1,5-Dipolar Electrocyclizations in Reactions of α-Thioxo Ketones and α-Thioxo Thioamides with Diazo Compounds

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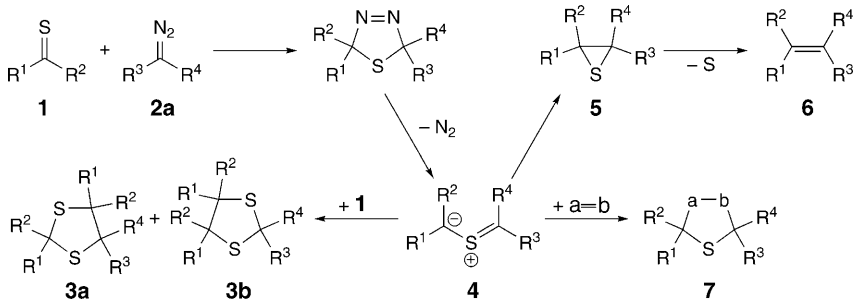
Several reactions of α-thioxo ketones and α-thioxo thioamides with diazo compounds were investigated. Most of them proceeded *via* a reactive thiocarbonyl ylide, which underwent a [2+3] cycloaddition with the α-thioxo ketone to give the '*Schönberg* products' **17**–**19** or a 1,5-dipolar electrocyclization to give the corresponding five membered 1,3-oxathioles (*i.e.*, **13**, **20a**, **20b**, **21**, and **25**) and 1,3-dithioles (*i.e.*, **33**, **34**, and **35**), respectively. In the case of thioamide **32**, the thiocarbonyl ylides underwent a competitive 1,3-dipolar electrocyclization to yield the corresponding thiiranes. In these cases, spontaneous desulfurization led to the corresponding alkenes **36** and **37**. The nature of the employed thiocarbonyl or diazo compounds seem to be decisive for the reaction pathway. When the diazo compound bears at least one H-atom in the β-position to the diazo group (*i.e.*, diazocyclohexane **15f**), no products of an electrocyclization could be isolated in the reactions with α-thioxo ketones or α-thioxo thioamides. The only products which were isolated in these cases were 2-[(cyclohex-1-enyl)sulfanyl]-1,2-diphenylethanone (**22**) and 2-[(cyclohex-1-enyl)sulfanyl]-*N*,*N*-dimethyl-2-phenylthioacetamide (**38**), which were formed by a [1,4]-H shift of the corresponding thiocarbonyl ylides.

Introduction. – The reactions of thiocarbonyl compounds **1** with diazo alkanes **2a** have been investigated extensively over the last few years. Most of the reactions led to 1,3-dithiolanes **3a** and **3b** by 1,3-dipolar cycloaddition of the intermediate thiocarbonyl ylide **4** with the original C=S compound (the so called *Schönberg* reaction [1][2]) or to thiiranes **5** by 1,3-dipolar electrocyclization. The latter form alkenes **6** by S-extrusion [2–4] (*Scheme 1*). Many studies have attempted to determine the intermediates of these reactions. All results indicated the formation of thiocarbonyl ylides **4** as intermediates, which react *via* several pathways to form the products (for reviews, see [5][6]). These intermediates could be intercepted by dipolarophiles to give the [2+3] adducts **7** in a 1,3-dipolar cycloaddition. This reaction led not only to the understanding of the reaction mechanism, but also opened new access to S-heterocycles.

Another goal was the incorporation of the dipolarophile into the thiocarbonyl ylide, in order to promote a ring closure *via* 1,5-dipolar electrocyclization. These studies have shown that 1,3-oxathioles **8** can easily be prepared by generation of a thiocarbonyl ylide **9** *via* a $Rh_2(OAc)_4$- or $LiClO_4$-catalyzed reaction of α-diazocarbonyl compounds **10** with thiocarbonyl compounds **1**, followed by a 1,5-dipolar electrocyclization [7–9]. In a few cases, it was shown that **8** can also be prepared by the reaction of α-thioxocar-

[1]) Part of the diploma work (2002) and the Ph.D. thesis of *D. H. E.*, University of Zürich, 2006.

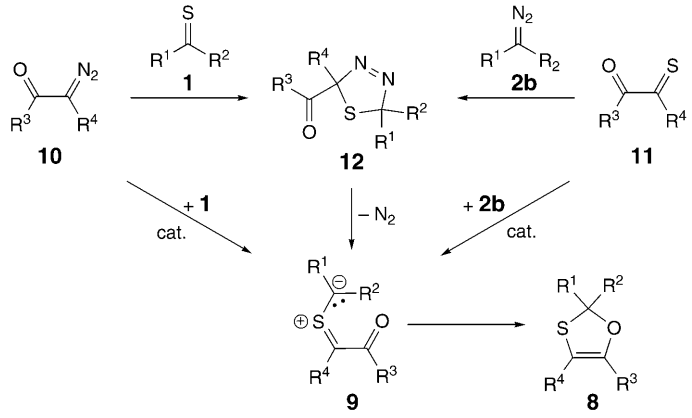
Scheme 1



bonyl compounds **11** with diazo compounds **2b** by using $Rh_2(OAc)_4$ as a catalyst [10][11]. This is not surprising, because the 2,5-dihydro-1,3,4-thiadiazole **12** and **9** are common intermediates in both reactions (*Scheme 2*).

The main target of the present study was to further investigate the scope and limitations of the 1,5-dipolar electrocyclization of thiocarbonyl ylides with a conjugated π-system and, in particular, the influence of this conjugated π-system in the thiocarbonyl compounds on the course of the reaction with diazo compounds.

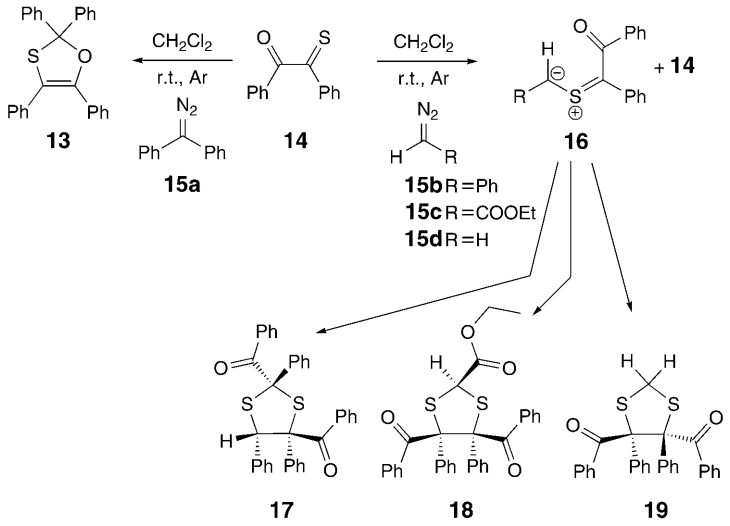
Scheme 2



Results and Discussion. – *Reactions with α-Thioxocarbonyl Compounds.* As 1,2-diphenyl-2-thioxoethanone (**14**) reacted cleanly with diazo(diphenyl)methane (**15a**) to give 2,2,4,5-tetraphenyl-1,3-oxathiole (**13**) as the only product [11] (*Scheme 3*)[2]), **14** was selected as a suitable candidate for the reaction with diazo(phenyl)methane (**15b**), ethyl-2-diazoacetate (**15c**), and diazomethane (**15d**), respectively. It was expected that these reactions would lead to the corresponding 1,3-oxathioles by 1,5-dipolar electrocyclization of the intermediate thiocarbonyl ylide **16**. Unexpectedly,

[2]) The repetition of the reaction reported in [11] yielded **13**, which was identical with the product obtained from the reaction of 2-diazo-1,2-diphenylethanone and thiobenzophenone [7].

Scheme 3



the products of the reaction in CH_2Cl_2 at room temperature obtained after chromatography on SiO_2 were not the expected ones. The main product in each case was a yellow stinky oil, which could not be analyzed because of decomposition. The results were the same when the reaction conditions were changed (low temperature, heating, catalysis with $Rh_2(OAc)_4$ or $LiClO_4$). In each case, the corresponding racemic *Schönberg* product, *i.e.*, **17**–**19**, was isolated as a minor product in 15 to 25% yield (*Scheme 3*).

The structures of **17**–**19** have been established by X-ray crystallography (*Fig. 1*). The five-membered ring of **17** has a half-chair conformation twisted on S(2)–C(3). The two benzoyl groups at C(2) and C(4) are *trans*-oriented, and the configuration of the Ph groups at C(2), C(4), and C(5) is *trans*, *cis*. In **18**, the Et group of the ester side chain is disordered over two orientations that differ slightly by a twist about this O–Et bond. Two equally occupied positions were refined for the terminal Me groups of this moiety. The five-membered ring has an envelope conformation with C(2) as the envelope flap. The two benzoyl groups at C(4) and C(5) are *cis*-oriented with respect to the ester group and to each other. The five-membered ring of **19** has a half-chair conformation twisted on C(1)–S(5). The benzoyl substituents lie *trans* to each other.

It is remarkable that the regioselectivity of the formation of the dithiolane ring of **17** is different from that of **18** and **19**. Furthermore, the relative configuration of the benzoyl groups at C(4) and C(5) is *cis* in **18**, but *trans* in **19**.

Since the results of the reactions under various conditions did not change, we tried to isolate a product from the yellow oil by varying the purification methods. Column chromatography on silica gel (acidic) or *Alox* (basic) did not lead to satisfying results; therefore, 1% Et_3N was added to the eluent of the chromatography on silica gel. This procedure showed considerable advantage over all methods previously used, and the best results were obtained with 3% Et_3N. By using the same reaction conditions as described above and the new conditions for the chromatographic workup, the reactions

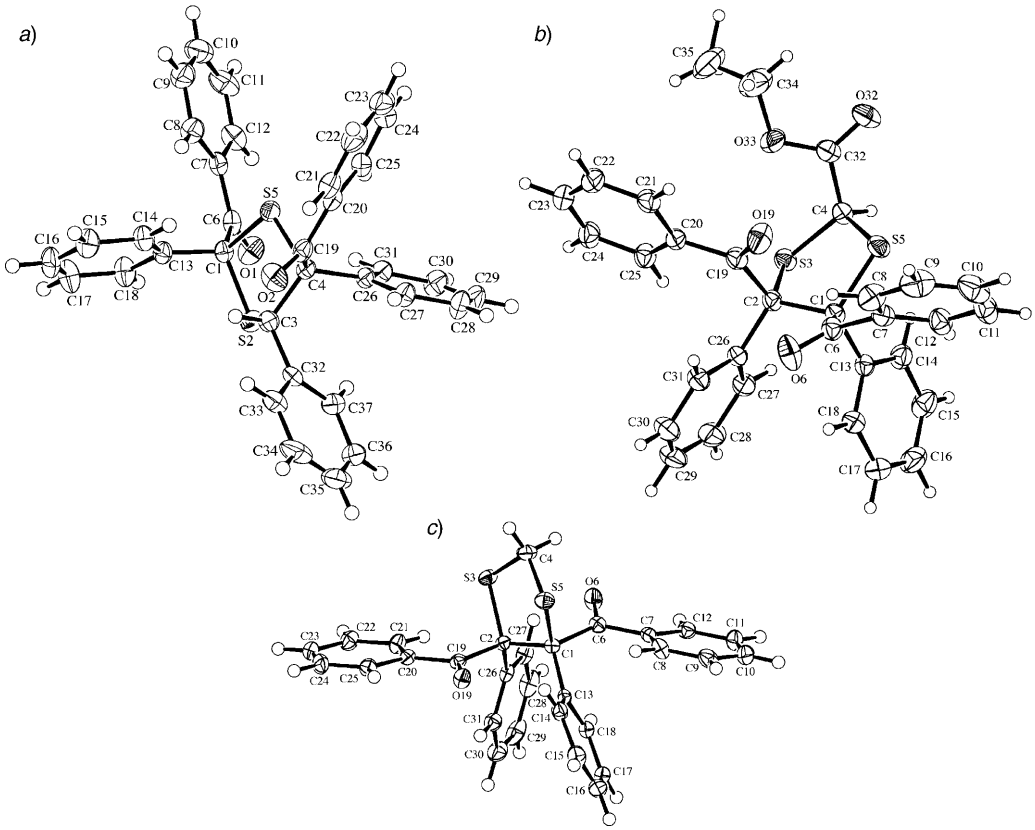


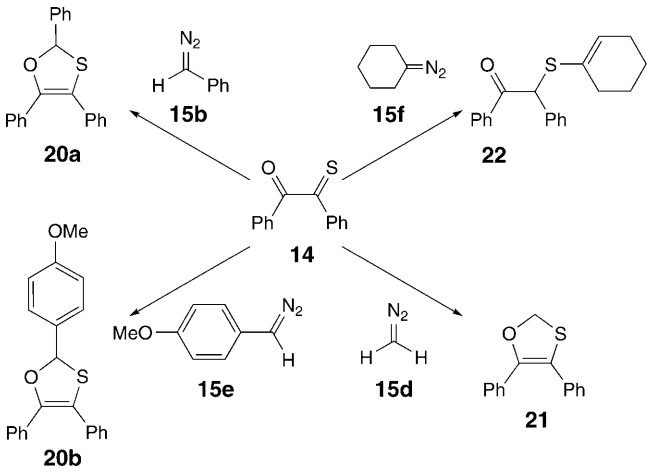
Fig. 1. *ORTEP Plots* [12] *of the molecular structure of* a) **17**, b) *one of the two conformations of* **18**, *and* c) **19** (50% probability ellipsoids, arbitrary numbering of the atoms)

of **14** with diazo(phenyl)methane (**15b**), diazomethane (**15d**), and diazo(4-methoxyphenyl)methane (**15e**) gave the expected 1,3-oxathiols **20a**, **21**, and **20b** in yields of 42, 40, and 60%, respectively (*Scheme 4*). In addition to the main product, namely the 1,3-oxathiols, the corresponding alkenes, which result from a 1,3-dipolar electrocyclization of the thiocarbonyl ylide, followed by a desulfurization, were observed as by-products, and not the *Schönberg* products. These by-products were themselves reactive and led to further by-products, which were neither isolated nor characterized.

The structure of **20b** was established by X-ray crystallography (*Fig. 2*). The five-membered ring has an envelope conformation with C(5) as the envelope flap. The planes of the Ph groups at C(2) and C(3) are twisted out of the plane defined by C(6), C(2), C(3), and C(12) by 57.6(2) and 33.1(2)°, respectively.

The results described above show that the synthesis of 1,3-oxathiols *via* 1,5-dipolar electrocyclization by starting from thioketones with a conjugated keto group is achievable with moderate-to-good yields. Under the chosen conditions, the 1,3-dipolar electrocyclization is a side reaction. Comparing the yields from the different experiments shows that the substituents of the diazo component have a significant influence on

Scheme 4



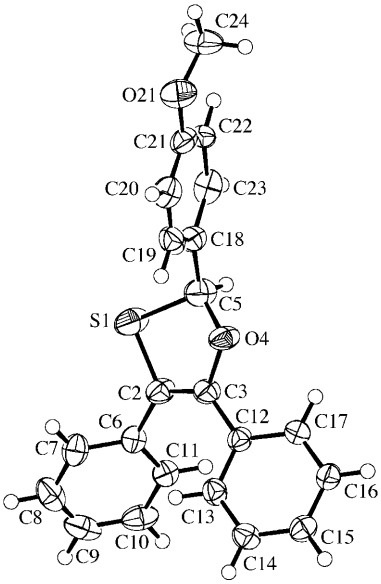
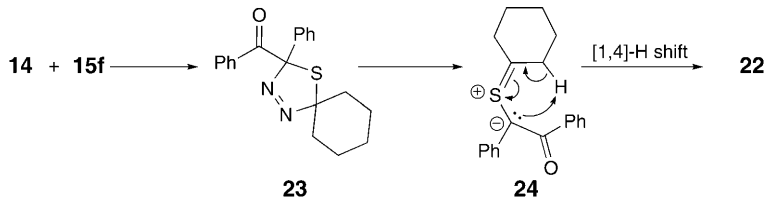


Fig. 2. *ORTEP Plot* [12] *of the molecular structure of* **20b** (50% probability ellipsoids, arbitrary numbering of the atoms)

the yields of the desired 1,3-oxathiols. The highest yield (81%) was observed in the already known reaction of **14** with **15a**, which leads to 1,3-oxathiol **13** [11] (*Scheme 3*).

The reaction of diazocyclohexane (**15f**) with **14** in CH_2Cl_2 at room temperature gave the sulfanyl derivative **22** in 40% yield (*Scheme 4*). The structure of **22** was again established by X-ray crystallography (*Fig. 3*). The cyclohexane ring has two equally occupied disordered orientations which differ by a rotation of *ca.* 180° about the S–C(15) bond. The formation of **22** is easily rationalized *via* the intermediate cycloadduct **23** and the thiocarbonyl ylide **24**, which does not undergo the 1,5-dipolar elec-

Scheme 5



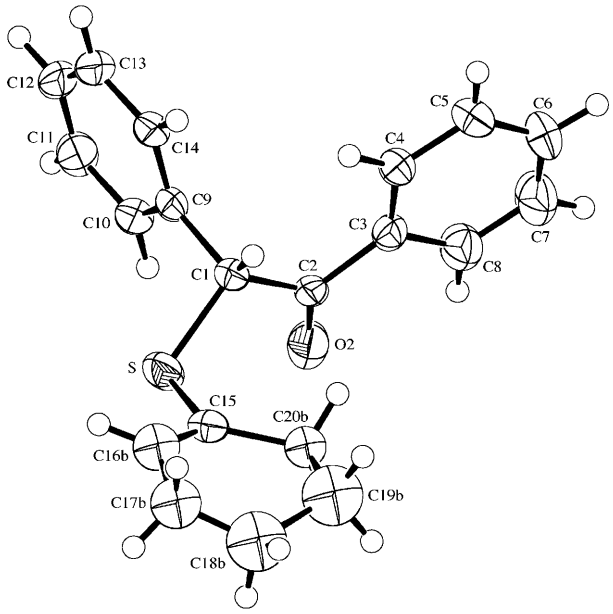


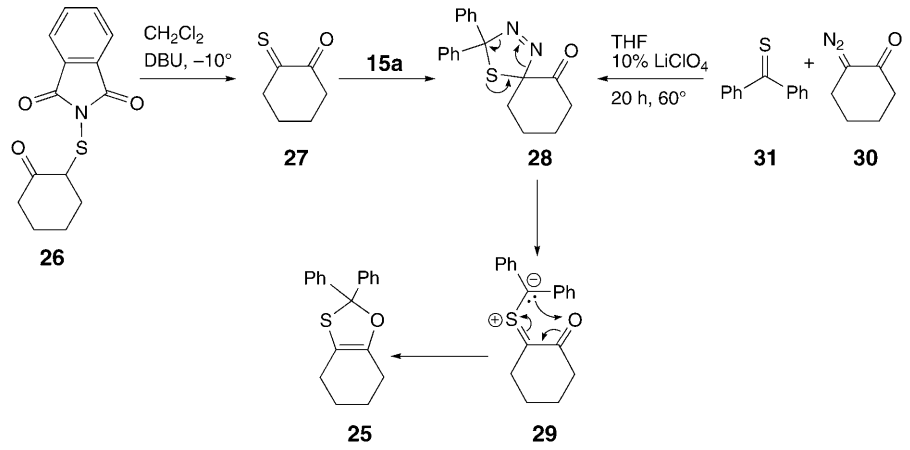
Fig. 3. *ORTEP Plot* [12] *of the molecular structure of one of the two disordered orientations of* **22** (50% probability ellipsoids, arbitrary numbering of the atoms)

trocyclization, but a [1,4]-H shift to give 2-[(cyclohex-1-enyl)sulfanyl]-1,2-diphenylethanone (**22**) (*Scheme 5*). Similar [1,4]-H shifts in thiocarbonyl ylides are known [5][6].

The synthesis of the fused 1,3-thioxole **25** was achieved by starting from 2-[(2-oxocyclohexyl)sulfanyl]-2*H*-isoindole-1,3-dione (**26**) and generating the intermediate 2-thioxocyclohexanone (**27**) by DBU-catalyzed elimination of phthalimide [13][14] (*Scheme 6*). In the presence of excess diazo(diphenyl)methane (**15a**), **27** underwent a cycloaddition to yield **28**, which eliminated N_2 spontaneously to give the thiocarbonyl ylide **29**. The subsequent reaction followed the expected pathway *via* 1,5-dipolar cyclization. The same 1,3-oxathiole, **25**, has been synthesized by *Kelmendi et al.* [9]. In this case, the starting material was 2-diazocyclohexanone (**30**), which reacted with thiobenzophenone (**31**) to give the same intermediate **28**. Because of the special reaction conditions, only the reaction with diazo(diphenyl)methane (**15a**) was successful.

The structure of **25** has been determined by X-ray crystallography (*Fig. 4*). The five-membered heterocycle has an envelope conformation with C(3) as the envelope flap, while the cyclohexene ring has a half-chair conformation twisted on C(7)–C(8).

Scheme 6



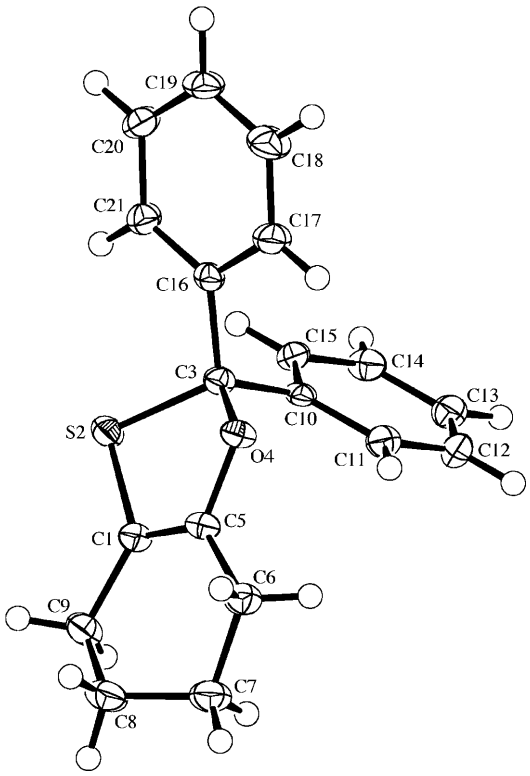
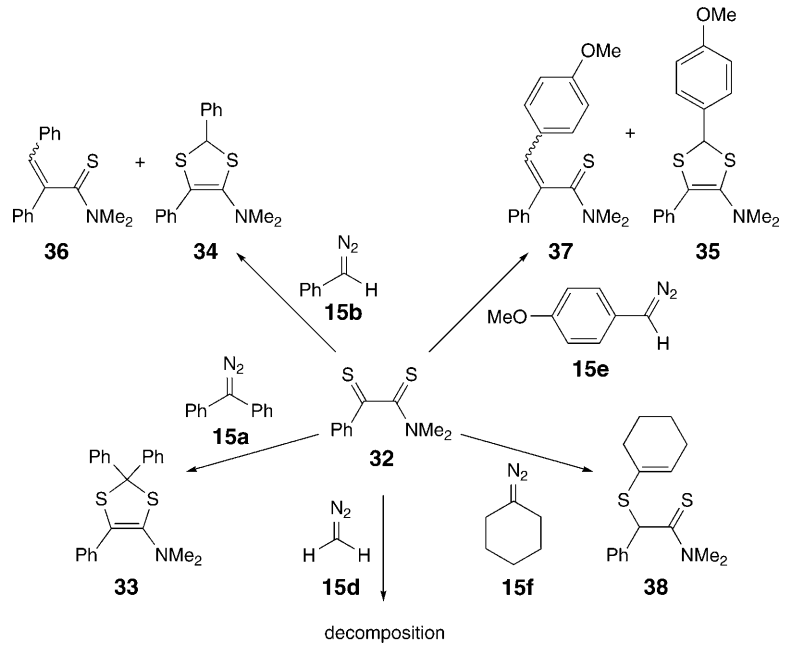


Fig. 4. *ORTEP Plot* [12] *of the molecular structure of* **25** (50% probability ellipsoids, arbitrary numbering of atoms)

Reactions with α-Thioxo Thioamides. After these encouraging results with α-thioxo ketones, we tried to find other systems, which would react analogously. α-Thioxo thio-

Scheme 7



amides of type **32** are easily available and possess an unsaturated system, the thioamide group, in conjugation with the C=S group. The reactions of **32** with diazo compounds showed that thiocarbonyl ylides are formed, which undergo a 1,5-dipolar electrocyclization to yield 1,3-dithiols **33**–**35** (*Scheme 7*). In all cases, the yields of the heterocyclic product were lower than with the thioxocarbonyl compound **14**. In the reactions of **32** with **15b** and **15e**, respectively, the 1,3-dipolar electrocyclization of the intermediate thiocarbonyl ylide is a more significant side reaction than in the case of **14**, and yields the corresponding α,β-unsaturated thioamides **36** and **37** after desulfurization[3]). The only reaction in which no side product was formed was that between diazo(diphenyl)methane (**15a**) and **32**. As in the case of α-thioxo ketone **14**, the reaction of **32** with diazocyclohexane (**15f**) led to the (cyclohexenyl)sulfanyl derivative **38** exclusively, which results from a [1,4]-H shift of the corresponding intermediate thiocarbonyl ylide. The reaction of **32** with diazomethane (**15d**) was carried out under the same conditions as those used in the case of **14**, but only decomposition was observed (TLC), and no reasonable product of a related reaction could be isolated.

The structures of the 1,3-dithiole **33** and α-sulfanyl thioamide **38** have been established by X-ray crystallography (*Fig. 5*).

Conclusions. – We have investigated several reactions of diazo compounds with thioketones, which contain a keto or a thioamide group in the α-position. The reactions

[3]) These side products could not be obtained in pure form, but only as mixtures of (*E*/*Z*)-isomers.

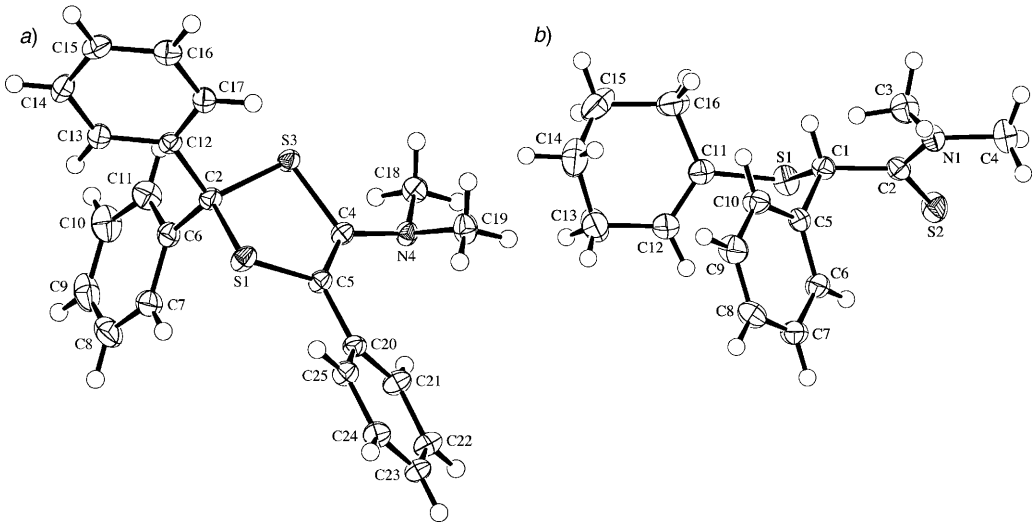


Fig. 5. *ORTEP Plot* [12] *of the molecular structure of* a) **33** *and* b) **38** (50% probability ellipsoids, arbitrary numbering of the atoms)

proceeded *via* thiocarbonyl ylides as intermediates, which, in most cases, underwent a 1,5-dipolar electrocyclization to give the corresponding five-membered ring containing the former thiocarbonyl S-atom, *i.e.*, 1,3-oxathioles and 1,3-dithioles, respectively. In some cases, a 1,3-dipolar electrocyclization of the thiocarbonyl ylide occurred to give the corresponding thiiranes, which spontaneously undergo desulfurization to yield the corresponding alkenes. Since 1,3-oxathioles with an H-atom in the ring are generally unstable under acidic conditions, they decomposed during chromatography on acidic or wet silica gel, and, in these cases, the *Schönberg* products **17**–**19** could be isolated, though in relatively low yields (10–25%).

The diazo compound used also seems to be decisive for the reaction pathway. When the diazo compound bears at least one H-atom in the β-position to the diazo group, *e.g.*, diazocyclohexane (**15f**), neither products of the 1,5- nor of the 1,3-dipolar electrocyclization could be isolated from the reaction with **14** or **32**. The only products isolated in these cases are products resulting from a [1,4]-H shift in the intermediate thiocarbonyl ylide. The behavior of the α-thioxo thioamide **32** under the chosen conditions is very much like that of α-thioxo ketones. However, the competition of the 1,3-dipolar electrocyclization of the thiocarboyl ylide, which produces the corresponding alkenes, is more pronounced.

We thank the analytical units of our institute for spectra and analyses, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for financial support.

Experimental Part

1. *General*. Solvents were purified prior to use by standard procedures. TLC: Glass plates covered with silica gel *60 F_{254}* (*Merck*); visualization by UV light or by spraying with 'mostain' soln. ($Ce(SO_4)_2$

(0.8 g), 10% H_2SO_4 (800 ml)) and heating (blue spots). Column chromatography (CC): silica gel *60* (*Merck*), 0.040 ± 0.063 mm. Medium-pressure liquid chromatography (MPLC): *Labomat VS-200* of *Labomatic* with a *HPP-VPC* column of *Kron-Lab* (length: 540 mm, inside Ø: 40 mm, max. pressure: 40 bar) was used. M.p. (not corrected): *Mettler FP 5/52*. IR Spectra: *Perkin-Elmer 1600 Series FT-IR* spectrometer; in cm^{-1}, characterization of the band intensities (transmission): 0–20% *vs*, 20–40% *s*, 40–60% *m*, 60–80% *w*. NMR Spectra: *Bruker ARX-300* (300 and 75.5 MHz, resp.); chemical shifts δ (in ppm) relative to $CDCl_3$ (7.27 resp. 77.0 ppm), coupling constants J in Hz; for assignments of ^{1}H-NMR signals, COSY, TOCSY, and NOESY 2D- or 1D-NMR methods were applied; for assignments of ^{13}C-NMR signals, HMBC and HSQC 2D-NMR methods were employed. If not stated otherwise, the spectra were recorded in $CDCl_3$. MS: *Varian SSQ 700*; ionization by EI (70 eV) or CI (NH_3); in *m/z*, rel. intensities (%).

2. *Starting Materials.* All thiocarbonyl derivatives or precursors, and the diazo compounds were prepared according to known protocols: *diazo(diphenyl)methane* (**15a**) [11], *diazo(phenyl)methane* (**15b**) [15], *diazomethane* (**15d**) [16], *diazocyclohexane* (**15f**) [17], *1,2-diphenyl-2-thioxoethanone* (**14**) [11], N,N-*dimethyl-2-phenyl-2-thioxothioacetamide* (**32**) [18], *2-[(2-oxocyclohexyl)sulfanyl]-2*H-*isoindole-1,3-dione* (**26**) [13][14]. All other reagents are commercially available.

3. *Yields.* Almost all of the diazo compounds are only stable in solution and were often used in excess. As most of the thiocarbonyl compounds were also only stable in solution, or they were synthesized *in situ*, the corresponding yields were approximated. The reported yields in these cases are based on experience [11] or on the volume of N_2 evolved. When this was not possible, *i.e.*, in cases of reactions lasting two or more days, yields were calculated over two or three reaction steps.

4. *General Procedure A* (*GP A*). To a soln. of thiocarbonyl compound (2–7 mmol) in CH_2Cl_2 (30–100 ml), the diazo compound (1–7 mmol) in toluene or benzene (30–130 ml) was added by means of a dropping funnel. After total conversion of the thiocarbonyl compound, monitored either by TLC, color change, or evolution of N_2[4]), the solvent was evaporated, and the mixture was analyzed and purified by chromatography using silica gel, which had been treated with 3% Et_3N. Furthermore, the solvent was doped with 1% of Et_3N.

General Procedure B (*GP B*). The same procedure as in *GP A* was followed, but the mixture was purified by chromatography without using Et_3N.

General Procedure C (*GP C*). To a suspension of 2*H*-isoindole-1,3-dione **26** (2–5 mmol) in CH_2Cl_2 (15–40 ml) at −10°, **15a** was added as a purple soln. in benzene (10–25 ml, 3–7 mmol). A catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added, and the evolution of N_2 was measured volumetrically. After stirring for a few min, the solvent was removed, and the mixture was analyzed and purified by chromatography.

5. *Reactions of 1,2-Diphenyl-2-thioxoethanone* (**14**) *with Diazoalkanes. (2,4-*trans-*4,5-*trans-*4-Benzoyl-2,4,5-triphenyl-1,3-dithiolane-2-yl)(phenyl)methanone* (**17**). According to *GP B*, **14** (3.9 mmol) in CH_2Cl_2 (60 ml) and **15b** (*ca.* 3.9 mmol) in toluene (150 ml) were used. The crude product was purified by CC (hexane/AcOEt 20:1) and recrystallized from hexane/AcOEt: 371 mg (20%) of **17**. Colorless crystals. M.p. 232–233°. IR (KBr): 3058*w*, 3028*w*, 2928*w*, 1679*vs*, 1595*s*, 1479*m*, 1489*m*, 1445*s*, 1395*w*, 1308*w*, 1228*vs*, 1184*s*, 1156*w*, 1080*w*, 1036*w*, 1018*m*, 1001*w*, 971*w*, 934*w*, 878*w*, 861*w*, 839*w*, 826*w*, 807*w*, 785*w*, 771*w*, 753*m*, 740*s*, 696*vs*, 685*s*, 658*s*, 650*s*. ^{1}H-NMR: 7.78–7.72 (*m*, 4 arom. H); 7.64–7.61 (*m*, 2 arom. H); 7.49–6.89 (*m*, 19 arom. H); 5.85 (*s*, H–C(5)). ^{13}C-NMR: 193.5, 191.5 (2*s*, 2 CO); 141.1, 135.8, 135.6, 134.1, 133.6 (5*s*, 5 arom. C); 133.3, 132.6, 130.7, 130.5, 130.1, 129.0, 128.4, 128.2, 128.0, 127.9, 127.8, 127.4, 126.6 (13*d*, 25 arom. CH); 79.5 (*s*, C(4)); 60.1 (*d*, C(5))[5]). CI-MS: 560 (100, $[M+NH_4]^+$), 543 (54, $[M+1]^+$), 317 (67, $[M-PhCOCSPh]^+$), 285 (41), 244 (28), 214 (19). Anal. calc. for $C_{35}H_{26}O_2S_2$ (542.72): C 77.46, H 4.83, S 11.82; found: C 77.51, H 4.91, S 11.80.

Crystals suitable for an X-ray crystal-structure determination were grown from CH_2Cl_2/hexane by slow evaporation of the solvent.

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[4]) The evolution of N_2 was determined volumetrically with a gas burette attached to the reaction vessel.

[5]) The signal for C(2) could not be detected.

Ethyl 2,4-cis-*4,5*-cis-*4,5-Dibenzoyl-4,5-diphenyl-1,3-dithiolane-2-carboxylate* (**18**). According to *GP B*, **14** (3.9 mmol) in CH_2Cl_2 (60 ml) and *ethyl diazoacetate* (**15c**; 1.02 g, 8.9 mmol) in Et_2O (20 ml) were used. The crude product was purified by CC (hexane/AcOEt 10:1), and the product was recrystallized from hexane/AcOEt: 458 mg (25%) of **18**. Colorless crystals. M.p. 195–197°. IR (KBr): 3058*w*, 3031*w*, 2984*w*, 2898*w*, 1710v*s*, 1697v*s*, 1673v*s*, 1595*m*, 1578*m*, 1490*m*, 1464*w*, 1445v*s*, 1395*w*, 1368*w*, 1221v*s*, 1182v*s*, 1160*m*, 1086*w*, 1022v*s*, 1002*w*, 971*w*, 959*w*, 933*w*, 900*w*, 872*w*, 850*w*, 806*w*, 790*w*, 766*s*, 715v*s*, 698v*s*, 660*m*, 642v*s*. ^{1}H-NMR ((D_6)DMSO): 7.57–6.61 (*m*, 20 arom. H); 5.89 (*s*, H–C(2)); 3.78 (*qd*-like, CH_2); 0.70 (*t*, $J=7.1$, Me). ^{13}C-NMR ((D_6)DMSO): 195.1, 191.8 (2*s*, 2 CO); 167.9 (*s*, C(O)O); 139.4, 136.6, 135.7, 133.2 (4*s*, 4 arom. C); 132.3, 131.4, 130.2, 129.2, 128.2, 127.9, 127.4, 127.2, 126.8 (9*d*, 20 arom. H); 80.8, 79.4 (2*s*, C(4), C(5)); 61.6 (*t*, CH_2); 47.6 (*d*, C(2)); 13.0 (*q*, Me)[6]. CI-MS: 556 (7, $[M+NH_4]^+$), 539 (9, $[M+1]^+$), 390 (31), 389 (100). Anal. calc. for $C_{32}H_{26}O_4S_2$ (538.69): C 71.35, H 4.87, S 11.91; found: C 71.37, H 4.68, S 11.62.

Crystals suitable for an X-ray crystal-structure determination were grown from CH_2Cl_2/AcOEt by slow evaporation of the solvent.

trans-*(5-Benzoyl-4,5-diphenyl-1,3-dithiolane-4-yl)(phenyl)methanone* (**19**). According to *GP B*, **14** (3.9 mmol) in CH_2Cl_2 (60 ml) and **15d** (*ca.* 4–6 mmol) in Et_2O (8 ml) were used. After 10 min stirring, a small amount of AcOH was added dropwise until the N_2 evolution ceased. The crude product was purified by CC (hexane/AcOEt 10:1): 302 mg (15%) of **19**. Colorless crystals. M.p. 189° (dec.). IR (KBr): 3087*w*, 3061*m*, 3030*w*, 2985*w*, 2929*w*, 1681v*s*, 1594*s*, 1578*s*, 1493*s*, 1444v*s*, 1414*m*, 1317*w*, 1302*w*, 1216v*s*, 1197v*s*, 1182v*s*, 1100*m*, 1085*m*, 1035*m*, 1010v*s*, 973*w*, 937*w*, 871*w*, 842*w*, 786*w*, 769*s*, 753*w*, 742*w*, 700v*s*, 638*w*, 611v*s*. ^{1}H-NMR: 7.39–7.35 (*m*, 8 arom. H); 7.25–7.15 (*m*, 8 arom. H); 7.08–7.03 (*m*, 4 arom. H); 3.96 (*s*, CH_2). ^{13}C-NMR: 190.0 (*s*, 2 CO); 136.2, 133.3 (2*s*, 4 arom. C); 132.9, 131.0, 130.1, 128.3, 127.3, 126.9 (6*d*, 20 arom. CH); 78.5 (*s*, C(4), C(5)); 32.3 (*t*, CH_2). EI- and CI-MS: no measurement possible. Anal. calc. for $C_{29}H_{22}O_2S_2$ (466.63): C 74.65, H 4.75, S 13.74; found: C 74.90, H 4.61, S 13.45.

Crystals suitable for an X-ray crystal-structure determination were grown from AcOEt by slow evaporation of the solvent.

4,5-Diphenyl-1,3-oxathiole (**21**). According to *GP A*, **14** (*ca.* 4 mmol) in CH_2Cl_2 (83 ml) and **15d** (*ca.* 5 mmol) in Et_2O (*ca.* 50 ml) were used. The crude product was purified by CC (hexane/AcOEt 4:1+3% Et_3N) and recrystallized from hexane/Et_2O: 368 mg (*ca.* 40%) of **21**. Yellowish crystals. M.p. 41–43°. IR (*Golden Gate*, ATR): 3057*w*, 3032*w*, 2915*w*, 2856*w*, 1691*w*, 1616*m*, 1593*m*, 1571*m*, 1494*m*, 1443*m*, 1329*m*, 1313*w*, 1297*w*, 1208*m*, 1072*w*, 1058*s*, 1028*m*, 1000*m*, 988*m*, 942*s*, 924*m*, 847*m*, 771*m*, 755v*s*, 742*s*, 693v*s*, 675*s*. ^{1}H-NMR: 7.36–7.18 (*m*, 10 arom. H); 5.69 (*s*, CH_2(2)). ^{13}C-NMR: 143.9 (*s*, C(5)); 132.4, 130.4 (2*s*, 2 arom. C); 129.0, 128.5, 128.2, 128.0, 127.7, 127.4 (6*d*, 10 arom. CH); 111.4 (*s*, C(4)); 72.7 (*t*, CH_2(2)). CI-MS (NH_3): 242 (17), 241 (100, $[M+1]^+$).

2,4,5-Triphenyl-1,3-oxathiole (**20a**). According to *GP A*, **14** (*ca.* 2.4 mmol) in CH_2Cl_2 (30 ml) and **15b** (*ca.* 3 mmol) in toluene (100 ml) were used. The crude product was purified by CC (hexane/AcOEt 5:1+3% Et_3N) and recrystallized from hexane/CH_2Cl_2: 317 mg (*ca.* 45%) of **20a**. Yellowish crystals. M.p. 74–75°. IR (*Golden Gate*, ATR): 3058*w*, 3034*w*, 2887*w*, 2868*w*, 1620*w*, 1598*w*, 1573*w*, 1494*w*, 1453*w*, 1444*w*, 1318*w*, 1248*m*, 1215*w*, 1056*m*, 1024*w*, 990*m*, 954*m*, 916*w*, 877*w*, 827*w*, 780*w*, 752*s*, 715*m*, 692*s*, 684*s*. ^{1}H-NMR: 7.66–7.21 (*d*-like, 2 arom. H); 7.44–7.17 (*m*, 13 arom. H); 7.04 (*s*, CH(2)). ^{13}C-NMR: 142.6 (*s*, C(5)); 139.6, 132.5, 130.6 (3*s*, 3 arom. C); 129.2, 129.1, 128.7, 128.3, 128.2, 127.8, 127.6, 126.4 (8*d*, 15 arom. CH); 111.3 (*s*, C(4)); 87.3 (*d*, CH(2)). CI-MS (NH_3): 318 (22), 317 (100, $[M+1]^+$). Anal. calc. for $C_{21}H_{16}OS$: C 79.71, H 5.10, S 10.13; found: C 79.62, H 4.95, S 10.17.

2-(4-Methoxyphenyl)-4,5-diphenyl-1,3-oxathiole (**20b**). According to *GP A*, **14** (*ca.* 2 mmol) in CH_2Cl_2 (30 ml) and **15e** (*ca.* 3 mmol) in benzene (20 ml) were used. The crude product was purified by CC (hexane/AcOEt 30:1+1% Et_3N) and recrystallized from hexane/CH_2Cl_2: 410 mg (40–55%) of **20b**. Yellowish crystals. M.p. 104–108°. IR (*Golden Gate*, ATR): 3056*w*, 3007*w*, 2956*w*, 2928*w*, 2906*w*, 2869*w*, 2834*w*, 1686*w*, 1625*w*, 1609*m*, 1585*w*, 1511*s*, 1494*m*, 1464*w*, 1443*m*, 1356*w*, 1317*w*, 1305*m*, 1289*w*, 1243v*s*, 1218*m*, 1171*s*, 1107*w*, 1082*w*, 1056*s*, 1026*s*, 984*m*, 956*m*, 915*w*, 881*w*, 833*s*, 777*m*, 763*m*, 754*s*, 697*s*, 683*s*. ^{1}H-NMR: 7.63–7.58 (*d*-like, 2 arom. H); 7.39–7.18 (*m*, 10 arom. H); 7.01 (*s*, CH(2));

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[6]) Because of the doubling of some signals, the compound is either a mixture of isomers or conformers.

6.96–6.91 (*d*-like, 2 arom. H); 3.82 (*s*, MeO). ^{13}C-NMR: 160.4 (*s*, 1 arom. C); 143.0 (*s*, C(5)); 132.6, 131.4, 130.7 (3*s*, 3 arom. C); 129.1, 128.6, 128.2, 128.1, 127.7, 127.6 (6*d*, 12 arom. CH); 114.0 (*d*, 2 arom. CH); 111.8 (*s*, C(4)); 87.4 (*d*, C(2)); 55.4 (*q*, MeO). CI-MS (NH_3): 348 (24), 347 (100, $[M+1]^+$), 315 (39, $[M-MeO]^+$). ESI-MS: 369 (100, $[M+Na]^+$).

Crystals suitable for an X-ray crystal-structure determination were grown from hexane/AcOEt by slow evaporation of the solvent.

2-[(Cyclohex-1-enyl)sulfanyl]-1,2-diphenylethanone (**22**). According to *GP B*, a soln. of **15f** (*ca.* 7 mmol) in CH_2Cl_2 (40 ml) was added dropwise to a soln. of **14** (*ca.* 6.4 mmol) in CH_2Cl_2 (100 ml). Purification of the crude product by MPLC (hexane/AcOEt 20:1) afforded 790 mg (40%) of **22**. Yellowish crystals. M.p. 61–63°. IR (KBr): 3062*w*, 3027*w*, 2936v*s*, 2909*s*, 2859*s*, 2834*m*, 1672v*s*, 1596*s*, 1580*s*, 1493*m*, 1451v*s*, 1433*m*, 1342*m*, 1322*m*, 1307*m*, 1296*m*, 1274*s*, 1212*m*, 1191*s*, 1169*s*, 1136*m*, 1075*m*, 1054*w*, 1007*s*, 999*s*, 929*w*, 914*m*, 868*w*, 844*w*, 831*w*, 797*w*, 782*w*, 758*s*, 723*s*, 694v*s*, 681*s*, 640*s*. ^{1}H-NMR ((D_6)DMSO): 8.09–8.06 (*m*, 2 arom. H); 7.64–7.59 (*m*, 1 arom. H); 7.52–7.47 (*m*, 4 arom. H); 7.35–7.24 (*m*, 3 arom. H); 6.22 (*s*, H–C(2)); 5.70–5.68 (*m*, =CH)[7]); 1.94–1.40 (*m*, 4 CH_2). ^{13}C-NMR ((D_6)DMSO): 195.0 (*s*, CO); 136.8, 135.3 (2*s*, 2 arom. C); 130.6 (*s*, =C–S); 133.5 (*d*, C(2)); 129.3, 128.7, 128.4, 127.6 (4*d*, 10 arom. CH); 54.1 (*d*, =CH); 30.1, 25.9, 22.8, 21.1 (4*t*, 4 CH_2). CI-MS: 310 (23), 309 (100, $[M+1]^+$), 214 (32). Anal. calc. for $C_{20}H_{20}OS$ (308.44): C 77.88, H 6.54, S 10.40; found: C 77.69, H 6.37, S 10.10.

Crystals suitable for an X-ray crystal-structure determination were grown from hexane/AcOEt by slow evaporation of the solvent.

6. *Reaction of 2-Thioxocyclohexanone* (**27**) *with Diazo(diphenyl)methane* (**15a**). *4,5,6,7-Tetrahydro-2,2-diphenyl-1,3-benzoxathiole* (**25**). According to *GP C*, a suspension of *2-[(2-oxocyclohexyl)sulfanyl]-2*H*-isoindole-1,3-dione* (**26**; 1.0 g, 3.6 mmol) [13][14] was treated with a catalytic amount of DBU and an excess of **15a** in Et_2O. CC (hexane/AcOEt 15:1) yielded 702 mg (51%) of **25**. Pale-bluish crystals. M.p. 107–109°. IR (KBr): 3080*w*, 3059*w*, 3019*w*, 3001*w*, 2950*s*, 2917*s*, 2884*m*, 2855*m*, 2841*s*, 1682*s*, 1598*w*, 1585*w*, 1488*s*, 1445v*s*, 1388*w*, 1353*w*, 1340*m*, 1313*w*, 1289*w*, 1261*w*, 1225*m*, 1206*s*, 1176v*s*, 1145v*s*, 1133*s*, 1109*w*, 1071*m*, 1028*s*, 997*m*, 986v*s*, 958*s*, 933*w*, 916*m*, 900*m*, 882*s*, 857*w*, 836*w*, 819*w*, 763v*s*, 754v*s*, 696v*s*. ^{1}H-NMR: 7.54–7.50 (*m*, 4 arom. H); 7.34–7.23 (*m*, 6 arom. H); 2.29–2.24 (*m*, 2 H); 2.17–2.12 (*m*, 2 H); 1.73–1.65 (*m*, 4 H). ^{13}C-NMR: 144.7 (*s*, 2 arom. C); 143.1 (*s*, C(7a)); 128.0, 127.9, 126.4 (3*d*, 10 arom. CH); 104.5, 100.7 (2*s*, C(2), C(3a)); 24.2, 23.5, 23.0, 22.4 (4*t*, 4 CH_2). EI-MS: 294 (26, $M^{+\cdot}$), 266 (11), 262 (23), 261 (100), 237 (28), 223 (13), 187 (15), 167 (18), 166 (10), 165 (49), 105 (21, $[PhCO]^+$), 77 (14, Ph^+). Anal. calc. for $C_{19}H_{18}OS$ (294.42): C 77.51, H 6.16; found: C 77.49, H 6.08.

Crystals suitable for an X-ray crystal-structure determination were grown from hexane by slow evaporation of the solvent.

7. *Reactions of* N,N-*Dimethyl-2-phenyl-2-thioxothioacetamide* (**32**) *with Diazoalkanes.* N,N-*Dimethyl*-N-*(2,2,5-triphenyl-1,3-dithiol-4-yl)amine* (**33**). According to *GP A*, a soln. of **32** (200 mg, 1.1 mmol) in CH_2Cl_2 (20 ml) and **15a** (*ca.* 1.5 mmol) in benzene (15 ml) were used. The crude product was purified by CC (hexane/AcOEt 10:1 to 4:1): 170 mg (*ca.* 43%) of **33**. Yellowish crystals. M.p. 122–125°. IR: 3053*w*, 3013*m*, 2986*m*, 2950*m*, 2923*m*, 2897*m*, 2862*m*, 2834*m*, 2792*m*, 1659*w*, 1590*m*, 1570*s*, 1553v*s*, 1483v*s*, 1452*s*, 1440v*s*, 1406*m*, 1311*s*, 1210*m*, 1071*s*, 1045*s*, 1033*s*, 998*m*, 961*m*, 902*m*, 861*s*, 833*m*, 800*w*, 756v*s*, 737v*s*, 698v*s*, 690v*s*, 658*s*, 629*m*, 618*m*, 608*m*. ^{1}H-NMR: 7.62–7.54 (*d*-like, 4 arom. CH); 7.43–7.37 (*d*-like, 2 arom. CH); 7.25–7.05 (*m*, 9 arom. CH); 2.42 (*s*, Me_2N). ^{13}C-NMR: 143.7 (*s*, 2 arom. C); 142.7 (*s*, arom. C); 134.5 (*s*, C(4)); 129.2, 128.3, 128.0, 127.9, 127.8, 127.4, 126.7 (7*d*, 15 arom. C); 117.6 (*s*, C(5)); 70.5 (*s*, C(2)); 44.2 (*q*, Me_2N). CI-MS (NH_3): 378 (12), 377 (28), 376 (100, $[M+1]^+$), 344 (24, $[M-S+1]^+$), 199 (17), 180 (15).

Crystals suitable for an X-ray crystal-structure determination were grown from hexane/CH_2Cl_2 by slow evaporation of the solvent.

N-*(2,5-Diphenyl-1,3-dithiol-4-yl)*-N,N-*dimethylamine* (**34**). According to *GP A,* a suspension of **32** (250 mg, 1.2 mmol) in toluene (20 ml) and **15b** (*ca.* 15 mmol) in toluene (100 ml) were used. The mixture was separated by CC (hexane/AcOEt 10:1+1% Et_3N): 90 mg (*ca.* 25%) of **34** and 80 mg (*ca.* 25%) of a mixture of *(*E*)-* and *(*Z*)-*N,N-*Dimethyl-2,3-diphenylprop-2-enethioamide* (**36**).

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[7]) When the spectrum was recorded in $CDCl_3$, the signals of CH(2) and =CH overlap.

Data of **34**. Yellowish oil. IR (KBr): 3059*m*, 3026*m*, 2932*m*, 2863*m*, 2788*w*, 1679*s*, 1647v*s* (enamine), 1597*s*, 1580*s*, 1554*m*, 1514*s*, 1493v*s*, 1451v*s*, 1392v*s*, 1333*w*, 1273*s*, 1206*m*, 1176*m*, 1142*s*, 1073*s*, 1030*m*, 1001*w*, 993*w*, 963*w*, 939*w*, 905*w*, 886*w*, 860*w*, 837*w*, 808*w*, 782*w*, 755*s*, 726*s*, 697v*s*. ^{1}H-NMR: 7.62–7.51 (*m*, 4 arom. H); 7.36–7.18 (*m*, 6 arom. H); 5.78 (*s*, CH(2)); 2.59 (*s*, Me_2N). ^{13}C-NMR: 141.4 (*s*, C(4)); 141.1, 134.1 (2*s*, 2 arom. C); 128.6, 128.2, 128.0, 126.9, 126.7 (5*d*, 10 arom. CH); 115.1 (*s*, C(5)); 50.0 (*d*, C(2)); 44.2 (*q*, Me_2N). CI-MS (NH_3): 301 (21), 300 (100, $[M+1]^+$).

Data of **36**. IR (KBr): 3078*m*, 3054*m*, 3022*m*, 2929*s*, 2857*m*, 1598*m*, 1574*w*, 1513v*s*, 1494v*s*, 1446v*s*, 1391v*s*, 1318*w*, 1269v*s* ($CSNMe_2$), 1203*w*, 1181*m*, 1146v*s*, 1116v*s*, 1076*s*, 1049*m*, 1030*m*, 1000*w*, 949*m*, 922*m*, 886*m*, 870*w*, 796*w*, 765v*s*, 714v*s*, 695v*s*. ^{1}H-NMR: 7.57–7.06 (*m*, 10 arom. H); 6.73, 6.69 (2*s* (1:3.5), =CH); 3.56, 3.49, 3.28, 3.12 (4*s* (1:3:3:1), Me_2N). ^{13}C-NMR (only the signals of the main isomer are given): 201.7 (*s*, CS); 143.4 (*s*, C(2)); 135.8, 135.5 (2*s*, 2 arom. C); 129.3, 128.7, 128.6, 128.5, 128.1, 127.8, 127.4 (7*d*, 10 arom. CH, =CH); 43.1, 42.9 (2*q*, Me_2N). CI-MS (NH_3): 269 (19), 268 (100, $[M+1]^+$).

N-*[2-(4-Methoxyphenyl)-5-phenyl-1,3-dithiol-4-yl]*-N,N-*dimethylamine* (**35**). According to *GP A*, a suspension of **32** (280 mg, 1.34 mmol) in toluene (20 ml) and **15e** (*ca.* 2 mmol) in benzene (20 ml) were used. The mixture was separated by CC (hexane/AcOEt 10:1+1% Et_3N): 80 mg (*ca.* 20%) of **35**, and 52 mg (*ca.* 13%) of *(*E/Z*)-3-(4-Methoxyphenyl)*-N,N-*dimethyl-2-phenylprop-2-enethioamide* (**37**).

Data of **35**. Yellowish oil. IR (*Golden Gate*, ATR): 3058*w*, 3026*w*, 2931*w*, 2362*w*, 1678*w*, 1645*m*, 1596*w*, 1579*w*, 1551*w*, 1492*w*, 1449*m*, 1393*w*, 1314*w*, 1266*w*, 1244*w*, 1206*w*, 1175*w*, 1144*w*, 1103*w*, 1073*w*, 1028*w*, 993*w*, 904*w*, 846*w*, 755*w*, 725*m*, 694*s*. ^{1}H-NMR: 7.55–7.51 (*m*, 4 arom. H); 7.32–7.18 (*m*, 3 arom. H); 6.88–6.83 (*m*, 2 arom. H); 5.80 (*s*, CH(2)); 3.79 (*s*, MeO); 2.59 (*s*, Me_2N). ^{13}C-NMR: 159.6 (*s*, arom. C); 141.4 (*s*, C(4)); 134.1, 133.0, 129.9 (3*s*, 3 arom. C); 128.2, 128.2, 128.0, 126.6 (4*d*, 7 arom. CH); 113.9 (*d*, 2 arom. CH); 55.2 (*q*, MeO); 49.9 (*d*, CH(2)); 44.2 (*q*, Me_2N). CI-MS (NH_3): 331 (21), 330 (100, $[M+1]^+$).

Data of **37**[8]). ^{1}H-NMR: 8.60 (*s*, =CH); 7.79–7.76 (*d*-like, arom. H); 7.54–7.51 (*d*-like, arom. H); 7.46–7.25 (*m*, arom. H); 7.03–6.81 (*m*, arom. H); 6.69–6.64 (*s*, =CH); 3.81, 3.74 (2*s* (1:4), MeO); 3.57, 3.48, 3.27, 3.13 (4*s* (1:3:3:1), Me_2N). ^{13}C-NMR: 202.1 (*s*, CS); 159.0 (*s*, arom. C); 141.6, 136.2 (2*s*, 2 arom. C); 130.7, 129.3, 128.6, 127.9 (4*d*, 7 arom. CH); 113.4 (*d*, 2 arom. CH); 55.2 (*s*, MeO); 43.2, 43.0 (2*q*, Me_2N). CI-MS (NH_3): 299 (21), 298 (100, $[M+1]^+$), 269 (14, $[M\text{-}Me_2NH+NH_3]^+$).

2-[(Cyclohex-1-enyl)sulfanyl]-N,N-*dimethyl-2-phenylethanethioamide* (**38**). According to *GP A*, a soln. of **32** (313 mg, 1.5 mmol) in CH_2Cl_2 (25 ml) and **15f** (*ca.* 2 mmol) in CH_2Cl_2 (15 ml) were used. The crude product was purified by CC (hexane/AcOEt 10:1 to 4:1): 240 mg (*ca.* 55%) of **38**. Yellowish crystals. M.p. 110–111°. IR: 3079*w*, 3053*w*, 3024*m*, 3002*w*, 2940v*s*, 2918v*s*, 2851*s*, 2826*s*, 2657*w*, 1636*w*, 1600*w*, 1511v*s*, 1493v*s*, 1452*s*, 1435*s*, 1413*s*, 1385v*s*, 1339*m*, 1267v*s*, 1237*s*, 1182*m*, 1133v*s*, 1110v*s*, 1072*m*, 1051*m*, 1036*m*, 911*w*, 901*w*, 846*w*, 830*w*, 796*m*, 752*m*, 728v*s*, 698*s*, 640*w*. ^{1}H-NMR: 7.55–7.52 (*d*-like, 2 arom. H); 7.35–7.23 (*m*, 3 arom. H); 5.86–5.83 (*m*, =CH); 5.59 (*s*, CH(2)); 3.47, 3.22 (2*s*, Me_2N); 2.22–2.00 (*m*, 4 H, cyclohexenyl); 1.69–1.49 (*m*, 4 H, cyclohexenyl). ^{13}C-NMR: 199.8 (*s*, C=S); 137.8 (*s*, arom. C); 132.0 (*d*, arom. C); 131.8 (*s*, =C–S); 128.3, 127.7, 127.6 (3*d*, 4 arom. C); 60.3 (*d*, C(2)); 45.3, 42.4 (*q*, Me_2N); 30.8, 26.6, 23.3, 21.5 (4*t*, 4 CH_2). EI-MS: 291 (9, M^+), 259 (40, $[M-S]^+$), 216 (20, $[M-S-Me_2N]^+$), 182 (22), 178 (52, $[M-S-$cyclohexenyl$]^+$) 146 (100, $[M-2S-$cyclohexenyl$]^+$), 131 (39), 116 (19).

Crystals suitable for an X-ray crystal-structure determination were grown from hexane/CH_2Cl_2, by slow evaporation of the solvent.

8. *X-Ray Crystal-Structure Determinations of* **17**, **18**, **19**, **20b**, **22**, **25**, **33**, *and* **38** (*Tables 1* and *2*, and *Figs. 1–5*)[9]). In the case of **17**, all measurements were made on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and a 12-kW rotating anode generator. In all other cases, all measurements were performed on a *Nonius KappaCCD* diffractometer [19] using graph-

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[8]) Some signals of the NMR spectra indicate the presence of (*E*/*Z*)-isomers of **37**. In the ^{13}C-NMR spectrum, only signals of the main isomer are given.

[9]) CCDC-608137–608144 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center via* http://www.ccdc.cam.ac.uk/data_request/cif.

ite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. The data collection and refinement parameters are given in *Tables 1* and *2*, and views of the molecules are shown in *Figs. 1–5*. For **17**, the intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Equivalent reflections were merged. For all other structures, data reduction was performed with *HKL Denzo* and *Scalepack* [20]. The intensities were corrected for *Lorentz* and polarization effects, and with the exception of **18**, an absorption correction based on the multi-scan method [21] was applied. Equivalent reflections were merged, except for the *Friedel* pairs in **20b** and **33**. The structures

Table 1. *Crystallographic Data of Compounds* **17**, **18**, **19**, **22**, *and* **25**

	17	**18**	**19**	**22**	**25**
Crystallized from	CH_2Cl_2/hexane	CH_2Cl_2/AcOEt	AcOEt	hexane/AcOEt	hexane
Empirical formula	$C_{35}H_{26}O_2S_2$	$C_{32}H_{26}O_4S_2$	$C_{29}H_{22}O_2S_2$	$C_{20}H_{20}OS$	$C_{19}H_{18}OS$
Formula weight [g mol^{-1}]	542.71	538.67	466.61	308.44	294.41
Crystal color, habit	colorless, tablet	colorless, prism	colorless, prism	pale-yellow, prism	colorless, prism
Crystal dimensions [mm]	0.18×0.30×0.43	0.22×0.30×0.30	0.15×0.15×0.20	0.12×0.18×0.27	0.20×0.22×0.25
Temp. [K]	173(1)	298(1)	160(1)	160(1)	160(1)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Z	4	2	4	4	4
Reflections for cell determination	25	6604	43672	34702	25782
2θ Range for cell determination [°]	21–37	5–74	2–60	2–55	4–60
Unit cell parameters					
a [Å]	19.819(3)	10.2453(2)	14.3898(1)	9.6064(2)	8.5780(1)
b [Å]	9.031(4)	10.4024(1)	9.5516(1)	10.4524(2)	12.5949(2)
c [Å]	16.328(3)	13.8478(2)	17.1675(2)	16.5859(3)	13.9084(2)
α [°]	90	100.2566(6)	90	90	90
β [°]	106.39(1)	98.8651(6)	105.2059(4)	101.7945(7)	96.2541(7)
γ [°]	90	106.5469(6)	90	90	90
V [Å^3]	2804(1)	1358.90(4)	2276.99(4)	1630.23(5)	1493.71(4)
D_x [g cm^{-3}]	1.285	1.316	1.361	1.257	1.309
μ(MoK_a) [mm^{-1}]	0.221	0.232	0.259	0.198	0.213
Scan type	$\omega/2\theta$	ω	ϕ and ω	ϕ and ω	ϕ and ω
$2\theta_{(max)}$ [°]	55	55	60	55	60
Transmission factors (min; max)	–	–	0.825; 0.964	0.861; 0.978	0.897; 0.959
Total reflections measured	7085	22427	59019	36152	39877
Symmetry independent reflections	6447	6226	6668	3734	4358
Reflections used [$I>2\sigma(I)$]	4411	4633	5450	2871	3384
Parameters refined	352	353	298	194	190
Final R	0.0661	0.0494	0.0398	0.0784	0.0433
wR	0.0691	0.0558	0.0466	0.0832	0.0414
Weights: p in $w=[\sigma^2(F_o)+(pF_o)^2]^{-1}$	0.005	0.01	0.01	0.007	0.005
Goodness-of-fit	2.401	2.162	2.302	4.726	2.484
Final Δ_{max}/σ	0.0003	0.02	0.001	0.0003	0.0004
$\Delta\rho$ (max; min) [e Å^{-3}]	0.71; −0.41	0.37; −0.26	0.38; −0.25	0.85; −0.47	0.31; −0.27

Table 2. *Crystallographic Data of Compounds* **20b**, **33**, *and* **38**

	20b	**33**	**38**
Crystallized from	hexane/AcOEt	hexane/CH_2Cl_2	hexane/CH_2Cl_2
Empirical formula	$C_{22}H_{18}O_2S$	$C_{23}H_{21}NS_2$	$C_{16}H_{21}NS_2$
Formula weight [g mol^{-1}]	346.44	375.55	291.47
Crystal color, habit	pale yellow, prism	yellow, plate	colorless, tablet
Crystal dimensions [mm]	$0.17\times0.20\times0.25$	$0.07\times0.27\times0.27$	$0.08\times0.20\times0.35$
Temp. [K]	160(1)	160(1)	160(1)
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$
Z	4	4	4
Reflections for cell determination	40845	21978	24601
2θ Range for cell determination [°]	4–55	4–60	4–60
Unit cell parameters			
a [Å]	5.5779(3)	9.2847(2)	6.4888(1)
b [Å]	8.1397(5)	12.7753(2)	16.6408(3)
c [Å]	38.894(2)	15.7321(3)	14.2958(2)
β [°]	90	90	99.210(1)
V [Å^3]	1765.9(2)	1866.06(6)	1523.74(4)
D_x [g cm^{-3}]	1.303	1.337	1.270
μ(MoK_a) [mm^{-1}]	0.195	0.292	0.336
Scan type	ϕ and ω	ϕ and ω	ϕ and ω
$2\theta_{(max)}$ [°]	55	60	60
Transmission factors (min; max)	0.844; 0.954	0.908; 0.982	0.895; 0.979
Total reflections measured	14153	36680	42595
Symmetry independent reflections	3957	5451	4459
Reflections with $I>2\sigma(I)$	2650	4864	3473
Reflections used in refinement	3955	5450	4457
Parameters refined	228	237	174
Final $R(F)$ ($I>2\sigma$ (I) reflections)	0.0630	0.0338	0.0404
$wR(F^2)$ (all data)	0.1608	0.0783	0.1104
Weighting parameters (a; b)[a]:	0.0649; 1.0748	0.0348; 0.4491	0.0517; 0.5980
Goodness-of-fit	1.040	1.053	1.040
Final Δ_{max}/σ	0.001	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.55; −0.24	0.21; −0.31	0.31; −0.38

[a]) $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$ where $P=(F_o^2+2F_c^2)/3$

were solved by direct methods using SHELXS97 [22] (**17** and **18**) and SIR92 [23] (**19**, **20b**, **22**, **25**, **33**, and **38**), which revealed the positions of all non-H-atoms. In the case of **18**, the terminal Me group of the ethyl ester side chain is disordered, and two equally occupied positions were refined for this group. The cyclohexene ring of **22** is also disordered, and the two conformations differ by a rotation of *ca.* 180° about the S–C(15) bond. Two positions with equal site-occupation factors were defined for each unsubstituted C-atom in the ring. However, some poor C–C bond lengths and elongated atomic displacement ellipsoids, when these atoms were refined anisotropically, suggest that the model does not fully describe the disorder, and that the ring may adopt several conformations. The non-H-atoms were refined anisotropically in all structures, except for the disordered atoms of **22**, which were refined only isotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups in **20b**, **33**, and **38**). The refinement of the structures **17**, **18**, **19**, **22**, and **25** was carried out on F using full-matrix least-squares procedures, which minimized the function

$\Sigma w(|F_o| - |F_c|)^2$. The refinement of **20b**, **33**, and **38** was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the cases of **18** and **20b**. Compound **33** is achiral, but crystallized in a non-centrosymmetric space group. Refinement of the absolute structure parameter [24] yielded a value of 0.00(5), which confidently confirms that the refined coordinates represent the true absolute structure. The absolute structure parameter for **20b** refined to 0.35(15), which is insufficiently precise to be able to deduce any information about the absolute configuration of the molecule. The presence of an inversion twin cannot be excluded. According to the preparation of the material, it has to be racemic. Neutral-atom scattering factors for non-H-atoms were taken from [25a], and the scattering factors for H-atoms were taken from [26]. Anomalous dispersion effects were included in F_c [27]; the values for f' and f'' were those of [25b]. The values of the mass attenuation coefficients are those of [25c]. All calculations were performed using the teXsan [28] (**17**, **18**, **19**, **22**, and **25**) or the SHELXL97 [29] program (**20b**, **33**, and **38**).

REFERENCES

[1] A. Schönberg, D. Cernik, W. Urban, *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2577.
[2] R. Huisgen, I. Kalvinsch, X. Li, G. Mlostoń, *Eur. J. Org. Chem*. **2000**, 1685.
[3] R. Huisgen, E. Langhals, *Tetrahedron Lett.* **1989**, *30*, 5369.
[4] G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **1996**, *79*, 1785.
[5] G. Mlostoń, H. Heimgartner, *Pol. J. Chem.* **2000**, *74*, 1503.
[6] G. Mlostoń, H. Heimgartner, in 'The Chemistry of Heterocyclic Compounds, Vol. 59, Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products', Eds. A. Padwa, W. H. Pearson, J. Wiley & Sons, New York, 2002, p. 315.
[7] M. Kägi, A. Linden, G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **1998**, *81*, 285.
[8] M. Kägi, A. Linden, G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **1996**, *79*, 855.
[9] B. Kelmendi, G. Mlostoń, H. Heimgartner, *Heterocycles* **2000**, *52*, 475.
[10] N. Tokitoh, T. Suzuki, A. Itami, M. Goto, W. Ando, *Tetrahedron Lett.* **1989**, *30*, 1249.
[11] C. Bak, K. Praefcke, *Chem. Ber.* **1979**, *112*, 2744.
[12] C. K. Johnson, *ORTEPII*, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
[13] M. U. Bombala, S. V. Ley, *J. Chem. Soc., Perkin Trans. 1* **1979**, 3013.
[14] G. Capozzi, S. Menichetti, C. Nativi, A. Rossi, *Tetrahedron* **1992**, *48*, 9023.
[15] D. S. Wulfman, S. Yousefian, J. M. White, *Synth. Commun.* **1988**, *18*, 2349.
[16] F. Arndt, *Org. Synth*. **1935**, *15*, 3.
[17] T. L. Holton, H. Shechter, *J. Org. Chem*. **1995**, *60*, 4725.
[18] G. Adiwidjaja, H. Günther, J. Voss, *Liebigs Ann. Chem*. **1983**, *7*, 1116.
[19] R. Hooft, KappaCCD Collect Software, Nonius BV, Delft, The Netherlands, 1999.
[20] Z. Otwinowski, W. Minor, in 'Methods in Enzymology', Vol. 276, 'Macromolecular Crystallography', Part A, Eds. C. W. Carter Jr., R. M. Sweet, Academic Press, New York, 1997, p. 307.
[21] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
[22] G. M. Sheldrick, SHELXS97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
[23] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *SIR92*, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[24] H. D. Flack, G. Bernardinelli, *Acta Crystallogr., Sect. A* **1999**, *55*, 908; H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **2000**, *33*, 1143.
[25] a) E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992. Vol. C, Table 6.1.1.1, p. 477; b) D. C. Creagh, W. J. McAuley, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.6.8, p. 219; c) D. C. Creagh, J. H. Hubbell, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.4.3, p. 200.
[26] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.

[27] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[28] teXsan: Single Crystal Structure Analysis Software, Version 1.10b, Molecular Structure Corporation, The Woodlands, Texas, 1999.
[29] G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttigen, Germany, 1997.

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