.06 (H-5'$_{exo}$), 2.93 ($^3J_{4',5'exo}$ = 4.0Hz, H-4'), 3.62 ($^3J_{2,SH}$ = 7.6 Hz, H-2), 4.11 ($^3J_{4,5exo}$ = 4.9 Hz, H-4). – ^{13}C NMR ($CDCl_3$):[15,16] δ = 13.0 (C-10), 13.3 (C-10'), 18.7 (C-8), 19.3 (C-9'), 19.6 (C-9), 20.1 (C-8'), 24.2 (C-6), 25.7 (C-5'), 28.3 (C-5), 35.4 (C-6'), 48.4 (C-7, exchangeable with C-7'), 48.7 (C-7', exchangeable with C-7), 51.0 (C-4), 51.5 (C-2), 52.3 (C-4'), 69.9 (C-1'), 50.2 (C-1), 145.5 (C-3), 157.8 (C-3'), 253.2 (C-2'). – Strong NOE between H-2 and H-4': (*E*)-configuration (compare finding for **16a**); NOE from H-2 to SH, H-8 and H-10, but not to H-6$_{endo}$: *exo*-position of H-2. – MS (70 eV), *m/z* (%): 334 (86) [M^+], 319 (43) [$M^+ - CH_3$], 301 (100) [$M^+ - SH$]. – $C_{20}H_{30}S_2$ (334.6): calcd. C 71.85, H 9.00, S 19.20; found C 72.17, H 9.06, S 19.41. – **[2'-Thioxo-3,3'-(*Z*)-bibornanylidene-2-(*endo*)yl] [2'''-thioxo-3'',3'''-(*E*)-bibornanylidene-2''-(*endo*)yl] disulfide (19)**; blue

flakes, m.p. 181-182°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε): 358 nm (4.51), 570 (3.02), 660 (2.91, sh.). – $[\alpha]_D^{20}$ = +369° ($CHCl_3$, c = 0.73 g/100 ml, d = 1 dm). – ^1H NMR ($CDCl_3$): δ = 0.67-2.45 (m, 52 H, aliphat.), including 0.67, 0.73, 0.78, 0.90, 0.93, 0.958, 0.961, 0.98, 0.99, 1.05, 1.107, 1.110 (12 s, 12 CH_3), 2.30 (d, J = 4.9 Hz), 2.66 (d, J = 3.8 Hz), 3.57 (d, J = 3.8 Hz), 4.14 (d, J = 4.9 Hz) (4 H; H-4, H-4', H-4'', H-4'''), 4.59, 4.67 (2 s, 2 H; CH-S-S-C-2, CH-S-S-C-2''). – ^{13}C NMR ($CDCl_3$): δ = 13.40, 13.41, 13.5, 15.4, 18.8, 19.30, 19.34, 19.38, 19.40, 19.42, 19.9, 20.7 (12 CH_3), 24.2, 24.3, 25.6, 26.6, 29.4, 30.4, 35.3, 36.0 (8 CH_2), 50.9, 51.7, 53.2, 54.3, 65.3, 65.3 (6 CH), 46.8, 48.8, 49.0, 50.0, 51.6, 52.8, 70.0, 70.1 (8 C), 144.6, 146.7, 155.0, 156.9 (4 C, olefin.), 246.8, 253.4 (2 C, C=S). – MS (70 eV), *m/z* (%): 666 (1) [M^+], 333 (58) [$M^+/2$], 301 (100) [$M^+/2$ – S]. – $C_{40}H_{58}S_4$ (667.1): calcd. C 72.28, H 8.73, S 19.28; found C 71.98, H 8.72, S 19.30. – *Regeneration of* **6**: A solution of 166 mg (0.25 mmol) **19** in 20 ml DMF is added to a stirred mixture of 120 mg (4 mmol) of NaH (80% suspension in paraffin oil) and 5 ml DMF under an argon atmosphere at room temperature. The mixture becomes dark violet in colour. After stirring 90 min, 50 ml of a 5-perc. aqueous solution of $K_3[Fe(CN)_6]$ is added with ice cooling. The precipitated **6** (contaminated with some **13**, **17**, and **19**) is extracted with diethyl ether (2 x 30 ml). The concentrated extracts are purified by CC. The first fraction (dark red) yields 51 mg (61%) **6**. – *Reduction to* **16a/18**: A suspension of 80 mg (0.12 mmol) **19** in 2 ml C_6H_6, 4 ml EtOH and 0.4 ml water is treated with $NaBH_4$ and the resulting mixture stirred at 35-40°C under an argon atmosphere during which time the solution becomes clear and the colour changes from blue to red-violet. Addition of 2 ml 2N H_2SO_4, extraction with C_6H_6 and CC [*n*-hexane/C_6H_6 (5:1)] yield 42 mg (52%) of a 1:1 mixture of **16a/18** (NMR detection).

B) By action of KF under PTC conditions: A mixture of 334 mg **3**, 290 mg (5 mmol) anhydrous KF, 132 mg 18-crown-6 and 30 ml anhydrous benzene is heated under reflux for 1 h during which time the colour changes to red-violet. After evaporation under reduced pressure the residue is separated by CC [*n*-hexane/C_6H_6 (3:1)]. 1st fraction (intensively yellow): **13** [EtOH/H_2O (6:1)], 51 mg (14%). 2nd fraction (red-violet): **17** [EtOH/H_2O (6:1)], 88 mg (29%). 3rd fraction (blue): **19**; 90 mg (25 %).

C) By consecutive deprotonation with NaH and reprotonation: A solution prepared from 334 mg (1 mmol) **3**, NaH and DMF as described above for **5b**, is treated with 50 ml of water, 30 ml 2N H_2SO_4 or 50 ml AcOH. The product is isolated by CC (as described above for the KF-PTC reaction). Yields (depending on the proton source): 44-65 mg (12-18%) **13**, 69-91% (23-30%) **17**, 67-90 mg (20-25%) **19**.

D) By influence of acids: A solution of 334 mg (1 mmol) **3** in 20 ml CH_2Cl_2 and 10 ml concd. HCl is vigorously stirred at 60°C for 7 h (colour changes from orange to blue-violet). The organic phase is washed with three 20 ml portions of water, concentrated and the residue recrystallized from EtOH/H_2O to afford a mixture of **16a/19** as violet flakes, 227 mg (68%); m.p. 115-125°C.

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References and Notes

☆ *Dedicated to Professor Richard Neidlein on the occasion of his 65th birthday*

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