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REACTIONS OF THIOKETEN S-OXIDES WITH DIAZO COMPOUNDS

A NOVEL SYNTHESIS OF HETEROCYCLIC SULFINES

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Abstract—Thioketen S-oxides **1** react with 2-diazopropane (**2a**) to give 1-pyrazoline-4-thione S-oxides **3**. Addition of diazomethane to **1** yields a stable 1:1-adduct only from the S-oxide **1c**. The constitution of both types of cycloadducts (**3**, **11**) was proven by X-ray diffraction. Irradiation of **3** leads to loss of nitrogen to afford the alkylidene thiirane S-oxides **12**.

Cycloaddition reactions of heterocumulenes with 1,3-dipoles provide an attractive method for the synthesis of a variety of heterocyclic compounds.[1] Also the bent heteroallene system of sulfines (thione S-oxides) is capable of this reaction mode as documented by the (2 + 3)-cycloadditions with diazoalkanes,[2] nitrile oxides,[3] nitrile ylides[4] nitrones[5] and diphenylnitrilimine.[6] Although the higher cumulated thioketen S-oxides are known for some time, namely those showing stabilization by steric effects,[7,8] the only reactions studied so far are cycloadditions with nitrones[9] or azomethines[10] and addition of phenyl[8] or methyl lithium[11] to give α,β-unsaturated sulfoxides. We now report on cycloaddition reactions of the thioketen S-oxides **1a**, **b**, and **c** with diazoalkanes **2**.

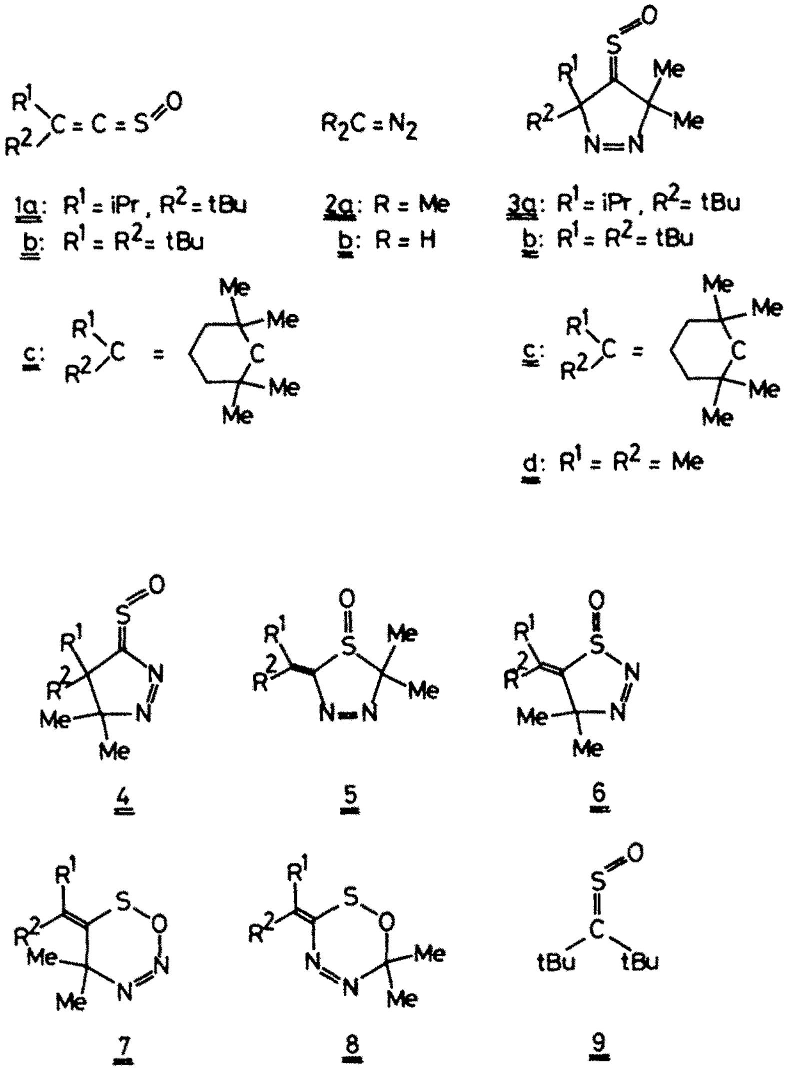
RESULTS

Cycloadditions of thioketen-S-oxides **1** *with 2-diazopropane* (**2a**). The thioketen S-oxides **1a**, **b**, and **c** react smoothly with the diazo compound **2a** to afford good to excellent yields of 1:1-adducts. Formulas **3**–**6** (Scheme 1) represent possible structures resulting from (2 + 3)-cycloaddition across the C=C bond (**3**, **4** plus their diastereomers) or the C=S bond (**5**, **6**) of the thioketen S-oxide. Besides, (3 + 3)-cycloaddition is conceivable, since compounds **1** can also react as 1,3-dipoles (structures 7 and 8).[10] In each case two regioisomers must be considered as diazoalkanes are known to be ambident nucleophiles.[12]

The IR spectra of the adducts show absorptions around 1060 cm^{-1} attributable either to the sulfine function in **3** or **4**, or to the sulfoxide group in **5** or **6**. In addition, N=N absorptions are present at about 1560 cm^{-1}, but no ν(C=C) could be detected. The ^{1}H NMR spectra exhibit one signal for the geminal Me protons adjacent to the diazo nitrogens of adducts derived from **1b** and **c**, and one signal for the t-Bu protons of the product derived from **1b**. Structures **5**–**8** are therefore less likely, because for these structures *two* singlets would be expected for the t-Bu groups. The UV spectra show maxima around 275 nm (ε *ca* 7000), which points to a nonconjugated sulfine moiety as in **3** (aliphatic sulfines show a UV absorption in the same region).[2b] Low field ^{13}C NMR signals were observed at δ 199.0 and 196.3 for **3b** and **c**, respectively. These values are in excellent agreement with δ 199.7 for the sulfine carbon in compound **3d**, which was recently obtained by peracid oxidation of the parent thione.[13] Among the other signals observed (see Experimental) the peaks around δ 100 agree reasonably well with those of the other ring C atom in **3d**.[13] However, in the acyclic aliphatic sulfine **9**[14] the C=SO resonance was found to occur at considerably lower field (δ 216.1).

Though the spectral data all suggest structure **3** for the cycloadducts, an X-ray structural investigation of the product obtained from **1c** was conducted to obtain unambigous proof of structure. The X-ray study confirms structure **3c** for this cycloadduct (Fig. 1, Table 1). The atoms of the pyrazolin ring as well as the exocyclic S and O atoms form a common plane with a maximum deviation of endocyclic torsional angles of 1.4° (for C5–N1–N2–C3). The oxygen of the sulfine moiety is directed towards the geminal Me groups on C3 giving the sterically more favourable *E*-configuration.

The S-C4 distance (Table 1) in **3c** falls within the usual range of 1.61–1.64 Å for the thiocarbonyl group in sulfines, whereas the S-O bond length is one of the longest observed for thione S-oxides.[15] The N1–N2 distance is almost identical with the calculated value[16]

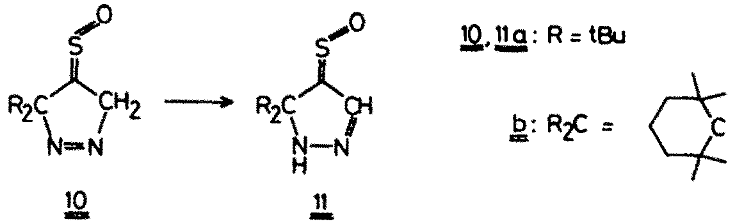


Scheme 1.

for an N=N bond of 1.24 Å, but the N2–C and N1–C5 distances considerable exceed the expected value of 1.46 Å for C(sp^3)-N= bonds,[15] probably because of the bulky substituents on C5 and particularly on C3. Similarly, the bond from C6 or C10 to the spiro carbon C3 are significantly stretched when compared to the other C–C distances in the cyclohexane ring (Table 1).

Cycloadditions of thioketen S-oxides **1** *with* diazomethane (**2b**). Addition of diazomethane to an ethereal solution of the S-oxid **1c** gives a red crystalline substance, which is rather unstable in solution and can be recrystallized only with difficulty. Thus the only spectroscopic data bearing on the structure of this product are the IR and ^{1}H NMR spectra (see Experimental), which do not lead to a unique structure. In any case, the presence of an NH group is obvious from an IR absorption at 3230 cm^{-1} and a broad ^{1}H NMR peak at δ 8.17 indicating that subsequent to the cycloaddition a tautomeric shift occurs.

An X-ray structural analysis revealed the product to be the pyrazoline-4-thione S-oxide **11b** (Scheme 2). Two slightly different molecules are present in the crystal (Fig. 2, Table 2).



Scheme 2.

The most remarkable feature of the structure is an H-bond between the NH and SO groups of neighbouring molecules as the symmetry-independent intermolecular O–H distance (Table 2) is well below the limiting value of 2.2 Å for an H-bond to oxygen.[17] Compound **11b** seems to gain some stability from this H-bonding in the crystal, whereas in solution, where the molecules are less associated, decomposition occurs. A parallel to the stabilization of **11b** by an NH–O bond can be found in the chemistry of thioamide S-oxides, where H-bond stabilization is important to make these compounds isolable.[18]

In spite of H-bonding, the S–O distance in **11c** is only slightly longer than in **3c**, but the C=S bond in **11b** (Table 2) is the longest reported for sulfines including **3c**.[15] This may result from some mesomeric interaction between the C=S and the C=N bonds, as the latter bond length well exceeds the normal value of 1.27 Å.[16] However, at the same time the N1–N2 distance is shorter than in hydrazones, where values in the order of 1.37–1.38 Å were observed,[16] and, consequently, mesomerism within the N2–N1–C5 unit may be discussed as well. In any case, a low-lying extended π* orbital must be available on excitation of an electron at sulphur as can be deduced from the red colour of the compound.

Surprisingly, the distance from N2 to the spiro atom C3 is shorter in **11b** than in **3c**, though in the latter case double-bonded nitrogen is involved. The other bond lengths in **11b** are similar to those in **3c** as discussed above.

The S-oxide **1b** and diazomethane appears to form cycloadduct **11a** as indicated by the red colour of the mixture. However, the colour rapidly fades, and only **1b** and decomposition product of the S-oxide **1b** can be detected (see Ref. 19).

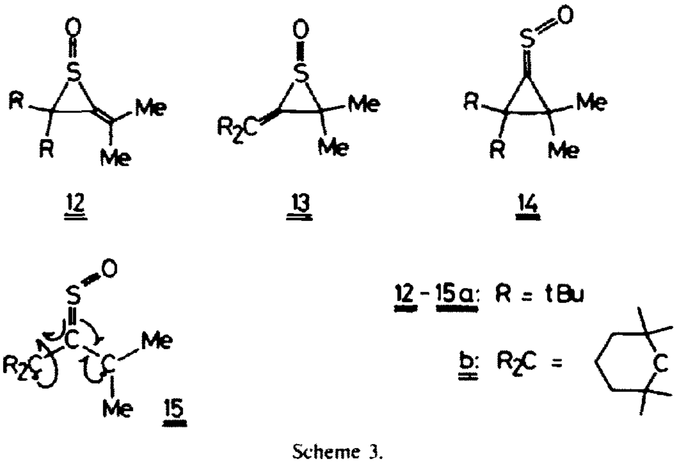
Photolysis of the cycloadducts **3b, c**. In an attempt to elucidate the chemistry of the heterocyclic sulfines **3** and because of the current interest in 1-pyrazoline photochemistry,[20] the photolysis of the cycloadducts **3b** and **c** was studied. Irradiation in benzene or carbon tetrachloride led to rapid loss of nitrogen. Consequently, structures **12–14** (Scheme 3) seem possible for the photoproducts. The IR spectra show absorptions at 1720 and 1050 cm^{-1}, which can be assigned to ν(C=C)[21] and ν(S=O), respectively. The presence of a C=C-band as well as the magnetic non-equivalence of the geminal substituents in the ^{1}H NMR spectra rule out the cyclopropane sulfine structure **14**. Distinction between the isomeric allene episulfoxides **12** and **13** is less straightforward. The ^{1}H NMR spectra in chloroform exhibit the signals for the Me protons at rather low field between δ 2.07 and 2.28, suggesting that the Me residues are attached to an olefinic carbon as in **12**. Furthermore, using benzene for the product from **3b**, the increased signal separation expected for thiirane S-oxide ring substituents[22] is observed for the t-Bu peaks. Structure **12** was unambigously proven with the aid the proton-undecoupled ^{13}C NMR spectrum of **12a**, where $^2J_{HC}$ and $^3J_{HC}$ coupling of the olefinic carbons with the Me hydrogens could be detected and the assignments substantiated by double resonance experiments (see Experimental). Thus the biradical **15** which probably forms from **3** after loss of nitrogen, undergoes a rearrangement in the manner indicated to give the episulfoxide **12** incorporating the carbon with the bulky substituents into the ring.

Prolonged irradiation of **3** results in further degradation to give hydrocarbons. This chemistry will be dealt with separately.[23]

DISCUSSION

Formation of the pyrazolinethione S-oxides **3**, **11** from thioketen S-oxides **1** and diazo compounds **2** implies that cycloaddition occurs across the C=C bond of the heterocumulene in spite of the strong steric shielding of this bond by the bulky substituents. This result is in apparent contrast to the reaction of the parent thioketens with **2**, which occurs across the C=S bond.[23] Also bis(trifluoromethyl)thioketen gives cycloadducts derived from C=S addition with diazomethane.[24] Apparently, electron distribution in thioketens differs significantly from the S-oxides as also indicated by the ^{13}C NMR data.[8]

Contrary to the behaviour of the tetramethylpyrazoline[13] **3d** towards 2-diazopropane (**2a**), we never observed formation of 1:2-adducts from **1** and **2a**. This can be attributed to the steric shielding of the C=S bond by the voluminous substituents on one side of the 5-membered ring. For the same reason, only the sterically favoured configuration (*E* for **3** could be detected in the cycloadducts *Z* for **11**).



Scheme 3.

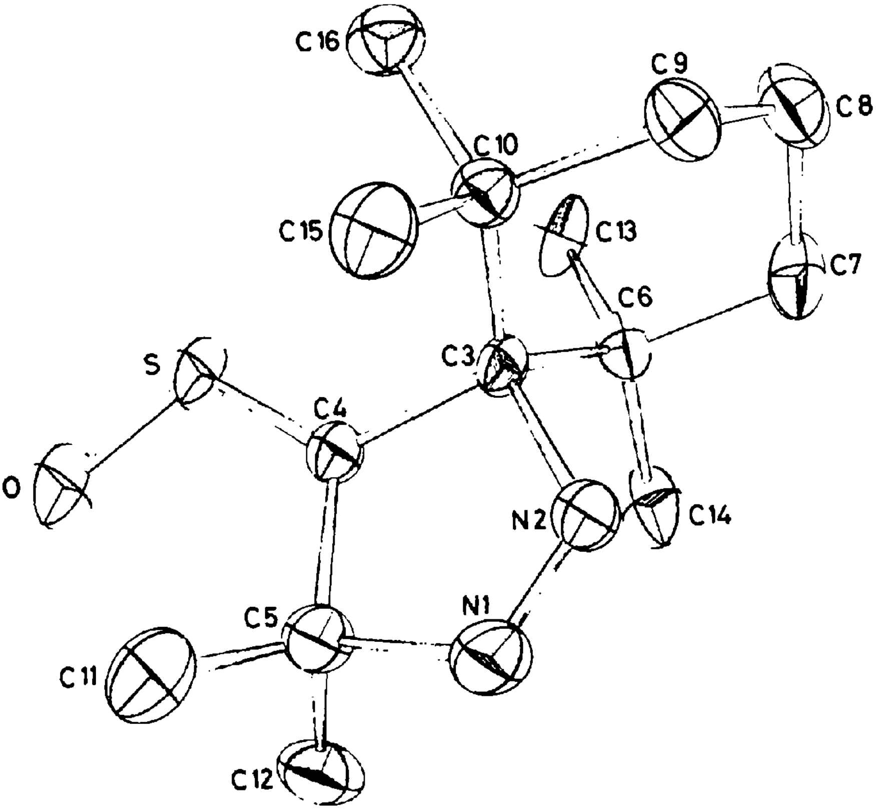


Fig. 1. ORTEP presentation[29] of the molecular structure of **3c**, showing 50% ellipsoids.

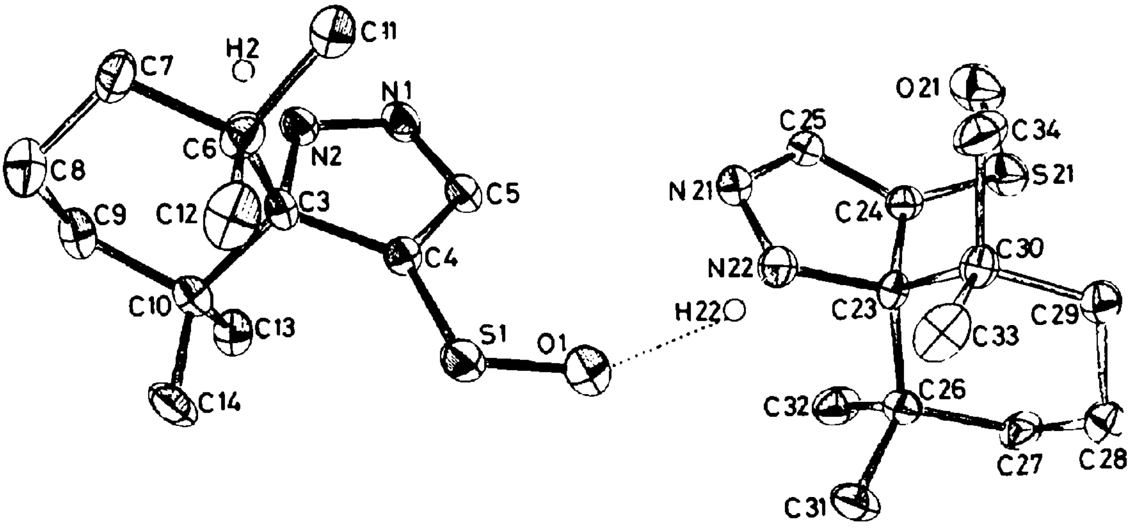


Fig. 2. ORTEP presentation[29] of the molecular structure and the arrangement of the two non-identical molecules of **11b**, showing 50% ellipsoids.

Table 1. Bond lengths (Å) and angles (°) with least-squares estimated standard deviations in parentheses for non-hydrogen atoms in **3c**. For numbering of atoms (see Fig. 1)

Bond lengths (Å)		Bond angles (°)			
S-O	1.491(3)	O-S-C4	112.5(2)	C3-C6-C13	114.3(4)
S-C4	1.632(4)	N2-N1-C5	113.4(4)	C7-C6-C13	107.8(4)
N1-N2	1.244(4)	N1-N2-C3	115.1(3)	C3-C6-C14	111.7(5)
N1-C5	1.522(5)	N2-C3-C4	100.0(3)	C7-C6-C14	108.2(4)
N2-C3	1.533(5)	N2-C3-C6	105.1(4)	C13-C6-C14	106.5(5)
C3-C4	1.529(5)	C4-C3-C6	114.1(4)	C6-C7-C8	114.6(5)
C3-C6	1.583(7)	N2-C3-C10	105.0(4)	C7-C8-C9	110.9(5)
C3-C10	1.566(7)	C4-C3-C10	115.2(4)	C8-C9-C10	113.9(5)
C4-C5	1.522(6)	C6-C3-C10	115.2(4)	C3-C10-C9	109.5(4)
C5-C11	1.540(8)	S-C4-C3	126.3(3)	C3-C10-C15	111.0(4)
C5-C12	1.513(8)	S-C4-C5	123.2(3)	C9-C10-C15	107.0(5)
C6-C7	1.566(6)	C3-C4-C5	110.0(3)	C3-C10-C16	113.7(4)
C6-C13	1.560(6)	N1-C5-C4	101.4(4)	C9-C10-C16	108.4(4)
C6-C14	1.541(6)	N1-C5-C11	106.7(5)	C15-C10-C16	107.0(5)
C7-C8	1.510(9)	C4-C5-C11	114.2(5)		
C8-C9	1.513(9)	N1-C5-C12	108.9(5)		
C9-C10	1.557(6)	C4-C5-C12	115.2(6)		
C10-C15	1.533(6)	C11-C5-C12	109.7(5)		
C10-C16	1.561(6)	C3-C6-C7	108.0(5)		

Table 2. Bond lengths (Å) and angles (°) with least-squares estimated standard deviations in parentheses for non-hydrogen atoms as well as H2 and H22 for the two non-identical molecules of **11b**. For numbering of atoms (see Fig. 2)

Bond lengths (Å)			Bond angles (°)					
	Atom X	Atom (X+20)		Atom X	Atom (X+20)		Atom X	Atom (X+20
S1-O1	1.499(2)	1.431(3)	O1-S1-C4	110.5(2)	110.6(2)	C3-C6-C12	113.3(3)	108.8(3)
S1-C4	1.654(3)	1.657(3)	S1-O1-H22	151.2(3)^{a}	152.2(3)^{a}	C7-C6-C12	110.2(3)	111.3(3)
O1-H22	2.014(44)^{a,b}	1.930(41)^{a,b}	N2-N1-C5	108.3(3)	108.3(3)	C11-C6-C12	107.2(3)	106.3(3)
N1-N2	1.321(4)	1.321(4)	N1-N2-C3	114.6(3)	114.7(3)	C6-C7-C8	113.8(4)	114.0(4)
N1-C5	1.317(4)	1.295(4)	N2-C3-C4	93.4(3)	93.0(3)	C7-C8-C9	111.1(4)	110.9(4)
N2-C3	1.469(4)	1.474(4)	N2-C3-C6	106.4(3)	110.3(3)	C8-C9-C10	114.4(4)	113.8(4)
N2-H2	0.949(44)	0.897(41)	C4-C3-C6	112.3(3)	111.9(3)	C3-C10-C9	107.7(3)	108.4(3)
C3-C4	1.523(5)	1.527(4)	N2-C3-C10	107.5(3)	109.7(3)	C3-C10-C13	109.5(3)	112.7(3)
C3-C6	1.600(5)	1.539(5)	C4-C3-C10	114.8(3)	111.1(3)	C9-C10-C13	108.7(3)	111.1(3)
C3-C10	1.575(5)	1.531(5)	C6-C3-C10	115.5(3)	114.5(3)	C3-C10-C14	113.4(3)	109.3(3)
C4-C5	1.408(4)	1.421(5)	S1-C4-C3	130.3(3)	130.5(3)	C9-C10-C14	110.1(3)	108.9(3)
C6-C7	1.546(5)	1.526(5)	S1-C4-C5	123.4(3)	123.5(3)	C13-C10-C14	107.4(3)	106.5(3)
C6-C11	1.528(5)	1.540(5)	C3-C4-C5	106.4(3)	106.0(3)			
C6-C12	1.539(5)	1.534(5)	N1-C5-C4	112.3(3)	112.5(3)			
C7-C8	1.509(6)	1.507(6)	C3-C6-C7	106.9(3)	108.5(3)			
C8-C9	1.519(6)	1.515(5)	C3-C6-C11	109.9(3)	112.6(3)			
C9-C10	1.544(5)	1.531(5)	C7-C6-C11	108.9(3)	109.4(3)			
C10-C13	1.537(5)	1.518(5)						
C10-C14	1.533(5)	1.548(5)						

[a] Error estimated. [b] Symmetry-independent distance. [c] Symmetry-dependent distance.

EXPERIMENTAL

M.ps were determined with a Leitz or Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 257 or 297 spectrometer in KBr discs unless otherwise noted. UV spectra were taken on a Zeiss PMQ-3 or a Perkin–Elmer/Hitachi spectrophotometer 200. ^{1}H NMR spectra were measured on a Varian T 60 or EM 360 spectrometer, and ^{13}C NMR spectra with a Bruker WP 60 or WH 270 instrument, using TMS as an internal standard in all NMR experiments and $CDCl_3$ as solvent unless otherwise noted. Mass spectra were obtained on a Varian MS-Ib or CH 7 mass spectrometer. Preparative tlc (ptlc) was carried out with silica gel PF_{254} as purchased from Merck, Darmstadt.

The S-oxides **1a–c** were obtained by oxidation of the parent thioketens[7,25] with *m*-chloroperbenzoic acid, preferably in pentane, from which the *m*-chlorobenzoic acid deposits.

Cycloadditions of **1** *with 2-diazopropane* (**2a**). An ethereal soln of **2a**[26] was added slowly at room temp to a soln of **1a, b** or **c** (2 mmol) in ether (15 ml) until the red colour of the diazo compound persisted. After stirring for 1 hr at room temp, drying ($MgSO_4$), and removal of ether, the solid residue of **3b** was recrystallized from pentane, whereas **3a** and **c** were isolated by ptlc using EtOAc–petrol ether (v/v, 1:3).

3-*t-Butyl-3-isopropyl-5,5-dimethyl-1-pyrazoline-4-thione S-oxide* (**3a**), yield 95%; b.p. 90°/0.01 Torr; IR (film) ν 1570 (N=N), 1070 (S=O); ^{1}H NMR δ 0.68 and 1.04 (each 3 H, d, *J* = 7 Hz, iPr–CH_3), 1.09 (9 H, s, tBu), 1.79 and 1.83 (each 3 H, s, 5-Me), 2.87 (1H, m, *J* = 7 Hz, iPr–CH). (Found: C, 59.43; H, 9.16; N, 11.16; S, 12.47. Calc. for $C_{12}H_{22}N_2OS$: C, 59.46; H, 9.15; N, 11.56; S, 12.83%).

3,3-*Di-t-butyl-5,5-dimethyl-1-pyrazoline-4-thione* S-*oxide* (**3b**), yield 70%, m.p. 79°; IR ν 1560 (N=N), 1065, 1040 (S=O); UV (hexane) λ_{max} 275 nm (3.84); ^{1}H NMR δ 1.16 (18 H, s, 2 tBu), 1.88 (6 H, s, 2 Me); ^{13}C NMR δ 22.2 (5–Me), 30.1 (tBu–CH_3), 405 (Ç–CH_3 of tBu), 99.3, 113.5 (C-3, C-5), 199.0 (C-4); MS *m/e* 211 (M–45), 200, 180, 172, 157, 137. (Found: C, 61.20; H, 9.58; N, 11.16; S, 12.53. Calc. for $C_{13}H_{24}N_2OS$: C, 60.90; H, 9.43; N, 10.93; S, 12.50%).

2,2,5′,5′,6,6-*Hexamethylcyclohexane-1-spiro-3′-1′-pyrazoline-4′-thione* S-*oxide* (**3c**), yield 95%; m.p. 63–64°; IR ν 1565 (N=N) 1070 (S=O); UV (isooctane) λ_{max} 277 nm (3.8), 330 nm (2.5); ^{1}H NMR δ 0.65 (6 H, s, 2 Me), 1.05 (6 H, s, 2 Me), 1.3–2.15 (6 H, m, 3 CH_2), 1.82 (6 H, s, 2 Me); ^{13}C NMR δ 18.5 (C-4), 20.8 (5′-Me), 25.1, 28.9 (2-Me, 6-Me), 36.2 (C-3, C-5) 38.1 (C-2, C-6), 98.4, 109.6 (spiro-C and C-5′), 196.3 (C-4′). (Found: C, 62.68; H, 9.31; N, 10.37; S, 11.95. Calc. for $C_{14}H_{24}N_2OS$: C, 62.65; H, 9.01; N, 10.44; S, 11.95%).

2,2,4,4-*Tetramethylpentane-3-thione* S-*oxide* (**9**).[14] ^{13}C NMR δ 29.3, 30.4 (tBu–CH_3), 40.3, 43.3 (Ç–CH_3 of tBu), 216.1 (C=S).

Cycloaddition of **1b** *with diazomethane* (**2b**). An ethereal soln of **2b** was added dropwise at room temp to a soln of **1b** (420 mg, 2.1 mmol) in ether (5 ml). The red crystals, which separated from the soln, were purified by careful recrystallization from $CHCl_3$/petrol ether to give 2,2,6,6-*tetramethylcyclohexane-1-spiro-3′-5′-pyrazoline-4′-thione* S-*oxide* (**11b**), yield 250 mg (55%); m.p. 112–115° (dec.); IR ν 3230, 3110 (NH) 1020, 1005 (S=O); ^{1}H NMR δ 0.85 (6 H, s, 2 Me), 0.90 (6 H, s, 2 Me), 1.3–1.7 (6 H, m, 3 CH_2), 7.85 (1 H, s, 5′-H), 8.17 (1 H, broad, NH). (Found: C, 59.98; H, 8.69; N, 11.66; S, 13.32. Calc. for $C_{12}H_{20}N_2OS$: C, 59.96; H, 8.39; N, 11.65; S, 13.34%).

Irradiation of **3b** *and* **c**. A 5×10^{-3} M soln of **3a** or **b** in benzene in a pyrex vessel was irradiated at 0° for 15 min using light from a Philips HPK 125 lamp. After evaporation of the solvent the products were isolated by ptlc using EtOAc–petrol ether (v/v, 1:3).

2,2-*Di-t-butyl-3-(1-methylethylidene)thiirane S-oxide* (**12a**), yield 13% (recovery of **3b**:30%); oil; IR ν 1720 (C=C), 1050 (S=O); ^{1}H NMR δ 1.00, 1.38 (each 9 H, s, tBu), 2.08, 2.20 (each 3 H, s, Me); in C_6D_6: δ 0.80, 1.35 (each 9 H, s, tBu), 1.72, 1.99 (each 3 H, s, Me); ^{13}C NMR (Multiplicity of undecoupled spectrum given) δ 22.2, 23.7 (q + m, ^{1}J = 125 Hz, ^{3}J ~ 4 Hz, =C–<u>Me</u>), 29.7, 31.5 (q + m, ^{1}J = 125 Hz, ^{3}J ~ 5 Hz, tBu–CH_3), 39.7, 39.9 (m, Ç–CH_3 of tBu), 79.3 (m, C-2), 134.9, 137.3 (m, J ~ 7 Hz, C-3, =Ç–Me), irradiation of the Me hydrogens at δ 2.1 led to 22.2, 23.7 (s), 29.7, 31.5 (broadened q), 39.7, 39.9 (broadened s), 79.3, 134.9, 137.3 (s), irradiation of the tBu hydrogens at 1.00 gave a high intensity signal at δ 79.3 and broadened peaks at δ 134.9, 137.3; MS *m/e* 228 (M^+), 180 (M–SO). (Found: C, 67.43; H, 10.56; S, 12.83. Calc. for $C_{13}H_{24}OS$: C, 68.36; H, 10.59; S, 14.04%).

2,2,6,6-*Tetramethyl-3′-(1-methylethylidene)cyclohexane*-1-*spiro-2′-thiirane* S-*oxide* (**12b**), yield 17%, m.p. 68–70°; IR ν 1720 (C=C), 1045 (S=O); ^{1}H NMR δ 0.33, 1.08, 1.42, 1.47 (each 3 H, s, Me), 1.70 (6 H, m, 3 CH_2), 2.07, 2.28 (each 3 H, s, Me); in C_6D_6: δ 0.23, 1.22, 1.28, 1.52 (each 3 H, s, Me), 1.50 (6 H, m, 3 CH_2), 1.68, 1.93 (each 3 H, s, Me). (Found: C, 69.01; H, 10.10; S, 13.52. Calc. for $C_{14}H_{24}OS$: C, 69.95; H, 10.06; S, 13.34%).

X-Ray structural analyses. Appropriate crystals of **3c** and **11b** were obtained by recrystallization from MeOH and $CHCl_3$/petrol ether, respectively. Rotating-crystal, Weissenberg and precession photographs gave approximate lattice constants and preliminary space groups. The crystals of **11b** were twinned with the (100) net being the twin plane. Refinement of the lattice constants led to the following cell dimensions:

3c:	$a = 28.272(3)$ Å	$V = 2995.5$ Å^3
	$b = 7.986(1)$ Å	$Z = 8$
	$c = 14.917(2)$ Å	$d_{calc.} = 1.20\ g \cdot cm^{-3}$
	$\beta = 117.2(3)°$	Space group $C2/c$
11b:	$a = 12.971(2)$ Å	$V = 2513.2$ Å^3
	$b = 14.984(2)$ Å	$Z = 8$
	$c = 15.006(2)$ Å	$d_{calc.} = 1.28\ g \cdot cm^{-3}$
	$\beta = 120.5(3)°$	Space group $P2_1/c$

A **3c**-crystal of dimensions 0.25 × 0.40 × 0.35 mm and an **11b**-crystal of dimensions 0.30 × 0.25 × 0.20 mm were employed for intensity measurements on a Syntex $P2_1$ single-crystal diffractometer using MoK_α radiation monochromated with graphite. The **3c**-crystal was destroyed during data collection. The intensity data were not corrected for absorption. The measured intensities were reduced to 1650 and 3188 symmetry-independent reflexions for **3b** and **11b**, respectively.

The structures were solved by the direct-methods program MULTAN.[27] The *E* maps revealed the positions of all the heavy atoms. After the refinement of these positions, the H atoms were found from a difference Fourier synthesis.[28] For **3c**, the final refinement[28] was carried out with the limitation that the H atoms of the methyl groups were kept fixed in a regular tetrahedral arrangement. Convergence was achieved at *R* 0.073 (R_w = 0.055) and 0.074 (R_w = 0.048) for **3c** and **11b**, respectively.

Final atomic positional and thermal parameters of both structures have been deposited with the Cambridge Data Centre.

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