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Cycloadditions of Thiocarbonyl Ylides with *N*-Sulfinylamines

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ABSTRACT: *Thiobenzophenone S-methylide* **(6)** *and 2,2,4,4-tetramethyl-3-thioxocyclobutanone S-methylide* **(17)** *were allowed to react with N-sulfinylaniline* **(7)** *and N-sulfinyltosylamide* **(8)** *furnishing 1,3,4-dithiazolidine 3-oxides. However, in the interaction* **17** + **8** *the main product was the 1,2,4-oxadithiolane 2-tosylimide* **(22)***; that is, the adduct to the S=O bond. An X-ray analysis confirmed structure* **22** *and revealed an envelope conformation of the heteroring. A tentative interpretation considers a switching from the concerted addition to the N=S bond of N-sulfinylamines to a two-step pathway via a zwitterion leading to* **22**.
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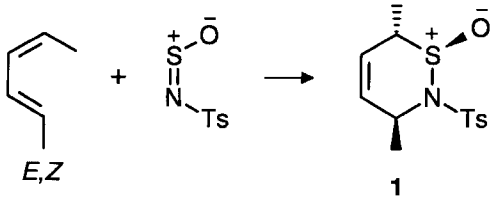
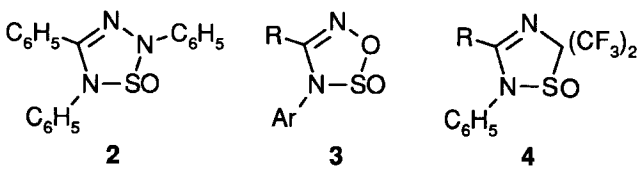
INTRODUCTION

N-Sulfinylamines are easily accessible by reaction of primary amines, carboxamides or sulfonamides with thionyl chloride [1]. The dienophilic activity of the RN=SO bond has been given much attention; several reviews concern its development for purposes of synthesis [2,3], including natural product synthesis [4].

The (4 + 2) cycloadditions of *N*-sulfinyl compounds show all the features of the "normal" Diels-Alder reaction, that is, the concerted interaction of electron-rich 1,3-dienes with electron-poor dienophiles. Whereas *N*-sulfinylalkylamines are inert, increasing dienophilic activity was observed for Ar-N=SO < RO_2C-N=SO < $ArSO_2N$=SO. Regiochemistry mirrors that of Diels-Alder reactions with C=C dienophiles. The retention of diene structure is illustrated in the formation of **1** from (*E,Z*)-2,4-hexadiene; this stereospecificity, however, finds a limit in the behavior of (*Z,Z*)-2,4-hexadiene, which can hardly assume the *s-cis* conformation required [5] and reacts in part in other ways.





1,3-Dipolar cycloadditions to the RN=SO bond have been studied only sporadically. The addition of diphenylnitrilimine with *N*-sulfinylaniline to give **2**

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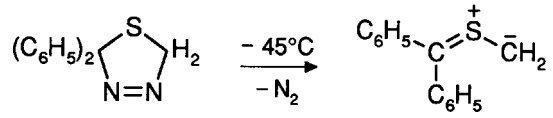
was the first example [6]. Several groups studied cycloadditions of nitrile oxides to form 1,2,3,5-oxathiadiazole *S*-oxides **3**. The thermolysis reactions of adducts of type **3** have received attention [7–9]. Nitrile ylides containing CF_3 groups can be generated as transitory intermediates and were intercepted by *N*-sulfinylaniline to furnish **4** [10].

In cycloadditions of nitrones to *N*-sulfinylbenzenesulfonamide, sulfur dioxide was eliminated with rearrangement to amidines [11–14]. Only in the case of pyridine *N*-oxide was the primary adduct isolable [12].

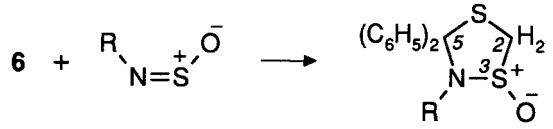
We report here on the cycloadditions of thiocarbonyl ylides to *N*-sulfinyl compounds and their mechanistic implications.

CYCLOADDITIONS AND PRODUCT STRUCTURES

The most variable pathway to thiocarbonyl ylides is nitrogen extrusion from 2,5-dihydro-1,3,4-thiadiazoles which, in turn, are formed by the cycloaddition of diazoalkanes to thiones [15].



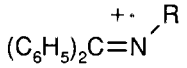
5 **6**



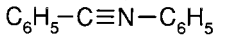
7 R = C_6H_5 **9**
8 R = Ts **10**

Thiadiazoline **5** was prepared from thiobenzophenone and diazomethane at −78°C; the 1,3-dipolar cycloreversion **5** → **6** proceeds with a half-life of 55 minutes at −45°C in tetrahydrofuran (THF) [16]. Thiobenzophenone *S*-methylide **(6)**, which is not isolable, was effectively captured in situ by 1.1 equiv of *N*-sulfinylaniline **(7)** or *N*-sulfinyltosylamide **(8)**. The ^{1}H NMR analysis with weight standard indicated 92% of **9** and 79% of **10**. The crystalline adducts were isolated in 69% and 66% yield, respectively.

Due to the adjacent sulfoxide function, the NMR spectra show the 3-H_2 as AB pattern and δ(C-2) at 55.9 **(9)** and 54.2 **(10)**. The ^{13}C parameters likewise indicate that the two phenyl groups are in different environments. The regiochemistry of **9** and **10** is clearly revealed by their mass spectra. The base peak of **9** is *m/z* 257 corresponding to **11** or an isomer, and the nitrilium ion **14** is a probable structure for *m/z* 180 (89%). Here as for the other cycloadducts, the formulae of the fragments were confirmed by the intensities of the ^{13}C and (^{34}S + $^{13}C_2$) isotope peaks.



11 R = C_6H_5 100%
12 R = Ts 17%
13 R = $C_6H_4CH_3$ 24%



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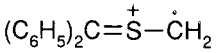
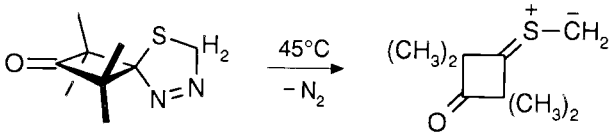


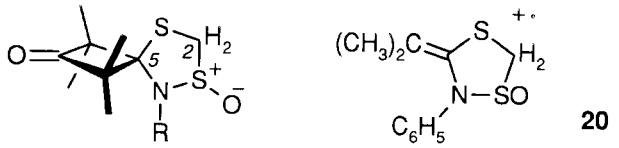
15

In the MS of **10**, the radical ion **12** is not prominent. The observed fragments of **12** are the tosyl radical cation (18%), $C_7H_7^+$ (39%), and **14** as the base peak. Interestingly, *m/z* 271 (24%) for $C_{20}H_{17}N^+$ suggests **13**, that is, the loss of SO_2 from **12**. 1,3-Cycloreversion plays a minor role: distonic radical ion **15** (*m/z* 212) was found with 16% (from **9**) and 3% (from **10**).

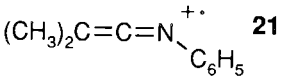
The structures of **9** and **10** indicate the CH_2 terminus to have been the nucleophilic center of the 1,3-dipole **6**. The same conclusion was drawn from the regiochemistry of the cycloadducts of **6** with methyl acrylate and acrylonitrile [17].



16 **17**



18 R = C_6H_5 **20**
19 R = Ts



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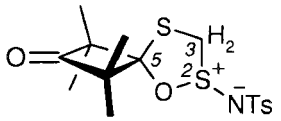
The thiadiazolines prepared from aliphatic thiones are isolable at room temperature. Dimeric dimethylketene is converted in two steps to the spirothiadiazoline **16**, which loses N_2 at 45°C with a half-life of 25 minutes (xylene) [18,19]. When **16** in THF was heated to 45°C for 6 hours in the presence of 1.1 equiv of **7**, the quantitative ^{1}H NMR analysis revealed 81% of **18** and 13% of a second, not isolated product.

The ^{1}H NMR spectrum of the main product **18** shows four different methyl signals and an AX pat-

tern for 2-H_2 (δ 3.60, 4.42), demonstrating chirality. Convincing evidence for the addition direction comes from the MS. **18** shares with the cycloadducts of **17** onto C=C bonds [20] the propensity to eliminate dimethylketene from the cyclobutanone ring. The successive loss of dimethylketene ($\rightarrow$ **20**) and $H_2C=S=O$ in parallel fragmentations disclose the connectivities in **18**. The base peak, *m/z* 145, agrees with $C_{10}H_{11}N^+$, which may be the ketene imine **21** or an isomer.

We have emphasized the evidence for the regiochemistry of **18**, because the properties of the main cycloadduct of **17** to *N*-sulfinyltosylamide **(8)**, were not in agreement with structure **19**, but rather with 1,2,4-oxadithiolane *N*-tosylimide **22**. NMR analysis of the crude product indicated 72% of **22** and 24% of the probable structure **19**. Both adducts are chiral, as demonstrated by the NMR parameters of four different methyl groups at the cyclobutane ring. The AB spectrum due to 3-H_2 of **22** appeared at δ 4.21 and 4.64, and the 2-H_2 of **19** led to an AX pattern at δ 3.63 and 4.60.



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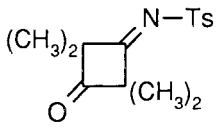
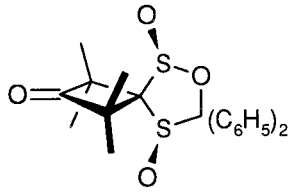


23

The δ_C due to C-3 of **22** and C-2 of **18**, 59.0 and 58.9 ppm, are nearly the same, but the spiro center of **22** (δ 111.4) is shifted to higher frequency, compared with δ(C-5) 96.5 for **18**. The radical cation $C_8H_{12}O_2^+$ suggests tetramethylcyclobutane-1,3-dione$^+$ (or an isomer); the connectivity has changed in **22**. An X-ray analysis confirmed structure **22**.

The minor product (24%) was not isolated, but converted to tetramethyl-3-tosyliminocyclobutanone (**23**, 19%) when the mother liquor of **22** was subjected to chromatography on silica gel. This is reconcilable with the hydrolysis of **19**. Equilibration of pure **22** with the minor product **19** at 130°C in $CDCl_3$ solution was found to occur. When pure **22** was heated under these conditions, a mixture of **22** and **19** in the ratio 53:47 was observed. The mechanism of the isomerization will be discussed below.



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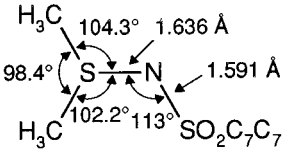

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No isomerization of **22** was observed in $CDCl_3$ at 50°C; thus, the product ratio of **22/19** from cycloaddition in THF ($\sim$ 79:21) represents kinetic control.

X-RAY STRUCTURE OF 1,2,4-OXADITHIOLANE 2-TOSYLIMIDE **22**

The heteroring of **22** has an envelope conformation. Atoms S4-C5-O1-S2 form a quasi-plane, and C3 is the "flap" with an out-of-plane distance of 0.76 Å (Fig. 1, Table 1). The torsion angle at C5-O1 in the ring amounts to only 6.5°, and those at S2-C3 ($-38.3°$) and C3-S4 (40.8°) are the largest. The folding angle of the ring is 44°. The ring conformation is related to that of the 1,2,4-oxadithiolane 2,4-dioxide **24**, wherein likewise C3 appeared as the "flap" of an envelope [21].

The bond system of S2 is strongly pyramidalized, as illustrated by an angle sum of 304.4°; if the bond system were tetrahedral, the angle sum would be 328.5°. The bond length N1-S2 of the sulfimide group is 1.567 Å which is shorter than that of N1-S3 of the sulfonamide group, 1.618 Å. It is also shorter than the S-N bond length of *S,S*-dimethyl-*N*-tosylsulfimide **(25)**, which is 1.636 Å [22]; in contrast to **25**, cycloadduct **22** harbors a cyclic sulfinimidate group. The angle sum of 304.9° at the S of **25** reveals a similar pyramidalization as observed in **22**.

DISCUSSION OF CYCLOADDITION MECHANISMS

Some mechanistic features that the (4 + 2) cycloadditions of *N*-sulfinylamines as dienophiles share with the concerted "normal" Diels-Alder reaction were mentioned in the introduction. We are not aware of any (4 + 2)-cycloaddition of a 1,3-diene to the S=O bond of a sulfinylamine. Among the limited number of 1,3-dipolar cycloadditions studied so far, the formation of the 1,2,4-oxadithiolane **22** appears to be unique. How is the kinetically controlled addition to the S=O bond, **17** + **8** $\rightarrow$ **22**, to be understood?

Many mechanistic criteria point to the concerted nature of 1,3-dipolar cycloadditions [23]. The PMO treatment of concerted cycloadditions [24] clarifies why, for example, electron-rich 1,3-dipoles react fast with electron-poor dipolarophiles. When the difference between the π-MO energies of the reactants becomes extreme, the concerted mechanism can slip to the two-step pathway, via a zwitterion. Such a switch requires assistance by steric hindrance.

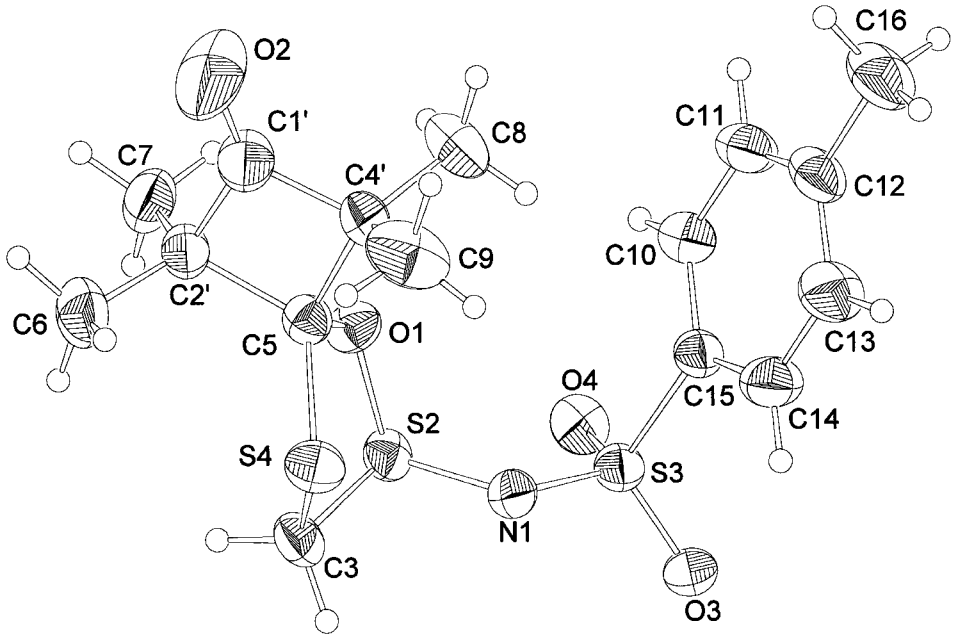
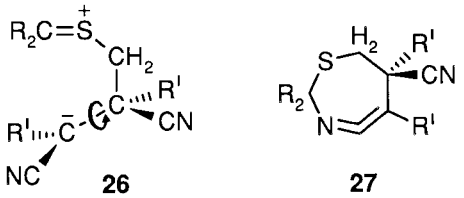
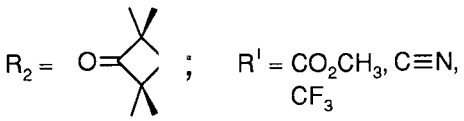
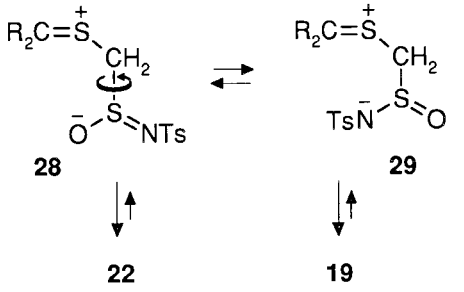


FIGURE 1 X-ray structure of 2′,2′,4′,4′-tetramethylspiro[(1,2,4)-oxadithiolane-5,3′-cyclobutane]-1′-one 2-tosylimide (**22**).



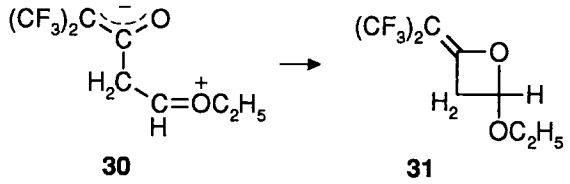




Thiocarbonyl ylides may be regarded as allyl anions in which the center carbon is replaced by a sulfonium function. Since sulfur has the same electronegativity as carbon, high π-MO energies are expected for this class of 1,3-dipoles. The π-MO energies of ethylenic dipolarophiles are severely diminished by introducing four acceptor substituents.

One of our model systems was the reaction of thiocarbonyl ylide **17**—one terminus sterically screened—with strongly electron-deficient ethylenes. The intermediacy of zwitterion **26** was recognized by loss of stereospecificity [25] and the reversible formation of 7-membered cyclic ketene imines **27** [26].

N-Sulfinyltosylamide (**8**) harbors a π system almost destitute of electrons. A plausible intermediate for the reaction **17** + **8** exists as the two rotamers **28** and **29**, which can close the 5-membered ring via bonding to oxygen (→ **22**) or to nitrogen (→ **19**). Whereas π-MO energies dominate the concerted process, control by charge density prevails in the collapse of the zwitterions and should favor the formation of **22**.



Ketene cycloadditions offer numerous precedents for switching from π-MO energy control to charge density control. As an example, concerted additions with vinyl ethers afford 3-alkoxycyclobutanones. Bis(trifluoromethyl)ketene, however, furnishes **31** [27], probably via the zwitterion **30** with ring closure at enolate oxygen.

TABLE 1 Selected Bond Lengths and Angles of **22** (In parentheses standard deviations on the last decimal)

Bond Lengths (Å)					
O1-S2	1.617(2)	S4-C5	1.805(3)	N1-S3	1.618(2)
S2-C3	1.802(3)	C5-O1	1.446(3)	C5-C2′	1.581(4)
C3-S4	1.780(3)	S2-N1	1.567(2)	C1′-C2′	1.503(4)
Bond Angles (°)					
O1-S2-C3	94.6(1)	S4-C5-O1	107.8(2)	C3-S2-N1	99.6(2)
S2-C3-S4	105.1(2)	C5-O1-S2	120.6(2)	S2-N1-S3	116.3(2)
C3-S4-C5	93.4(2)	O1-S2-N1	110.2(1)	N1-S3-C15	103.7(2)
Dihedral Angles (°)					
O1-S2–C3-S4	−38.3(2)	S4-C5–O1-S2	6.5(3)		
S2-C3–S4-C5	40.8(2)	C5-O1–S2-C3	20.0(2)		
C3-S4–C5-O1	−29.5(2)	C3-S2–N1-S3	163.3(2)		

Thus, the cycloadditions of thiobenzophenone *S*-methylide **(6)** to *N*-sulfinylamines **7** and **8** appear to follow the concerted pathway. In contrast, the exceptional formation of **22** suggests the intermediacy of zwitterion **28/29**. We thus understand that the change in mechanism was forced by the electron paucity of the π-bond of **8**, coupled with strong steric hindrance at one terminus of the electron-rich 1,3-dipole **17**.

EXPERIMENTAL

General

IR spectra were recorded on a Perkin-Elmer FT model 1000. All NMR spectra were taken in acid-free $CDCl_3$, if not otherwise stated; a Bruker WP80 CW instrument was used for 80 MHz ^1H NMR spectra and Bruker WP80 DS for 20 MHz ^{13}C NMR spectra (H-decoupled and off-resonance). Routinely, the crude products were ^1H NMR-analyzed by comparison of a suitable signal with that of *sym*-tetrachloroethane as weight standard (machine integrals). The MS are EI spectra with 70 eV recorded on a Finnigan MAT 90 instrument; intensities of isotope peaks are given in the mode, for example, ^{13}C% calcd/% found. PLC is preparative thick-layer (1 or 2 mm) chromatography on silica gel Merck $PF_{254,366}$. Melting points are uncorrected.

4,5,5-Triphenyl-1,3,4-dithiazolidine 3-oxide (**9**)

The solution of 396 mg (2.00 mmol) of thiobenzophenone in 2 mL of CH_2Cl_2 was cooled to −78°C. Ethereal diazomethane was added until the deep-blue color disappeared. After removing some of the ether at −70°C/4 mm, 306 mg (2.20 mmol) of *N*-sulfinylaniline (**7**, distilled at 84°C/10 mm and stored under argon) [28] was introduced, and the temperature was raised to −40°C; 2 mmol of N_2 was set free within 4 hours. The solution was kept at room temperature for 12 hours, and the solvent was completely removed in vacuo. The ^1H NMR analysis in $CDCl_3$ with weight standard indicated 92% of **9** (AB at δ 3.96). After evaporation, 485 mg (69%) of **9** crystallized from ethanol, m.p. 133–136°C (dec.); the recrystallized specimen showed m.p. 136–137°C (dec.). IR (KBr): $\tilde{\nu}$ 693 cm^{-1}, 732 st, 754 m (C_6H_5 out-of-plane deform.); 1004, 1059 m; 1109 st (S=O), 1235 st; 1444, 1448 m, 1489 st, 1595 m (C_6H_5 ring vibr.). ^1H NMR: δ 3.92, 4.00 (AB, close to A_2, ^2J = 11.8 Hz, 2-H_2), 6.75–7.75 (m, 3 C_6H_5); (C_6D_6): 3.19, 3.28 (AB, ^2J = 11.5 Hz, 2-H_2). ^{13}C NMR: δ 55.9 (t, C-2), 91.8 (s, C-5), 124.9, 127.6, 127.9, 128.0, 128.3, 129.0, 130.7 (7 d instead of expected 9 signals, CH of 3 different C_6H_5), 137.5, 139.7, 140.5 (3 s, 3 arom. C_q). MS (75°C); *m/z* (%): 351 (0.05) [M^+], 305 (13) [$C_{19}H_{15}NOS^+$, M^+-CH_2S; ^{13}C 2.7/3.0, (^{34}S + $^{13}C_2$) 0.86/0.78], 257 (100) [$C_{19}H_{15}N^+$, **11**; ^{13}C 21/19], 256 (37), 212 (16) [$C_{14}H_{12}S^+$, **15**; (^{34}S + $^{13}C_2$) 0.88/0.96], 211 (14), 180 (89) [$C_{13}H_{10}N^+$, **14**; ^{13}C 12.9/12.2; $^{13}C_2$ 0.9/1.1, no S], 165 (42) [$C_{13}H_9^+$, 9-fluorenyl$^+$, ^{13}C 6.0/6.2], 77 (39) [$C_6H_5^+$], 51 (10) [$C_4H_3^+$], 45 (5) [$HC{\equiv}S^+$]. Anal. calcd for $C_{20}H_{17}NOS_2$ (351.5): C, 68.34; H, 4.88; N, 3.99; S, 18.25; found: C, 68.43; H, 4.89; N, 3.76; S, 18.39.

5,5-Diphenyl-4-tosyl-1,3,4-dithiazolidine 3-oxide (**10**)

N-Sulfinyltosylamide **(8)** [1b] was distilled at 152°C/10^{-3} mm as a pale-yellow oil that solidifies (m.p. 50–53°C) when stored under argon. **8** (477 mg, 2.20 mmol) was reacted with 2.00 mmol of **5** by the procedure described previously. The quantitative ^1H NMR analysis showed 79% of **10** by the integral of the 2-H_2 at δ 3.79 ($CDCl_3$). Triturating the residue after evaporation with cold ethanol furnished 570 mg (66%) of **10** as colorless crystals, m.p. 192–194°C (dec.). The analytical specimen, m.p. 194–195°C (dec.), was obtained by PLC (CH_2Cl_2/acetone 98:2).

IR (KBr): $\tilde{\nu}$ 546 cm^{-1}, 574, 667 st; 700 st, 737 m, 800, 815 st (arom. CH out-of-plane deform.); 959, 988, 1089 st; 1125, 1136 st (S=O); 1164, 1351 vst (SO_2); 1446, 1449 st, 1495, 1599 m (arom. ring vibr.). ^{1}H NMR: δ 2.30 (s, CH_3), 3.79 (br s, 2-H_2), 6.70–7.60 (m, 14 arom. H); the AB pattern of 2-H_2 is clear in C_6D_6:2.86, 2.99 with ^2J = 12.8 Hz. ^{13}C NMR: δ 21.5 (q, CH_3), 54.2 (t, C-2), 90.4 (s, C-5), 127.15, 127.27, 127.43, 2 × 128.9, 131.8 (6 d, 12 *o*-CH, *m*-CH), 128.9, 128.2 (2 d, 2 *p*-CH), 133.2, 137.1, 139.6, 143.3 (4 s, arom. C_q); the phenyl groups are diastereotopic. MS (95°C); *m/z* (%): 429 (0.2) [M^+], 335 (17) [$C_{20}H_{17}NO_2S^+$, **12**; ^{13}C 3.9/4.6, (^{34}S + $^{13}C_2$) 1.2/1.4], 271 (24) [$C_{20}H_{17}N^+$, 335 − SO_2, **13**; ^{13}C 5.3/4.9; $^{13}C_2$ 0.57/0.43, no S], 212 (3) [**15**], 180 (100) [$C_{13}H_{10}N^+$, **14**; ^{13}C 15/17], 179 (9), 155 (18) [$C_7H_7O_2S^+$, Tos^+; ^{13}C 1.4/1.8, (^{34}S + $^{13}C_2$) 0.83/0.88], 91 (39) [$C_7H_7^+$, *p*-tolyl], 85 (10), 83 (16), 77 (35) [$C_6H_5^+$], 45 (7) [$HC{\equiv}S^+$?]. Anal. calcd for $C_{21}H_{19}NO_3S_3$ (429.6): C, 58.71; H, 4.46; N, 3.26; S, 22.39; found: C, 58.77; H, 4.40; N, 3.15; S, 22.41.

2′,2′,4′,4′-Tetramethyl-4-phenylspiro[(1,3,4)-dithiazolidine-5,3′-cyclobutane]-1′-one 3-oxide (**18**)

Freshly recrystallized thiadiazoline **16** [19] (396 mg, 2.00 mmol) in 2 mL of THF was stirred with 306 mg (2.20 mmol) of **7** at 45°C; the evolution of 2.0 mmol of N_2 in 6 hours was checked by nitrometer. The solvent was evaporated in vacuo. The NMR analysis showed 81% of **18** (d at δ 3.60, branch of AB). A second AB spectrum at δ 4.42 and 4.60 with J = 12.0 Hz was attributed to 13% of an unknown cycloadduct. The methanolic solution deposited **18** as colorless crystals (305 mg, 49%), m.p. 129–131°C (dec., gas evolution). IR (KBr): $\tilde{\nu}$ 701 cm^{-1}, 778. 798 m; 1069, 1081 m, 1125 vst (S=O); 1458 m, 1488 st, 1592 w (C_6H_5 ring vibr.), 1782 st (C=O). ^{1}H NMR: δ 0.82, 1.35, 1.47, 1.49 (4 s, 4 CH_3), 3.60, 4.42 (AB, ^2J = 11.2 Hz, 2-H_2), 7.27–7.55 (m, C_6H_5). ^{13}C NMR: δ 19.7, 23.4, 24.0, 25.2 (4 q, 4 CH_3), 58.9 (t, C-2), 64.5, 71.2 (2 s, C-2′, C-4′), 96.5 (s, C-5), 127.5, 128.1, 129.6 (3 d, 5 arom. CH, 2:1:2), 141.1 (s, arom. C_q), 217.7 (s, C=O). MS (55°C); *m/z* (%): 247 (40), [$C_{14}H_{17}NOS^+$, M^+-$H_2C{=}S{=}O$; ^{13}C 6.4/6.3, (^{34}S + $^{13}C_2$) 2.2/2.2], 239 (19) [$C_{11}H_{13}NOS_2^+$, M^+-dimethylketene, **20**; ^{13}C 2.3/2.6, ($^{34}S_2$ + $^{13}C_2$) 1.8/1.8], 215 (10) [$C_{14}H_{17}NO^+$, tetramethyl-3-phenyliminocyclobutanone$^+$; ^{13}C 1.5/1.6, $^{13}C_2$ 0.11/0.13], 177 (17) [$C_{10}H_{11}S^+$, 247-dimethylketene; ^{13}C 1.9/2.2, (^{34}S + $^{13}C_2$), 0.83/0.83], 145 (100) [$C_{10}H_{11}N^+$, **21**; ^{13}C 11/11, $^{13}C_2$ 0.56/0.54], 144 (25), 130 (15) [145-CH_3], 104 (9). 77 (20) [C_6H_5]. Anal. calcd for $C_{15}H_{19}NO_2S_2$ (309.4): C 58.22, H 6.19, N 4.53, S 20.73; found: C 58.41, H 6.29, N 4.24, S 20.71.

2′,2′,4′,4′-Tetramethylspiro[(1,2,4)-oxadithiolane-5,3′-cyclobutane]-1′-one 2-tosylimide (**22**)

For the reaction of 2.00 mmol of **16** with 396 mg (2.20 mmol) of **8**, the protocol of the preceding experiment was followed. In the analysis with weight standard, comparison of the ^{1}H NMR integrals indicated 72% of **22** (s δ 0.90 for CH_3) and 24% of **19** (s δ 1.74). After evaporation the residue was triturated with pentane/diethyl ether and gave 598 mg of colorless product, m.p. 90–100°C. Recrystallization from ethanol furnished 328 mg (42%) of **22** as coarse crystals, m.p. 124–125°C. PLC (CH_2Cl_2) of the mother liquor provided 110 mg (19%) of **23** and another 130 mg of **22** (in toto 59%).

Properties of **22**. IR (KBr): $\tilde{\nu}$ 667 cm^{-1} st, 817, 893 st; 1001, 1035 st (C-O); 1150 vst, 1302, 1312 st (SO_2); 1465 m, 1496 w, 1598 w (arom. ring vibr.), 1782 vst (C=O). ^{1}H NMR: δ 0.90, 1.22 (2 s, 2 CH_3), 1.27 (s, 2 CH_3), 2.37 (s, CH_3 of tolyl), 4.21, 4.64 (AB, J = 12.0 Hz, 3-H_2), 7.12–7.33, 7.66–7.85 (2 m, C_6H_4). ^{13}C NMR: δ 19.7, 20.6, 21.4, 21.5, 22.6 (5 q, 5 CH_3), 59.0 (t, C-3), 66.2, 66.4 (2 s, C-2′, C-4′), 111.4 (s, C-5), 126.6, 129.4 (2 d, 4 arom. CH), 139.6, 143.0 (2 s, 2 arom. C_q), 215.5 (s, C=O). − MS (95°C); *m/z* (%): 317 (0.7) [M^+-dimethylketene], 215 (3.1) [$C_8H_9NO_2S_2^+$, Ts-N=S=CH_2^+], 171 (35) [$C_7H_9NO_2S^+$, $TsNH_2^+$], 155 (67) [tosyl$^+$; ^{13}C 5.3/6.8], 140 (11) [$C_8H_{12}O_2^+$, tetramethylcyclobutanedione$^+$; ^{13}C 1.0/1.3], 139 (11), 107 (10), 91 (100) [$C_7H_7^+$, *p*-tolyl], 85 (14) [$C_4H_5S^+$, dimethylthioketene-H], 83 (22) [$C_6H_{11}^+$], 76 (18), 70 (90) [$C_4H_6O^+$, dimethylketene; ^{13}C 4.0/4.0], 69 (13) [70-H], 65 (17), 45 (10), 42 (40) [$C_3H_6^+$], 41 (23) [allyl$^+$]. Anal. calcd for $C_{16}H_{21}NO_4S_3$ (387.5): C, 49.59; H, 5.46; N, 3.61; S, 24.82; found: C, 49.75; H, 5.43; N, 3.63; S, 24.82.

2,2,4,4-Tetramethyl-3-tosyliminocyclobutanone (**23**)

m.p. 136–138°C (ethanol), was isolated after the PLC, without appearing in the crude reaction product above. IR (KBr): $\tilde{\nu}$ 555 cm^{-1}, 609, 655, 689, 732 st; 812, 840 st, 1046, 1090 st; 1177, 1310, 1319 st (-SO_2-N); 1459 st, 1495 w, 1597 m (arom. ring vibr.), 1664 vst (C=N), 1810 st (C=O). ^{1}H NMR: δ 1.35, 1.60 (2 s, 4 CH_3), 2.42 (s, arom. CH_3), 7.16–7.40, 7.66–7.93 (AA′BB′, C_6H_4). MS (50°C); *m/z* (%): 293 (3.8) [M^+, ^{13}C 0.64/0.75], 225 (4.2) [M^+-dimethylketene + H], 155 (100) [tos$^+$, ^{13}C 7.8/8.9; (^{34}S + $^{13}C_2$) 4.7/5.1], 138 (25) [$C_8H_{12}NO^+$], 110 (9). 91 (94) [$C_7H_7^+$], 69 (15) [$C_4H_5O^+$], 65 (11) [$C_5H_5^+$], 41 (14) [allyl$^+$]. Anal. calcd for $C_{15}H_{19}NO_3S$ (293.4): C, 61.41; H, 6.53; N, 4.77; S, 10.93; found: C, 61.30; H, 6.63; N, 4.58; S, 10.92.

Equilibration of **22** *and* **19**

On heating pure **22** in $CDCl_3$ in a closed NMR tube at 130°C, new signals that corresponded to the side product obtained above from **16** and **8** appeared. After 1 hour the ratio of 53:47 for **22/19** was attained, which remained unchanged after 12 hours at 130°C; no further signals were observed. The isolation of **19** did not succeed. ^{1}H NMR of **19** (deduction of the signals of **22**): δ 1.38, 1.46, 1.53, 1.74, 2.45 (5 s, 5 CH_3), 3.63, 4.60 (AX, ^2J = 11.2 Hz, 2-H_2). The assignment as 2′,2′,4′,4′-tetramethyl-4-tosylspiro[(1,3,4)-dithiazolidine-5,3′-cyclobutane]-1′-one 3-oxide **(19)** is tentative, although supported by hydrolysis to **23**.

The reaction of **16** with **8** was repeated without solvent at 45°C, that is, in molten **8**; the ^{1}H NMR spectrum indicated **22/19** = 3:1 besides unidentified products. A further cycloaddition experiment was run in acetonitrile at 50°C; it afforded **22** and some side products, but no **19**.

X-Ray Structure Analysis of **22** *[29]*

$C_{16}H_{21}NO_4S_3$, monoclinic, space group C2/c No. 15. Unit cell dimensions: a = 2418.8(6), b = 1083.4(3), c = 1486.2(3) pm, α = 90.00(2)°, β = 92.33(2)°, γ = 90.00(2)°, volume 3.8916 nm^3, Z = 8, D_C = 1.323 g/cm^3; $F(000)$ = 1632, T = 274(1) K, μ(Mo K_α) = 3.83 cm^{-1}. Data collection: CAD4 diffractometer, colorless crystal (.37 × .40 × .20 mm), mounted in a glass capillary, cell constants from 25 centered reflexions. Mo K_α radiation, λ = 71.073 pm, graphite monochromator, ω − 2 Θ scan, scan width (0.80 + 0.35 tan Θ)°, maximum measuring time 75 seconds, intensity of three standard reflexions checked every hour 2 Θ range 4–46° for all $\pm hl + kl + l$ reflexions, 3001 reflexions measured, 2547 unique, and 2207 with $I > 2\,\sigma\,(I)$. Structure solution and refinement: direct methods of the SHELXTL program package [30], nonhydrogen atoms refined anisotropically, hydrogens isotropically with $U_i = 1.2 \times U_{eq}$ of the adjacent carbon atoms, full matrix refinement. Final $R1$ = 0.037 and w$R2$ = 0.101 for 2207 reflexions with I > 2σ(I) and 222 refined variables. The final difference map was featureless; O2 is disordered. The thermal ellipsoids of the ZORTEP plot [31] in Fig. 1 represent 30% probability.

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