REACTIONS OF α-DIAZOCYCLOALKANONES WITH THIOCARBONYL COMPOUNDS

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(Dedicated to Prof. T. Mukaiyama on the occasion of his 73rd birthday)

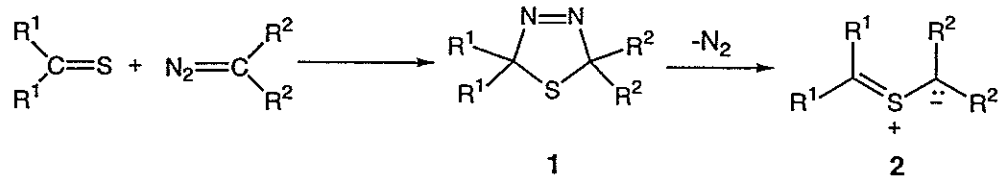
Abstract - Reactions of 2-diazocyclohexanone (**7**) with thioketones and a 1,3-thiazole-5(4*H*)-thione in THF at 50-60°C in the presence of 10% $LiClO_4$ proceeded by elimination of N_2 and yielded 4,5,6,7-tetrahydro-1,3-benzoxathiole derivatives (**13-17**). In the case of 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**12**), a 1:5 mixture of *cis*- and *trans*-bisadducts (*cis*/*trans*-**17**) was obtained. Under analogous conditions, no reactions occurred with 5,5-dimethyl-2-diazocyclohexane-1,3-dione (**18**). Only in the presence of 2% $Rh_2(OAc)_4$, **18** reacted with dithione (**12**) yielding the 1,3-benzoxathiole derivative (**19**).

INTRODUCTION

First reports on reactions of diazo compounds with thioketones were published by *Staudinger*[2] and *Schönberg*[3] many years ago, but mechanisms of the formation of the isolated products were unknown until the early eighties. Then, *Huisgen* and coworkers studied the reaction of thiobenzophenone and diazomethane at low temperature and identified 2,5-dihydro-2,2-diphenyl-1,3,4-thiadiazole (**1**, R^1 = Ph, R^2 = H) (*Scheme 1*) as the primary adduct.[4] A thiocarbonyl ylide (**2**), formed by thermal N_2 elimination, was recognized as the crucial reactive intermediate involved in the formation of all isolated products. Further studies showed that the stability of the primarily formed 2,5-dihydro-1,3,4-thiadiazoles of type (**1**) depends on the substitution pattern. On the one hand, aromatic substituents lower the stability and, on the other hand, sterically crowded systems are more stable.[5] For example,

the product of the reaction of di(*tert*-butyl)diazomethane and 2-benzyl-4,4-dimethyl-1,3-thiadiazole-5(4*H*)-thione was isolated as a fairly stable substance and its structure was confirmed by X-Ray crystallography[6] (for a second example see ref. [7]).

Scheme 1

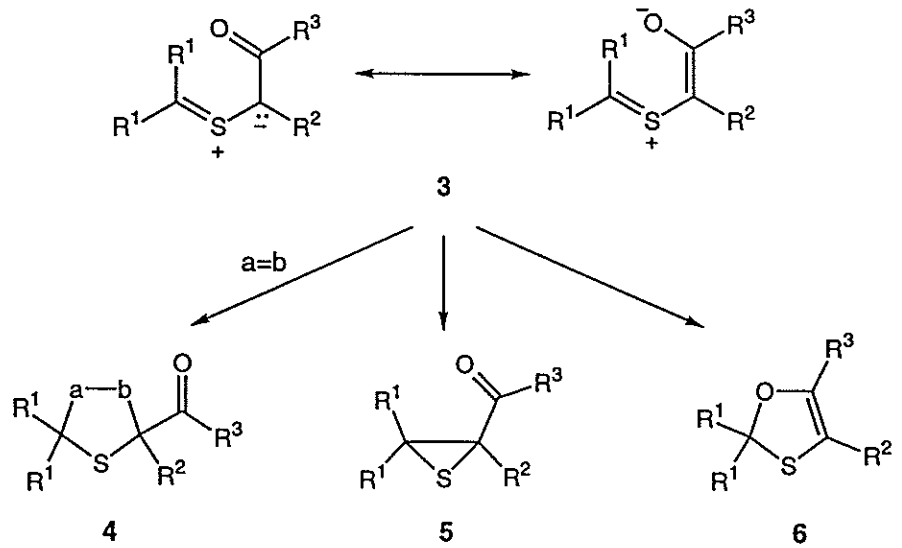


1 2

Diazomethane is very reactive towards thioketones, but its derivatives with electron-withdrawing substituents show a reduced reactivity, in accordance with general rules.[8,9] *E.g.*, methyl diazomalonate does not react at room temperature with thiobenzophenone, which is one of the most reactive thioketones.[10] In such cases, the corresponding thiocarbonyl ylides can be generated *via* $Rh_2(OAc)_4$-catalyzed processes in which carbenoids are formed by spontaneous N_2 elimination.[11,12]

Reactive thiocarbonyl ylides of type (**2**)[13] generated *in situ* undergo easily [2+3] cycloadditions with various dipolarophiles to give adducts of type (**4**), dimerize or yield thiiranes (**5**) *via* 1,3-dipolar ring closure.[15,16] Carbonyl-substituted analogues (**3**) react mainly *via* a 1,5-dipolar electrocyclization[17] to form 1,3-oxathiole derivatives (**6**, *Scheme 2*).[7,18,19]

Scheme 2



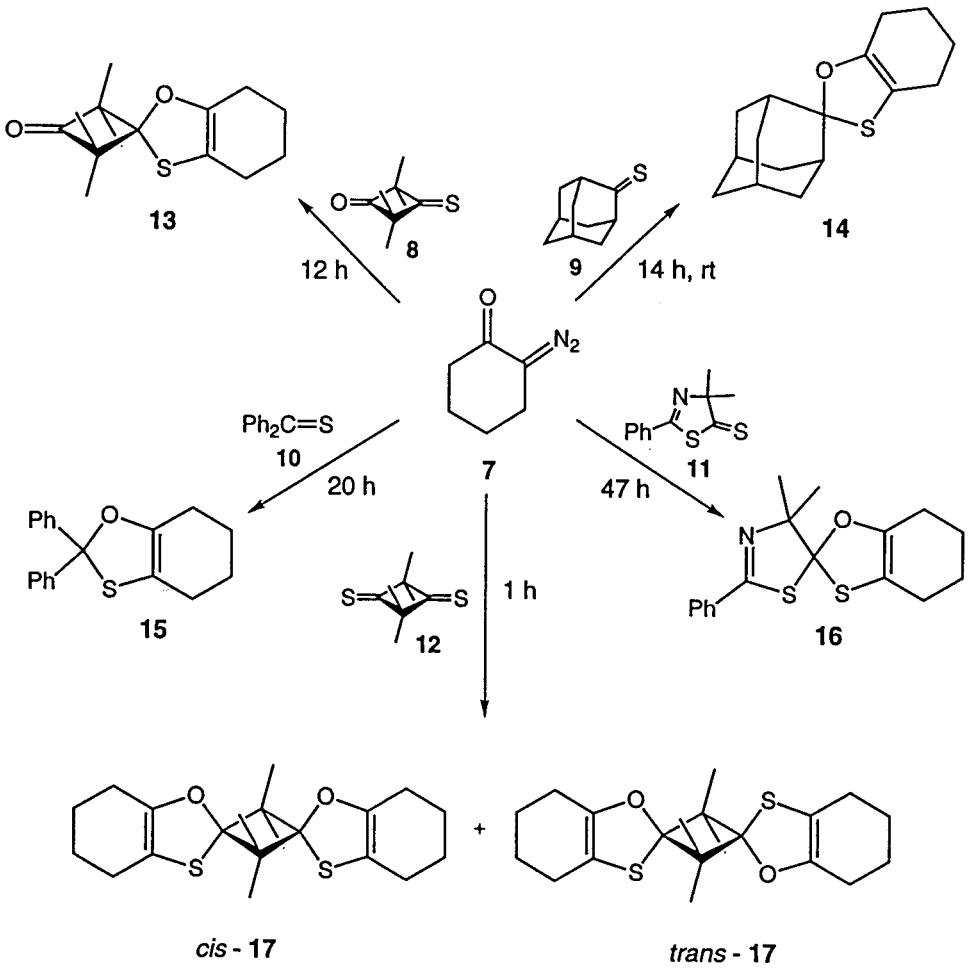
3 4 5 6

In our recent papers we described reactions of open chain α-diazo carbonyl compounds with C=S bonds.[7,18] Generally, the major product originated from the 1,5-ring closure. Thiiranes resulting from 1,3-ring closure were also found in some cases, and the ratio of the two products depended on the substitution pattern of both reagents. Considering the mechanisms of the ring closure reactions leading to **5** or **6**, respectively, we concluded that rigid α-diazocycloalkanones with a fixed (*Z*)-arrangement of diazo- and carbonyl groups should lead preferably to 1,3-oxathioles (**6**).

RESULTS AND DISCUSSION

Reactions of 2-diazocyclohexanone (**7**)[20] with thiocarbonyl compounds (**8-12**) (*Scheme 3*) were typically carried out in a THF solution containing 10% $LiClO_4$ at 50-60°C. The mixture was stirred until the color of the thiocarbonyl compound faded. The disappearance of the color was accompanied by the evolution of N_2.[21] After usual workup, the products were isolated using column chromatography, and solid materials were recrystallized from methanol. Reactions with **8-11** afforded single products identified as 1,3-oxathiole derivatives (**13-16**) (*Scheme 3*). The structures were determined on the basis of their spectral data which were in good agreement with those of previously reported analogues.[7,18]

Scheme 3

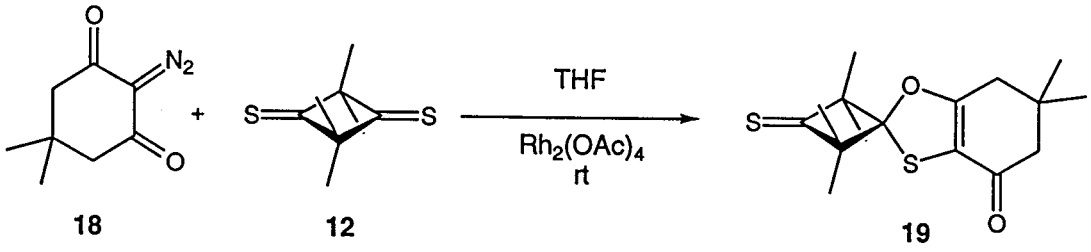


Reaction conditions: THF, 10% $LiClO_4$, 50-60°C

In the case of dithione (**12**) reaction was performed with molar excess of **7**. The reaction was complete after 1 h and a mixture of two isomeric 1:2 adducts was isolated in 93% yield.[22] Based on ^{1}H-NMR analysis of the analytically pure mixture, the ratio of *cis*-**17**/*trans*-**17** was determined to 1:5. The isomers were separated using HPLC, and differentiation of the two structures was easily achieved as *trans*-**17** shows only one Me absorption whereas *cis*-**17** shows two Me signals (^{1}H- and ^{13}C-NMR).

The second rigid α-diazo compound we selected for our studies was 2-diazo-5,5-dimethylcyclohexane-1,3-dione (diazodimedone (**18**)).[23] Under conditions used for the reaction with **7**, this compound did not react with thiocarbonyl compounds (**8-12**). For this reason, the methodology was changed, and $Rh_2(OAc)_4$ was used as a catalyst, but **18** failed to react with **8-11**. Only in the case of dithione (**12**), used in a 1:1 ratio with **18**, after stirring at room temperature for 5 h, a red crystalline product was isolated in modest yield.[24] ^1H- and ^{13}C-NMR spectral data indicated two non-equivalent CH_2 groups. Moreover, IR and ^{13}C-NMR spectral data suggested the presence of an α,β-unsaturated carbonyl function. These data, together with the molecular ion peak in the CI-MS and elemental analysis led to the formulation of the 1,3-oxathiole structure (**19**) (*Scheme 4*). This proposal is further supported by the presence of only three Me absorptions for six Me groups in the ^1H-NMR spectrum as well as two singlets for Me_2C atoms in the ^{13}C-NMR. The key intermediate leading to **19** is again a thiocarbonyl ylide resulting from the addition of a carbenoid generated *in situ* at the C=S group of **12**.

Scheme 4



18 **12** **19**

A similar process has been described recently:[25] heating of **18** in nitriles as the solvent in the presence of $Rh_2(OAc)_4$ to 60°C gave 2-substituted 4,5,6,7-tetrahydro-1,3-benzoxazoles, most likely *via* a 1,5-dipolar electrocyclization of an intermediate acylated nitrile ylide.

In conclusion, we have shown that rigid α-diazoketones with a fixed (*Z*) geometry react with thiocarbonyl compounds to give intermediate thiocarbonyl ylides which undergo exclusively a 1,5-dipolar electrocyclization yielding 1,3-oxathiole derivatives.

EXPERIMENTAL

General remarks. See ref.[26] Melting points were determined on a *Mettler FP-5* apparatus and are uncorrected. Elemental analyses with an *Elementar Analysator EL, Gerber Instruments*. If not otherwise stated, IR spectra were recorded on a *Perkin-Elmer-781* instrument (KBr, cm^{-1}), ^1H-NMR (300 MHz) and ^{13}C-NMR (75.5 MHz) spectra on a *Bruker-ARX-300* instrument ($CDCl_3$, δ in ppm, *J* in Hz) with TMS as internal standard (= 0 ppm), and MS spectra on a *Finnigan-TSQ-700* instrument (EI: 70 eV, CI with NH_3). Column chromatography (CC) or prep. TLC on silica gel (SiO_2).

Starting materials. The α-diazocycloalkanones were prepared following known procedures: 2-diazocyclohexanone (**7**)[20] and 2-diazo-5,5-dimethylcyclohexane-1,3-dione (**18**)[23] were obtained *via* diazo transfer with tosylazide to 2-formylcyclohexanone and dimedone, respectively. The syntheses of the thiocarbonyl compounds 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**8**), adamantanethione (**9**), thiobenzophenone (**10**), 4,4-dimethyl-1,3-thiazole-5(4*H*)-thione (**11**), and 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**12**) have already been described (cf. refs.[7,18]).

Reactions of 2-diazocyclohexanone (**7**) *with thiocarbonyl compounds* (**8**-**12**). *4,5,6,7-Tetrahydro-2',2',4',4'-tetramethylspiro[1,3-benzoxathiole-2,1'-cyclobutane]-3'-one* (**13**). A solution of **7** (124 mg, 1 mmol) and **8** (156 mg, 1 mmol) in THF/10% $LiClO_4$ (2 mL) was heated in an N_2-atmosphere to 60°C. After 12 h, the initially red mixture was colorless. Work-up by filtration, evaporation of the solvent, chromatography (SiO_2, hexane/CH_2Cl_2 1:1), and recrystallization from methanol gave **13** (170 mg, 67%) as colorless crystals, mp 82-84°C. IR: 2961*s*, 2937*vs*, 2858*s*, 2842*s*, 1773*vs*, 1689*s*, 1450*s*, 1376*m*, 1363*m*, 1342*m*, 1251*s*, 1220*w*, 1205*s*, 1176*s*, 1147*vs*, 1051*m*, 959*w*, 922*w*, 866*w*. ^{1}H-NMR: 2.2-2.1 (*m*, 4 H); 1.7-1.4 (*m*, 4 H); 1.66, 1.23 (2*s*, 2 Me). ^{13}C-NMR: 220.5 (*s*, C=O); 144.4 (*s*, C(7a)); 103.1 (*s*, C(3a)); 102.2 (*s*, spiro-C); 65.9 (*s*, 2 Me_2C); 23.4 (*t*, CH_2(7)); 23.3 (*t*, CH_2(4)); 22.9 (*t*, 2 CH_2); 22.2, 18.2 (2*q*, 4 Me). CI-MS: 254 (16), 253 (100, $[M + 1]^+$), 182 (22). Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.70; H, 7.99. Found: C, 66.92; H, 7.73.

4,5,6,7-Tetrahydrospiro[1,3-benzoxathiole-2,2'-tricyclo[3.3.1.1^{3,7}]decane] (**14**). A solution of **7** (124 mg, 1 mmol) and **9** (166 mg, 1 mmol) in THF/10% $LiClO_4$ (2 mL) was stirred at rt. After 14 h, **9** had been consumed (TLC). The mixture was filtered, the solvent evaporated, and the residue purified by chromatography (SiO_2, hexane/CH_2Cl_2 1:1) and recrystallization from methanol. Yield of **14**: 190 mg (72%). Colorless crystals, mp 77-79°C. IR: 2911*vs*, 2853*vs*, 1687*w*, 1470*s*, 1464*w*, 1357*s*, 1348*s*, 1306*w*, 1277*w*, 1209*s*, 1178*s*, 1153*s*, 1140*m*, 1103*vs*, 941*m*, 895*m*, 879*w*, 801*w*, 772*w*, 698*w*, 678*w*. ^{1}H-NMR: 2.3-2.0 (*m*, 8 H); 1.91 (*m*, 14 H). ^{13}C-NMR: 143.4 (*s*, C(7a)); 104.1 (*s*, C(3a)); 102.0 (*s*, spiro-C); 39.5 (*d*, CH(1'), CH(3')); 37.5 (*t*, CH_2); 35.7 (*t*, 2 CH_2); 33.6 (*t*, 2 CH_2); 26.6 (*d*, CH); 26.3 (*d*, CH); 24.2 (*t*, CH_2(7)); 23.6 (*t*, CH_2(4)); 23.1, 22.4 (2*t*, 2 CH_2). EI-MS: 264 (18), 262 (100, $M^{+\cdot}$), 166 (6), 91 (8), 79 (5). Anal. Calcd for $C_{16}H_{22}OS$: C, 73.31; H, 8.46. Found: C, 73.32; H, 8.30.

4,5,6,7-Tetrahydro-2,2-diphenyl-1,3-benzoxathiole (**15**). A solution of **7** (124 mg, 1 mmol) and **10** (198 mg, 1 mmol) in THF/10% $LiClO_4$ (2 mL) was heated under N_2 (60°C). After 20 h, the starting materials had disappeared (TLC) and the mixture was filtered, the solvent evaporated, and the residue purified by chromatography (CC, hexane/ethyl acetate 10:1, and prep. TLC, hexane/CH_2Cl_2 1:2). Recrystallization from methanol yielded **15** (150 mg, 52%). Colorless crystals, mp 107-109°C. IR: 2950*s*, 2916*s*, 2853*s*, 2840*w*, 1681*s*, 1599*m*, 1487*vs*,

1339*m*, 1260*s*, 1224*s*, 1206*s*, 1176*s*, 1145*s*, 1132*vs*, 1070*vs*, 1027*vs*, 985*vs*, 957*m*, 932*s*, 915*s*, 856*vs*, 818*vs*, 763*vs*, 753*vs*. ^{1}H-NMR: 7.6-7.5 (*m*, 4 arom. H); 7.45-7.4 (*m*, 6 arom. H); 2.3-2.25 (*m*, H_2C(7a)); 2.25-2.15 (*m*, H_2C(3a)); 1.75-1.65 (*m*, 2 H_2C). ^{13}C-NMR: 144.6 (*s*, 2 arom. C); 143.1 (*s*, C(7a)); 127.9, 127.8, 126.4 (3*d*, 10 arom. CH); 104.5 (*s*, C(3a)); 100.7 (*s*, spiro-C); 24.2 (*t*, CH_2(7)); 23.5 (*t*, CH_2(4)); 23.0, 22.4 (2*t*, 2 CH_2). CI-MS: 296 (22), 295 (100, [*M* + 1]+). Anal. Calcd for $C_{18}H_{18}OS$: C, 77.53; H, 6.15. Found: C, 77.36; H, 6.39.

4,4',5,5',6,7-Hexahydro-4',4'-dimethyl-2'-phenylspiro[1,3-benzoxathiole-2,5'-(1,3)thiazole] (**16**). A solution of **7** (93 mg, 0.75 mmol) and **11** (110 mg, 0.5 mmol) in THF/10% $LiClO_4$ (1 mL) was heated to 60°C under N_2. After 47 h, the initially orange color changed to yellow and no **11** could be detected by TLC. Filtration of the mixture, evaporation of the solvent, and chromatography (CC, hexane/ethyl acetate 3:1, and prep. TLC, hexane/CH_2Cl_2 1:2) gave 70 mg (50%) of **16** as a yellowish oil. IR (neat): 2931*s*, 1622*s*, 1598*s*, 1577*s*, 1520*s*, 1489*s*, 1447*s*, 1355*m*, 1259*m*, 1209*m*, 1065*m*, 1033*m*, 996*s*, 919*m*, 876*m*, 830*s*, 802*m*, 772*m*, 728*m*, 689*s*, 660*s*, 634*s*, 611*s*. ^{1}H-NMR: 7.8-7.75 (*m*, 2 arom. H); 7.45-7.35 (*m*, 3 arom. H); 2.35-2.3 (*m*, CH_2); 2.2-2.1 (*m*, CH_2); 1.8-1.75 (*m*, 2 CH_2); 1.68, 1.46 (2*s*, 2 Me). ^{13}C-NMR: 163.9 (*s*, C=N); 143.4 (*s*, C(7a)); 133.7 (*s*, 1 arom. C); 131.2, 128.4, 128.1 (3*d*, 5 arom. CH); 122.8 (*s*, spiro-C); 106.1 (*s*, C(3a)); 81.7 (*s*, Me_2C); 24.8, 21.2 (2*q*, 2 Me); 23.9 (*t*, CH_2(7)); 23.2 (*t*, CH_2(4)); 22.9, 22.1 (2*t*, 2 CH_2). EI-MS: 317 (10, $M^{+\cdot}$), 177 (15), 145 (100), 104 (25).

cis- *and* trans-*4,4",5,5",6,6",7,7"-Octahydro-2',2',4',4'-tetramethyldispiro[1,3-benzoxathiole-2,1'-cyclobutane-3',2"-(1,3)benzoxathiole]* (*cis*- and *trans*-**17**). A solution of **7** (248 mg, 2 mmol) and **12** (172 mg, 1 mmol) in THF/10% $LiClO_4$ (2 mL) under N_2 was stirred for 30 min at rt. Filtration of the mixture and evaporation of the solvent yielded a crude product mixture in which a monoadduct was the major compound (CI-MS: *m/z* 269, [*M* + 1]+). After dissolving in THF/10% $LiClO_4$ (2 mL), a second portion of **7** (124 mg, 1 mmol) was added and the solution was heated to 50°C for 1 h. Then, no monoadduct could be detected by TLC, and the mixture was filtered, the solvent evaporated, and the residue purified by CC (hexane/CH_2Cl_2 1:1), leading to a 1:5 mixture of *cis*- and *trans*-**17**[27] (340 mg, 93%). CI-MS: 367 (10), 366 (21), 365 (100, [*M* + 1]+). Anal. Calcd for $C_{20}H_{28}O_2S_2$: C, 65.93; H, 7.74. Found: C, 65.83; H, 7.74.
The isomers were separated by means of HPLC and recrystallized from methanol.
cis-**17**: Colorless crystals, mp 138-140°C. IR: 2973*s*, 2930*vs*, 2880*s*, 2854*vs*, 2836*vs*, 1683*vs*, 1458*vs*, 1445*vs*, 1375*s*, 1364*s*, 1353*s*, 1341*s*, 1329*s*, 1263*vs*, 1233*vs*, 1202*vs*, 1129*m*, 1069*vs*, 1031*s*, 980*vs*, 953*s*, 864*vs*, 833*m*, 664*m*. ^{1}H-NMR: 2.2-2.05 (*m*, 4 CH_2); 1.7-1.6 (*m*, 4 CH_2); 1.26 (*s*, 2 Me); 1.14 (*s*, 2 Me). ^{13}C-NMR: 144.6 (*s*, C(7a), C(7a")); 106.8 (*s*, C(3a), C(3a")); 102.0 (*s*, 2 spiro-C); 55.3 (*s*, 2 Me_2C); 26.9 (*q*, 2 Me); 23.6 (*t*, CH_2(7,7")); 23.3 (*t*, CH_2(4,4")); 23.1, 22.5 (2*t*, 4 CH_2); 17.6 (*q*, 2 Me).
trans-**17**: Colorless crystals, mp 140-141°C. IR: 2973*vs*, 2931*vs*, 2855*vs*, 2837*vs*, 1768*m*, 1684*s*, 1653*vs*, 1459*vs*, 1445*vs*, 1375*s*, 1365*s*, 1353*s*, 1342*m*, 1330*m*, 1295*s*, 1264*s*, 1233*m*,

1202*s*, 1176*s*, 1145*vs*, 1130*vs*, 1104*vs*, 1087*s*, 1062*vs*, 1031*s*, 1015*s*, 980*s*, 954*s*, 937*s*, 915*s*, 865*m*, 817*m*. ^{1}H-NMR: 2.15-2.1 (br *s*, 4 CH_2); 1.75-1.25 (br *s*, 4 CH_2); 1.24 (*s*, 4 Me). ^{13}C-NMR: 144.0 (*s*, C(7a), C(7a")); 105.9 (*s*, C(3a), C(3a")); 102.9 (*s*, 2 spiro-C); 55.5 (*s*, 2 Me_2C); 23.4 (*t*, CH_2(7,7")); 23.3 (*t*, CH_2(4,4")); 23.1, 22.4 (2*t*, 4 CH_2); 22.9 (*q*, 4 Me).

Reactions of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (**18**) *with* **8**-**12**. Solutions of **18** (166 mg, 1 mmol) and an equimolar amount of the thiocarbonyl compound in THF/10% $LiClO_4$ (2 mL) were heated to 50-60°C. In none of the experiments could an adduct be detected.

4,5,6,7-Tetrahydro-2',2',4',4',6,6-hexamethyl-3'-thioxospiro[1,3-benzoxathiole-2,1'-cyclobutan]-4-one (**19**). To a solution of **18** (166 mg, 1 mmol) and **12** (172 mg, 1 mmol) in THF (2 mL), $Rh_2(OAc)_4 \cdot 2\ H_2O$ (9.56 mg, 0.02 mmol) was added and the mixture was stirred at rt until **12** was completely consumed (TLC; the red color of the mixture turned to pale rosa). After filtration of the mixture and evaporation of the solvent, the residue was chromatographed (CC, hexane/CH_2Cl_2 1:4) and recrystallized from methanol. Yield of **19**: 120 mg (38%).[28] Pale red crystals, mp 115°C. IR: 2964*s*, 2928*m*, 2868*w*, 1650*vs*, 1619*vs*, 1461*m*, 1450*m*, 1388*s*, 1364*s*, 1351*m*, 1331*s*, 1305*w*, 1241*w*, 1161*m*, 1146*m*, 1122*m*, 1054*s*, 1028*vs*, 984*m*, 954*w*. ^{1}H-NMR: 2.42 (*s*, 2 H); 2.33 (*s*, 2 H); 1.36 (*s*, 2 Me); 1.30 (*s*, 2 Me); 1.13 (*s*, 2 Me). ^{13}C-NMR: 191.2 (*s*, C=O); 166.5 (*s*, C(7a)); 110.5 (*s*, C(3a)); 110.1 (*s*, spiro-C); 69.8 (*s*, 2 Me_2C); 34.1 (*s*, Me_2C); 50.4, 38.7 (2*t*, 2 CH_2); 28.4, 26.8, 22.0 (3*q*, 3 Me_2C).[29] CI-MS: 312 (18), 311 (100, [*M* + 1]+), 297 (21). Anal. Calcd for $C_{16}H_{22}O_2S_2$: C, 61.96; H, 7.15. Found: C, 61.82; H, 7.44.

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21. In the case of the reaction of **7** and **8**, respectively, a *ca.* equimolar amount of N_2 was determined volumetrically by using a gas-burette.
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27. Heating of a 2:1 mixture of **7** and **12** in THF/10% $LiClO_4$ to 50°C for 1 h yielded an analogous mixture.
28. No other product could be isolated.
29. The thiocarbonyl C-atom (C3')), absorbing usually at *ca.* 280 ppm,[30] was not detected.
30. G. Mlostoń, J. Romański, A. Linden, and H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 1499.

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