Trapping of a Thiocarbonyl Ylide with Imidazolethiones, Pyrimidinethione, and Thioamides

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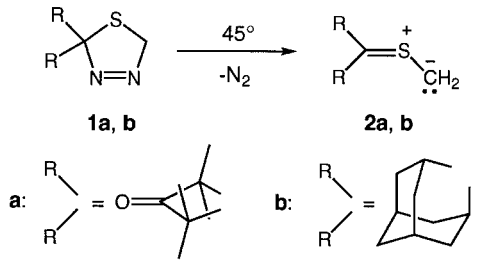
The reactions of 1,1,3,3-tetramethyl-8-thia-5,6-diazaspirol[3.4]oct-5-en-2-one (**1a**) with imidazole-2-thiones **3** and pyrimidine-2(1*H*)-thione (**6**) in $CHCl_3$ at 40–50° yield 2,2,4,4-tetramethylcyclobutanone dithioacetals of type **4** and **7**, respectively, by interception of the intermediate thiocarbonyl ylide **2a** (*Scheme 2*). Thiirane **5** is formed as a minor product by 1,3-dipolar electrocyclization of **2a**. When thioacetamide (**8a**) and thiobenzamide (**8b**) are used as trapping reagents, the primary adduct **10** undergoes a spontaneous cyclization by intramolecular nucleophilic addition of the imino group at the carbonyl group to yield bicyclic products of type **9**. The structure of **9a** has been established by X-ray crystallography.

Introduction. – In a series of recent contributions, we have used the thermal decomposition of 2,5-dihydro-1,3,4-thiadiazoles of type **1** to generate reactive thiocarbonyl ylides[2]) **2** (*Scheme 1*). These 1,3-dipolar species with a central S-atom were shown to form [3+2] cycloadducts with various dipolarophiles in high yields [2–5], to intercept RXH compounds with X = N,O,S (azoles, alcohols, phenol, thiophenol) [6–8], or to undergo 1,3- or 1,5-dipolar electrocyclizations [9][10].

Scheme 1



A frequently used precursor of **2a** is the spirocyclic 1,3,4-thiadiazole derivative **1a**, a fairly stable compound obtained from 2,2,4,4-tetramethyl-3-thioxocyclobutanone and CH_2N_2. In THF solution, **1a** extrudes N_2 at 45° with $\tau_{1/2} = 35$ min forming **2a** as a reactive intermediate [11]. Thioketones, thioesters, and 1,3-thiazole-5(4*H*)-thiones were shown to react highly regioselectively with **2a** to give 1,3-dithiolanes *via* 1,3-

[1]) Part of the planned Ph.D. thesis of *T.G.*, University of Łódź.

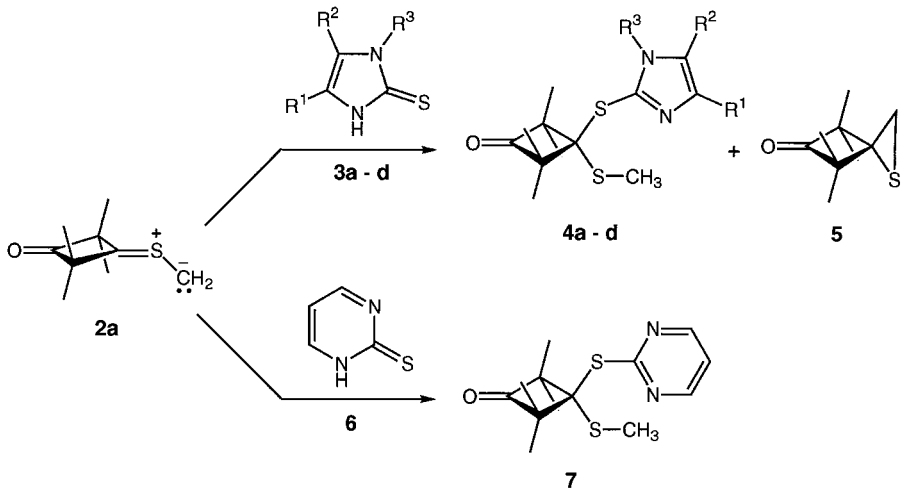
[2]) The convenient name 'thiocarbonyl ylide' is used for thiocarbonyl methanides (*cf.* [1]).

dipolar cycloadditions [2] [11]. Generally, these thiocarbonyl compounds reacted very well, not only with thiocarbonyl ylides, but also with other 1,3-dipoles. Thioketones showed remarkably high reactivity and, therefore, were named 'superdipolarophiles' [12]. On the other hand, thioamides are considered as very poor dipolaro- and dienophiles. Only recently have the first reports appeared on the use of some thioamides substituted with electron-withdrawing groups in *Lewis*-acid-catalyzed hetero *Diels-Alder* reactions [13].

In the present paper, we describe for the first time reactions of thiocarbonyl ylide **2a** with selected compounds containing a $-C(S)NH-$ group, leading to 1:1 adducts in good-to-excellent yields.

Results and discussion. – As the first group of compounds to be tested in the reaction with **2a**, we selected imidazole-2(3*H*)-thiones **3**, which are easily accessible by the method already reported [14]. Solutions of **1a** and **3** in $CHCl_3$ were heated to 40–50° until the evolution of N_2 ceased. In the crude mixture, 1:1 adducts of type **4** along with small amounts of thiirane **5** were detected by ^{1}H-NMR (*Scheme 2*). In the reaction with **3a**, for example, the ratio of **4a**/**5** was 86:14. For all adducts **4**, the presence of a MeS signal at 2.14–2.06 ppm was characteristic. These products were isolated as colorless crystalline materials in good yields.[3]) An analogous procedure with pyrimidine-2(1*H*)-thione (**6**) yielded the interception product **7**, which was isolated in excellent yield; in this case, no **5** was detected in the crude mixture.

Scheme 2

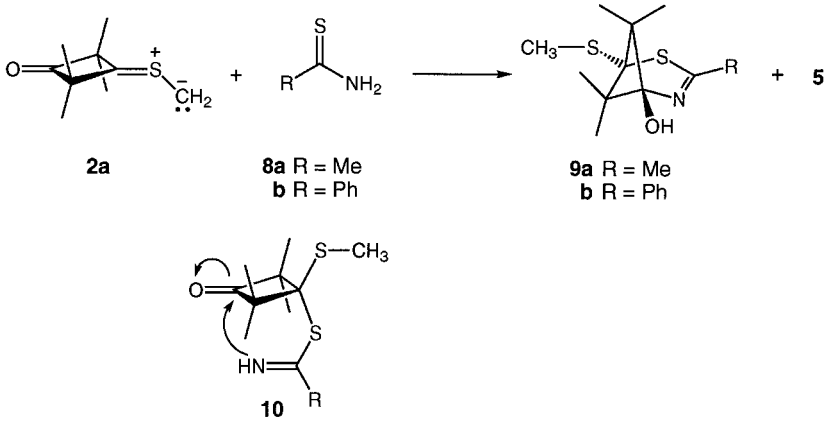


[3]) In an analogous reaction of **3a** with the adamantane derivative **1b** at 45°, no interception product was formed (^{1}H-NMR). Only decomposition products of **1b**, described earlier [15], were detected.

Both, imidazolethiones **3** and pyrimidinethione **6** showed the same reaction pattern as thiols, described some years ago [7], *i.e.*, after protonation of **2a**, the anion of **3** or **6** adds to the intermediate sulfonium ion. This is an indication that **3** and **6**, which, in solution exist in a tautomeric equilibrium of the thione and thiol forms, react with **2a** as mercapto-substituted azaaromatic compounds.

Prompted by the successful interceptions of **2a** by **3** and **6**, we also tested *N*-unsubstituted thiocarboxamides as reaction partners. Thermal decomposition of **1a** in the presence of thioacetamide (**8a**) in $CHCl_3$ was completed after 3 h. The solvent was removed, and the viscous oily residue was identified as a mixture of **5** and a 1:1 adduct (^{1}H-NMR). The latter showed four *singlets* for Me groups at 2.26, 2.07, 1.54, and 1.07 ppm in the ratio of 1:1:2:2. After removing **5**, the crystalline 1:1 adduct was obtained in 64% yield (*Scheme 3*).

Scheme 3



Unexpectedly, this product showed no C=O absorption in the IR spectrum (KBr) but a very broad band at 3280 cm^{-1} for an OH group. The ^{13}C-NMR spectrum confirmed the absence of a C=O group[4]); instead, an absorption for an sp^2-C-atom was found at 165.7 ppm. Two quaternary C-atoms absorbed at 91.7 and 68.5 ppm, in a region characteristic for acetal- and dithioacetal-type structures. Based on the IR and ^{13}C-NMR data, we concluded that the isolated material did not correspond to the expected structure of the primary interception product **10**, and subsequently the structure **9a** was established by X-ray crystallography (*Fig.*).

The structure of **9a** consists of a 2-thia-4-azabicyclo[3.1.1]hept-2-ene skeleton, and it is isomeric with the primary adduct **10a** (*Scheme 3*). This bicyclic product results from an intramolecular cyclization of **10a** leading to a 'hemiaminoacetal' structure (ring-chain tautomerism). This bicyclic structure, established for the crystalline state, is preserved in $CDCl_3$ solution, and no 'open-chain' structure **10a** could be detected by ^{1}H-NMR spectroscopy at room temperature. To the best of our knowledge, this is the first example of a nucleophilic addition onto the C=O group of a tetramethylcyclobutanone derivative without cleavage of the four-membered ring.

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[4]) The C=O group of 2,2,4,4-tetramethylcyclobutanones appears typically at *ca.* 220 ppm.

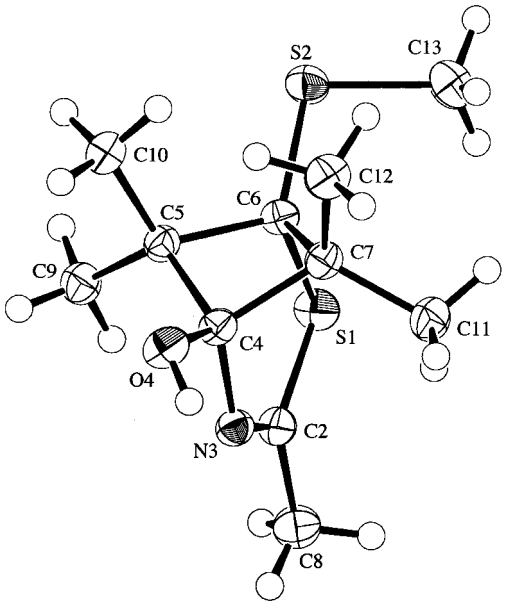

Fig. *ORTEP Plot* [16] *of the molecular structure of* **9a** (arbitrary numbering of the atoms; atomic displacement ellipsoids with 50% probability)

The analogous reaction of thiobenzamide (**8b**) with **2a** afforded the corresponding bicyclic adduct **9b** which was identified by comparison of the spectral data with those of **9a**.

In summary, we described a new type of interception of thiocarbonyl ylide **2a** with compounds which can exist, potentially, in solution as an equilibrium of a 'thioamide' and a 'mercapto imine' (iminothiol) structure (*cf.* [17]). These thiocarbonyl groups are not able to enter into cycloaddition reactions with **2a**, but trapping of **2a** by protonation to give a sulfonium ion, followed by a nucleophilic addition of the iminothiolate, is possible. The latter additions are relatively slow as the formations of **4**, **7**, and **10**/**9** were accompanied by 1,3-dipolar electrocyclization of **2a** to give thiirane **5**. According to earlier observations, adamantanethione *S*-methanide (**2b**) differs in reactivity compared with **2a** and easily undergoes intramolecular conversions [17]. This is probably the reason that it cannot be intercepted by less reactive compounds with a thioamide structure.

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Experimental Part

1. *General.* See [18]. M.p.: in capillary, *Büchi-SMP 20* apparatus, uncorrected. IR Spectra: *Perkin-Elmer 781* spectrometer; in KBr; in cm^{-1}. NMR Spectra: *Bruker B-ACS-60* spectrometer (300 MHz (^1H) and 76.5 MHz (^{13}C)); $CDCl_3$ soln.; TMS as an internal standard ($\delta(TMS) = 0$). EI-MS: *Varian MAT-112S* spectrometer; at 70 eV; CI-MS with NH_3. Elemental analyses were performed in the microanalytical laboratories of the Institute of Organic Chemistry of the University of Zürich and the Polish Academy of Sciences in Łódź.

2. *Starting materials. Thioacetamide* (**8a**), *thiobenzamide* (**8b**), and *pyrimidine-2-thione* (**6**) were commercially available (*Aldrich*) and used without further purification. Imidazole-2(3*H*)-thiones **3a**–**d** were prepared from the corresponding imidazole 3-oxides and 2,2,4,4-tetramethyl-3-thioxocyclobutanone following the protocol described in [14]. 2,5-Dihydro-1,3,4-thiadiazol **1a** was obtained in a known manner by treating the red soln. of 2,2,4,4-tetramethyl-3-thioxocyclobutanone in Et_2O with CH_2N_2 at 0° until the color disappeared. M.p. 41–42° (pentane, dry ice; [11]: m.p. 40–42°).

3. *Reactions of 2,5-Dihydro-1,3,4-thiadiazole* **1a** *with Thioamides* **8a**,**b**. *General Procedure.* Freshly recrystallized *1,1,3,3-tetramethyl-8-thia-5,6-diazaspiro[3.4]oct-5-en-2-one* (**1a**; 397 mg, 2 mmol) and 2 mmol of the corresponding thioamide were dissolved in dry $CHCl_3$ (6 ml), and the clear soln. was kept in an oil bath at 45° and stirred until the N_2 evolution ceased (*ca.* 5 h). Volumetrical control of the evolved gas showed in both reactions *ca.* 50 ml of N_2, corresponding fairly well to the expected amount. After evaporation of the solvent, the thick, colorless oils were washed with $CHCl_3$ to remove *4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexan-2-one* (**5**; identified by TLC and ^{1}H-NMR in the crude mixture), and the crude crystalline products were recrystallized from MeOH to yield anal. pure samples. Reported yields refer to crude products.

3,6,6,7,7-Pentamethyl-1-(methylthio)-2-thia-4-azabicyclo[3.1.1]hept-3-en-5-ol (**9a**): Yield: 314 mg (64%). Colorless crystals. M.p. 125–127° (MeOH). IR: 3280*vs* (OH), 1600*s* (C=N), 1420*s*, 1390*s*, 1350*s*, 1200*s*, 1170*s*, 1140*s*, 970*s*, 930*s*, 705*s*. ^{1}H-NMR: 5.85 (br. *s*, OH); 2.26 (*s*, Me); 2.07 (*s*, MeS); 1.54, 1.07 (2*s*, 4 Me). ^{13}C-NMR: 165.7 (*s*, C(3)); 91.7 (*s*, C(5)); 68.5 (*s*, C(1)); 45.8 (*s*, C(6), C(7)); 23.3 (*q*, Me); 24.0, 20.1 (2*q*, 4 Me); 11.6 (*q*, MeS). CI-MS: 246 (100, $[M+1]^+$), 171 (9), 76 (100), 75 (6). Anal. calc. for $C_{11}H_{19}NOS_2$ (245.41): C 53.84, H 7.80, N 5.71, S 26.13; found: C 53.81, H 7.85, N 5.85, S 25.95.

6,6,7,7-Tetramethyl-3-phenyl-1-(methylthio)-2-thia-4-azabicyclo[3.1.1]hept-3-en-5-ol (**9b**): Yield: 424 mg (69%). Colorless crystals. M.p. 129–130° (MeOH). IR: 3250*s* (OH), 1600*m* (C=N), 1490*m*, 1460*s*, 1360*m*, 1270*s*, 1195*s*, 1150*s*, 1050*m*, 975*m*, 950*s*, 920*m*. ^{1}H-NMR: 7.85–7.8, 7.5–7.4 (2 *m*, 5 arom. H); 2.10 (*s*, MeS); 1.50, 1.08 (2*s*, 4 Me). ^{13}C-NMR: 165.1 (*s*, C(3)); 135.3 (*s*, 1 arom. C); 131.2, 128.6, 126.4 (*3d*, 5 arom. CH); 92.1 (*s*, C(5)); 68.6 (*s*, C(1)); 45.9 (2*s*, C(6), C(7)); 23.9, 19.9 (2*q*, 4 Me); 11.7 (*q*, MeS). CI-MS: 308 (100, $[M+1]^+$), 260 (6, $[M-\text{MeS}]^+$), 205 (7), 171 (24), 143 (9), 139 (7), 138 (88), 121 (7). Anal. calc. for $C_{16}H_{21}NOS_2$ (307.46): C 62.50, H 6.89, N 4.56, S 20.85; found: C 62.55, H 6.60, N 4.62, S 20.98.

4. *Reactions of* **1a** *with Imidazole-2(3*H*)-thiones* **3a**–**d**. The reactions were carried out according to the *General Procedure* (*cf. Sect. 3*). Crude products were purified by recrystallization from hexane/CH_2Cl_2.

2,2,4,4-Tetramethyl-3-(methylthio)-3-[(1,4,5-trimethylimidazol-2-yl)thio]cyclobutanone (**4a**). Yield: 387 mg (62%). Colorless crystals. M.p. 150–152°. IR: 2860*s*, 1760*vs* (C=O), 1580*m*, 1460*s*, 1440*s*, 1390*s*, 1380*s*, 855*m*. ^{1}H-NMR: 3.56 (*s*, MeN); 2.14 (*s*, MeS); 2.12 (*s*, 2 Me); 1.75, 1.39 (2*s*, 4 Me). ^{13}C-NMR: 219.2 (*s*, C=O); 135.3, 134.8, 125.3 (3*s*, 3 imidazole C); 74.2 (*s*, C(3)); 68.1 (*s*, C(2), C(4)); 31.6 (*q*, MeN); 24.6, 20.6 (2*q*, 4 Me); 15.9 (*q*, MeS); 13.1, 9.6 (2*q*, 2 Me). EI-MS: 312 (3, $M^{+\bullet}$), 171 (29), 143 (82), 142 (30), 141 (14), 109 (5), 101 (9), 96 (9), 95 (100), 86 (9), 85 (8), 81 (7), 67 (12). Anal. calc. for $C_{15}H_{24}N_2OS_2$ (312.49): C 57.65, H 7.74, N 8.96; found: C 57.33, H 7.64, N 8.82.

3-[(1,4-Dimethyl-5-phenylimidazol-2-yl)thio]-2,2,4,4-tetramethyl-3-(methylthio)cyclobutanone (**4b**). Yield: 612 mg (82%). Colorless crystals. M.p. 184–186°. IR: 2870*m*, 1770*vs* (C=O), 1600*s*, 1495*m*, 1460*s*, 1370*s*, 1030*m*, 780*s*, 705*s*. ^{1}H-NMR: 7.2–7.7 (*m*, 5 arom. H); 3.62 (*s*, MeN); 2.42 (*s*, 2 Me); 2.12 (*s*, MeS); 1.80, 1.44 (2*s*, 4 Me). ^{13}C-NMR: 219.3 (*s*, C=O); 138.8 (*s*, 1 arom. C); 128.9, 127.9, 126.8 (3*d*, 5 arom. CH); 136.9, 135.4, 125.9 (3*s*, 3 imidazole C); 74.3 (*s*, C(3)); 68.1 (*s*, C(2), C(4)); 31.6 (*q*, MeN); 24.6, 20.9 (2*q*, 4 Me); 15.9 (*q*, MeS); 11.0 (*q*, Me). EI-MS: 374 (4, $M^{+\bullet}$), 289 (5), 204 (32), 171 (38), 145 (23), 144 (17), 143 (100), 103 (5), 101 (7), 95 (90), 67 (11), 55 (17). Anal. calc. for $C_{20}H_{26}N_2OS_2$ (374.56): C 64.13, H 7.00, N 7.48; found: C 64.18, H 6.82, N 7.68.

2,2,4,4-Tetramethyl-3-[(1-methyl-4,5-diphenylimidazol-2-yl)thio]-3-(methylthio)cyclobutanone (**4c**). Yield: 566 mg (65%). Colorless crystals. M.p. 214–215°. IR: 2860*m*, 1770*vs* (C=O), 1600*m*, 1500*s*, 1450*s*, 1440*s*, 1370*s*, 1140*m*, 1030*s*, 795*s*, 710*s*. ^{1}H-NMR: 7.5–7.15 (*m*, 10 arom. H); 3.48 (*s*, MeN); 2.14 (*s*, MeS); 1.82, 1.50 (2*s*, 4 Me). ^{13}C-NMR: 219.1 (*s*, C=O); 138.8, 138.6 (2*s*, 2 arom. C); 130.7, 129.1, 128.8, 126.3 (4*d*, 10 arom. CH); 134.6, 131.3, 126.6 (3*s*, 3 imidazole C); 74.3 (*s*, C(3)); 68.2 (*s*, C(2), C(4)); 32.2 (*q*, MeN); 24.6, 20.9 (2*q*, 4 Me); 15.9 (*q*, MeS). EI-MS: 436 (14, $M^{+\bullet}$), 389 (6, $[M-\text{MeS}]^+$), 266 (35), 265 (18), 207 (28), 171 (29), 144 (14), 143 (100), 118 (15), 101 (10), 95 (80), 77 (13), 67 (15). Anal. calc. for $C_{25}H_{28}N_2OS_2$ (436.63): C 68.77, H 6.46, N 6.42; found: C 68.79, H 6.18, N 6.29.

3-[(1-Benzyl-4,5-diphenylimidazol-2-yl)thio]-2,2,4,4-tetramethyl-3-(methylthio)cyclobutanone (**4d**). Yield: 738 mg (72%). Colorless crystals. M.p. 159–161°. IR: 2970*s*, 2930*s*, 1770*vs* (C=O), 1600*s*, 1440*vs*, 1370*s*, 1340*vs*, 1330*s*, 1160*s*, 1130*s*, 1020*s*, 970*s*, 950*s*, 770*s*. ^{1}H-NMR: 7.55–6.85 (*m*, 15 arom. H); 4.56 (*s*, CH_2); 2.06 (*s*, MeS); 1.79, 1.51 (2*s*, 4 Me). ^{13}C-NMR: 219.5 (*s*, C=O); 139.5 (*s*, 3 arom. C); 131.0, 128.9, 128.6, 128.1, 127.5

Table. *Crystallographic Data of Compound* **9a**

Crystallized from	pentane
Empirical formula	$C_{11}H_{19}NOS_2$
Formula weight [g mol^{-1}]	245.40
Crystal color, habit	colorless, prism
Crystal dimensions [mm]	$0.25 \times 0.40 \times 0.48$
Temperature [K]	173(1)
Crystal system	monoclinic
Space group	*C*2/*c*
Z	8
Reflections for cell determination	25
2θ range for cell determination [°]	38 – 40
Unit cell parameters *a* [Å]	26.781(3)
b [Å]	8.215(2)
c [Å]	12.615(2)
β [°]	112.11(1)
V [Å^3]	2571.3(8)
D_x [g cm^{-3}]	1.268
μ(MoK_α) [mm^{-1}]	0.390
$2\theta_{(max)}$ [°]	55
Total reflections measured	3238
Symmetry independent reflections	2964
Reflections used [$I > 2\sigma(I)$]	2473
Parameters refined	141
Final *R*	0.0366
wR ($w = [\sigma^2(F_o) + (0.005\,F_o)^2]^{-1}$)	0.0400
Goodness of fit	2.209
Secondary extinction coefficient	$2.2(3) \times 10^{-7}$
Final Δ_{max}/σ	0.0002
$\Delta\rho$ (max; min) [e Å^{-3}]	0.32; −0.32

(5*d*, 15 arom. CH); 137.0, 134.5, 126.3 (3*s*, 3 imidazole C); 74.5 (*s*, C(3)); 68.3 (*s*, C(2), C(4)); 48.2 (*t*, CH_2); 24.6, 20.9 (2*q*, 4 Me); 15.9 (*q*, MeS). EI-MS: 513 (8, $[M+1]^+$), 512 (21, $M^{+\cdot}$), 465 (16, $[M-\text{MeS}]^+$), 427(9), 342(20), 309(9), 287(7), 193(28), 178(6), 144(20), 143(100), 95(88), 91(74), 67(15). Anal. calc. for $C_{31}H_{32}N_2OS_2$ (512.73): C 72.62, H 6.29, N 5.46; found: C 72.58, H 6.02, N 5.48.

5. *Reaction of* **1a** *with Pyrimidine-2-thione* (*2-Mercaptopyrimidine*, **6**). Freshly recrystallized **1a** (198 mg, 1 mmol) and **6** (112.2 mg, 1 mmol) were dissolved in abs. acetone (5 ml), and the soln. was heated in an oil bath (45°) under stirring for *ca.* 5 h. After this time, N_2 evolution was completed (*ca.* 24 ml of N_2, 98% of theory). After evaporation of the solvent, the solid residue was treated with MeOH (5 ml), and the crude product was filtered: 257 mg (91%) of yellowish crystals. An anal. pure sample of *2,2,4,4-tetramethyl-3-(methylthio)-3-[(pyrimidin-2-yl)thio]cyclobutanone* (**7**) was obtained by recrystallization from MeOH. M.p. 96 – 98°. IR: 2980*m*, 1770v*s* (C=O), 1550*s*, 1480v*s*, 1180*s*, 1030*m*. ^{1}H-NMR: 8.57 (*d*, $J = 4.8$, 2 arom. H); 7.05 (*dd*, $J_1 \approx J_2 \approx$ 4.8, 1 arom. H); 2.13 (*s*, MeS); 1.57, 1.54 (2*s*, 4 Me). ^{13}C-NMR: 219.1 (*s*, C=O); 170.8 (*s*, 1 arom. C); 156.9, 117.3 (2*d*, 3 arom. CH); 70.2 (*s*, C(3)); 68.0 (*s*, C(2), C(4)); 23.8, 20.9 (2*q*, 4 Me); 16.0 (*q*, MeS). CI-MS: 283 (100, $[M+1]^+$), 171(30), 143(9), 113(11). Anal. calc. for $C_{13}H_{18}N_2OS_2$ (282.31): C 55.28, H 6.42, N 9.92, S 22.71; found: C 55.27, H 6.47, N 10.00, S 22.44.

6. *Crystal-Structure Determination of* **9a** (see *Table* and *Fig.*)[5]. All measurements were made on a *Rigaku AFC5R* diffractometer in the $\omega/2\theta$-scan mode using graphite-monochromated MoK_α radiation (λ 0.71069 Å) and a 12-kW rotating anode generator. The intensities were corrected for *Lorentz* and polarization effects, but

[5]) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-111992. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

not for absorption. Data collection and refinement parameters are listed in the *Table*, a view of the molecule is shown in the *Figure*. The structure was solved by direct methods using SHELXS86 [19], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. The OH H-atom was placed in the position indicated by a difference electron-density map, and its position was refined together with an isotropic displacement parameter. All other H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95Å), and they were assigned fixed isotropic displacement parameters with a value equal to 1.2 U_{eq} of the parent atom. Refinement of the structure was carried out on F using full-matrix least-squares procedures. A correction for secondary extinction was applied. Neutral atom scattering factors for non-H-atoms were taken from [20a] and the scattering factors for H-atoms from [21]. Anomalous dispersion effects were included in F_{calc} [22]; the values for f' and f'' were those of [20b]. All calculations were performed using the TEXSAN crystallographic software package [23].

The OH group forms an intermolecular H-bond with the N-atom of a neighboring molecule, thereby linking the molecules into dimeric units which possess a 2-fold axis; graph set [24]: $R_2^2(8)$.

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