Chemoselectivity of the Reactions of Diazomethanes with 5-Benzylidene-3-phenylrhodanine

by **Martin S. Seyfried**[a])[1]), **Anthony Linden**[a]), **Grzegorz Mlostoń**[b]), and **Heinz Heimgartner***[a])

[a]) Organisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich (phone: +41-44-6354282; fax: +41-44-6356812; e-mail: heimgart@oci.uzh.ch)

[b]) University of Łódź, Department of Organic and Applied Chemistry, Narutowicza 68, PL-90-136 Łódź

Dedicated to Professor *Valerij A. Nikolaev*, Saint Petersburg, on the occasion of his 70th birthday

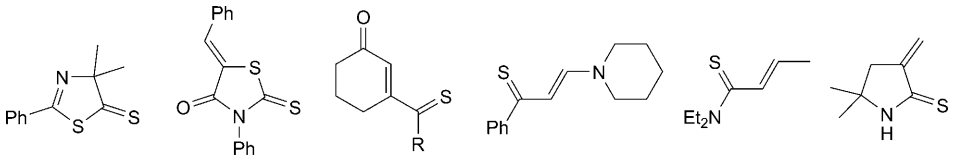
The reactions of 5-benzylidene-3-phenylrhodanine (**2**; rhodanine = 2-thioxo-1,3-thiazolidin-4-one) with diazomethane (**7a**) and phenyldiazomethane (**7b**) occurred chemoselectively at the exocyclic C=C bond to give the spirocyclopropane derivatives **9** and, in the case of **7a**, also the *C*-methylated products **8** (*Scheme 1*). In contrast, diphenyldiazomethane (**7c**) reacted exclusively with the C=S group leading to the 2-(diphenylmethylidene)-1,3-thiazolidine **11** *via* [2+3] cycloaddition and a 'two-fold extrusion reaction'. Treatment of **8** or **9b** with an excess of **7a** in refluxing CH_2Cl_2 and in THF at room temperature in the presence of $[Rh_2(OAc)_4]$, respectively, led to the 1,3-thiazolidine-2,4-diones **15** and **20**, respectively, *i.e.*, the products of the hydrolysis of the intermediate thiocarbonyl ylide. On the other hand, the reactions with **7b** and **7c** in boiling toluene yielded the corresponding 2-methylidene derivatives **16**, **21a**, and **21b**. Finally, the reaction of **11** with **7a** occurred exclusively at the electron-poor C=C bond, which is conjugated with the C=O group. In addition to the spirocyclopropane **23**, the *C*-methylated **22** was formed as a minor product. The structures of the products (*Z*)-**8**, **9a**, **9b**, **11**, and **23** were established by X-ray crystallography.

1. Introduction. – The concept of the 1,3-dipolar cycloaddition, *i.e.*, the [2+3] cycloaddition, which has been formulated and evolved by *Huisgen* [1], is one of the most powerful synthetic approaches to five-membered heterocycles [2]. The general reactivity and the selectivities observed in the concerted reactions are nowadays well-understood on the basis of the Frontier Molecular Orbital (FMO) theory [3]. But, there is also an increasing number of formal 1,3-dipolar cycloadditions known, in which the five-membered product is formed in a non-concerted, two-step mechanism [4] with either a biradical [5] or a zwitterion [6] as the crucial intermediate.

An ideal system for the experimental and theoretical study of a concerted *vs.* two-step mechanism of 1,3-dipolar cycloaddition proved to be the reactions with C=S dipolarophiles [7]. It has been shown that thioketones, especially aromatic thioketones, exhibit an outstanding reactivity in cycloadditions with, *e.g.*, nitrones [5d][8], diazo compounds [9], and sulfines [10]. For this reason, thiocarbonyl compounds are named 'superdipolarophiles'. This high reactivity is the result of the low-lying LUMO of the C=S dipolarophile and the high-lying HOMO of the dipole and, therefore, is influenced by substituents in both reaction partners [9][11].

[1]) Part of the diploma thesis of *M. S. S.*, Universität Zürich, 2005.

In our studies on 1,3-dipolar cycloadditions with C=S compounds, we have also used 1,3-thiazole-5(4*H*)-thiones of type **1** (*Fig. 1*) as dipolarophiles. All reactions with nitrile imines [12], nitrile ylides [12][13], thiocarbonyl ylides [14], carbonyl ylides [15], azomethine ylides [16], and diazo compounds [17] occurred at the C=S bond leading to spirocyclic products. Similarly, organic azides and benzonitrile oxide underwent a cycloaddition with the C=S bond of **1**, but the initially formed spirocyclic products were not stable, and the corresponding 1,3-thiazol-5(4*H*)-imines [18] and 1,3-thiazol-5(4*H*)-one [19], respectively, were obtained. In none of the reactions was the C=N bond involved.



1 **2** **3a** R = Ph **3b** R = CO_2Et **4** **5** **6**

LUMO Energies [3f]	$H_2C=O$	$H_2C=CH_2$	$H_2C=S$
	1.79 eV	1.44 eV	–0.54 eV

Fig. 1. *Some C=S dipolarophiles and LUMO energies of π-bonds* [3f]

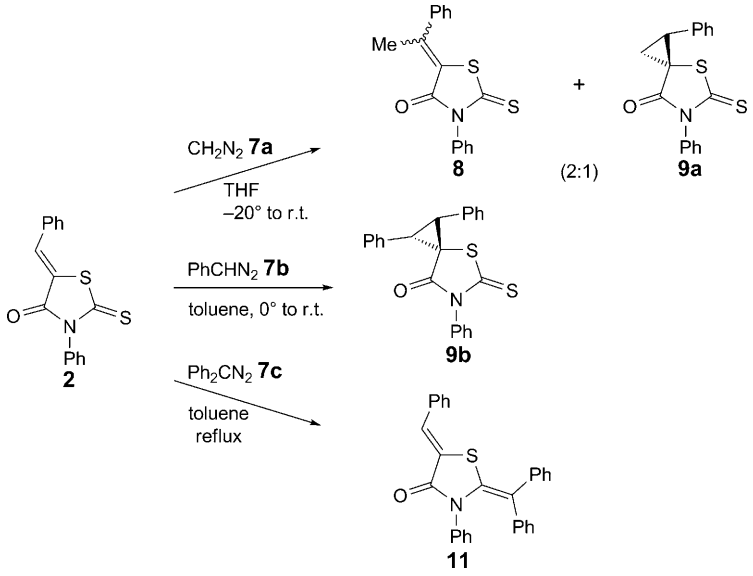
Another heterocyclic C=S compound, which in addition contains an exocyclic C=C and a C=O bond, is 5-benzylidene-3-phenylrhodanine (rhodanine = 2-thioxo-1,3-thiazolidin-4-one; **2**; *Fig. 1*). Whereas reactions with nitrile imines took place exclusively at the C=S group [20], thiocarbonyl ylides added onto the C=S and C=C bond competitively in favor of the latter [21]. The chemoselectivity in the case of the nitrile imines was rationalized with the low-lying LUMO of the C=S bond [3f][20a] (*Fig. 1*). Another indication of the low-lying LUMO of the C=S group of **2** is the chemoselectivity of the *Lewis* acid-catalyzed reaction with oxiranes leading to spirocyclic products with a 1,3-oxathiolane ring [22]. However, as mentioned above, substituents can strongly modify this general reactivity [9][11][21]. For example, it has been shown recently that compounds **3** and **4** with conjugated C=S groups, and diazo compounds react selectively at the C=S group [23], but, in the reactions with the α,β-unsaturated thioamide **5**, only dihydropyrazole-3-thiocarboxamides are formed *via* addition at the C=C bond [24]. On the other hand, the products formed in the reaction between benzonitrile oxides and 5,5-dimethyl-3-methylidenepyrrolidine-2-thione (**6**), which also possess the structure elements of an α,β-unsaturated thioamide, were explained *via* initial [2 + 3] cycloaddition at the C=S bond and subsequent reactions [25].

Here, we describe the results of 1,3-dipolar cycloadditions of **2** with CH_2N_2, $PhCHN_2$, and Ph_2CN_2.

2. Results and Discussion. – 2.1. *Reactions of* **2** *with Diazomethanes.* In analogy to the reactions of diazo compounds with 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (**1**) [17b–d], we chose CH_2N_2 (**7a**), $PhCHN_2$ (**7b**), and Ph_2CN_2 (**7c**) as 1,3-

dipolar species for the reactions with **2** (*Scheme 1*). In the case of **1**, all reactions took place with the C=S bond exclusively and were rationalized *via* an initial [2+3] cycloaddition leading to an unstable spirocyclic 2,5-dihydro-1,3,4-thiadiazole derivative. Subsequent elimination of N_2 generated *in situ* reactive thiocarbonyl ylides, which reacted further to give spirocyclic thiiranes *via* 1,3-dipolar ring closure (with **7b** and **7c**) or the corresponding methylidene derivative (with **7a**) after elimination of sulfur. On the other hand, the [2+3] cycloadducts could be isolated when **1** was reacted with 2-diazopropane [17a] or $(t\text{-Bu})_2CN_2$ [17c].

Scheme 1



The reaction of **2** with **7a** was started by dropwise addition of a 5M solution of **7a** in Et_2O to a solution of **2** in THF at $-20°$ under Ar. After a few min, **2** was completely consumed, and a new product was detected by TLC. During the warming of the mixture to room temperature, this intermediate disappeared, and two new products **8** and **9a** were formed, which were separated by column chromatography and isolated in 65 and 35% yield, respectively. Elemental analyses and mass spectra indicated that the isomeric compounds were CH_2 adducts of **2**. Furthermore, the ^{13}C-NMR spectra evidenced that in both products the C=S and the C=O group were retained, *i.e.*, the reaction of **7a** had occurred at the benzylidene group. Whereas the spectroscopic data of the minor product were in accordance with the spirocyclic structure **9a**, the major product exhibited the signals of a Me group at 2.76 (^{1}H) and 21.8 (^{13}C)[2]) (*Scheme 1*). Finally, the structures (*Z*)-**8** and **9a** were unambiguously established by X-ray crystallography (*Fig. 2*). The crystal structures showed clearly that the exocyclic

[2]) The ^{1}H-NMR spectrum of crude **8** also showed a minor signal at 2.35 ppm, which indicates the presence of the (*E*)-isomer as a minor component (*ca.* 25%); (*Z*)-**8** was obtained in pure form by recrystallization from AcOEt/pentane.

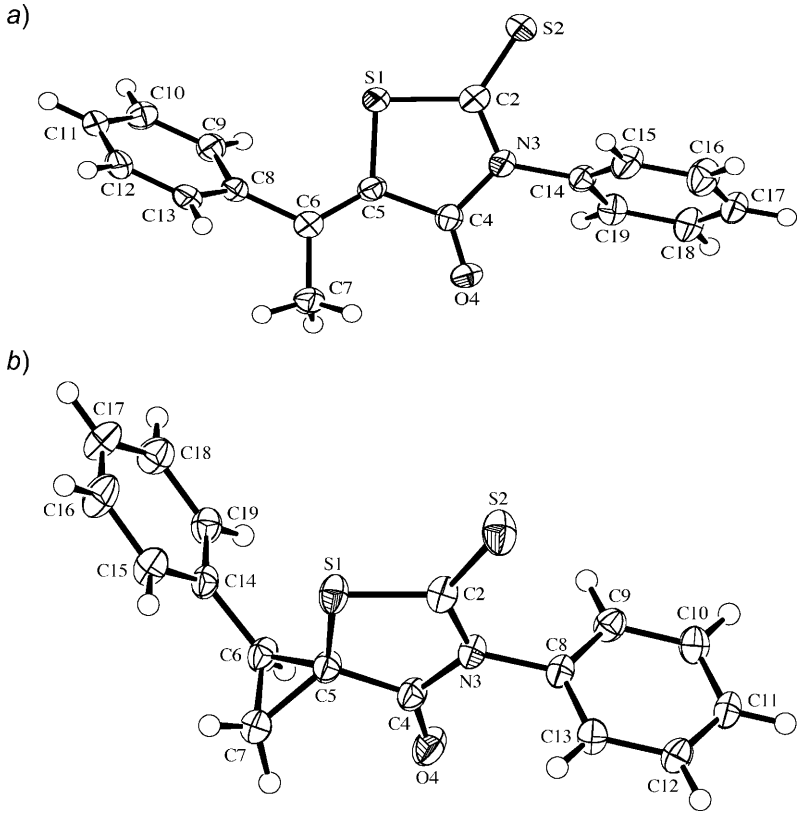


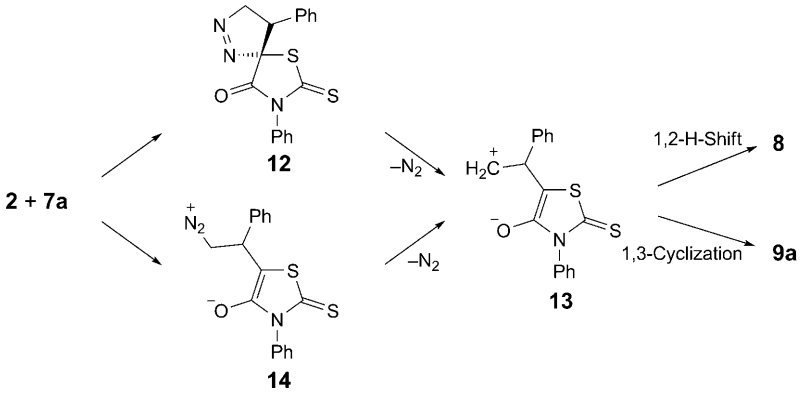
Fig. 2. *ORTEP Plots* [26] *of the molecular structures of* a) *one of the two symmetry-independent molecules of* (*Z*)-**8** *and* b) **9a** (arbitrary numbering of the atoms; 50% probability ellipsoids)

C=C bond of (*Z*)-**8** is (*Z*)-configured, and the Ph residue on the cyclopropane ring of **9a** is *cis*-oriented with respect to the S-atom of the 1,3-thiazolidine.

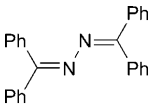
All attempts to isolate the initially formed product were in vain, although it was stable in solution at $-20°$. Attempted crystallization and even concentration of the solution by evaporation of the solvent led to the formation of **8** and **9a**. The ^{1}H-NMR spectrum of the crude mixture showed a *triplet* at 3.95 ppm and a *doublet* at 5.28 ppm in a ratio of *ca.* 1:2. These signals could be assigned to the PhCH–CH_2 fragment of the [2 + 3] cycloadduct of **7a** at the benzylidene group, *i.e.*, the spirocyclic 4,5-dihydro-3*H*-pyrazole **12**, but not the opposite regioisomer (*Scheme 2*). The ratio of the two products **8** and **9a** was almost independent of the temperature of the reaction. Furthermore, the reaction in the presence of [Rh_2(OAc)$_4$], *i.e.*, the reaction of **2** with the carbenoid, gave the same products **8** and **9a**, which were isolated in 64 and 34% yield, respectively.

In line with our expectation, the reaction of **2** with **7b** was more sluggish and, therefore, was performed in toluene at 0°. No [2 + 3] cycloadduct could be detected, and only a single product, **9b**, was obtained in 91% yield (*Scheme 1*). Its structure was again determined by X-ray crystallography (*Fig. 3*). The orientation of the two Ph groups on the cyclopropane ring was determined as *trans.*

Scheme 2



Surprisingly, **7c** reacted with **2** in a different way. Under mild conditions, in toluene at room temperature or at 50°, no reaction with **2** was observed but only a slow decomposition of **7c**. Addition of $LiClO_4$ or $[Rh_2(OAc)_4]$ led to a faster decomposition of **7c**, but again no reaction with **2** took place. The major product in the $[Rh_2(OAc)_4]$-catalyzed reaction was benzophenonazine (**10**)[3]), and tetraphenylethene was identified in the mixture from the reaction with $LiClO_4$ by ^{13}C-NMR spectroscopy and mass spectroscopy. Finally, a solution of **2** and 1.3 equiv. of **7c** in toluene was heated under reflux overnight. Evaporation of the solvent and washing of the residue with boiling hexane gave **11** in 93% yield (*Scheme 1*). The structure was confirmed by the ^{13}C-NMR, elemental-analysis, and MS data, and was established by X-ray crystallography (*Fig. 3*). In contrast to the reactions with **7a** and **7b**, **7c** underwent a [2 + 3] cycloaddition with the C=S group of **2**, followed by a 'two-fold extrusion reaction' (*Barton–Kellogg* reaction) [30].



10

Whereas the transformation **2** + **7c** → **11** is the expected one, in which the diazo compound reacts with the C=S group of **2** in analogy to previously described reactions with **1** [17], the formation of **8** and **9** deserves a comment. In reactions of **2** with thiocarbonyl ylides, it has been observed that the C=C bond is the preferred dipolarophile [21]. This also holds true for the reactions with **7a** and **7b**. Therefore, the spirocyclic 4,5-dihydro-3*H*-pyrazole **12** is a reasonable intermediate in the case of **7a**, which, *via* elimination of N_2, could lead to **13** (*Scheme 2*). Ring closure *via* 1,3-

[3]) The formation of **10** from **7c** in the presence of $[Rh_2(OAc)_4]$ has been described repeatedly [27]. Because the ^{13}C-NMR data of our compound did not correspond to those described in the literature [28], we synthesized **10** independently from benzophenone and $NH_2NH_2 \cdot H_2O$ in EtOH at 160° according to [29] and from **7c** according to the procedure described in [27b]. The ^{13}C-NMR data given in [28] correspond to those of benzophenone.

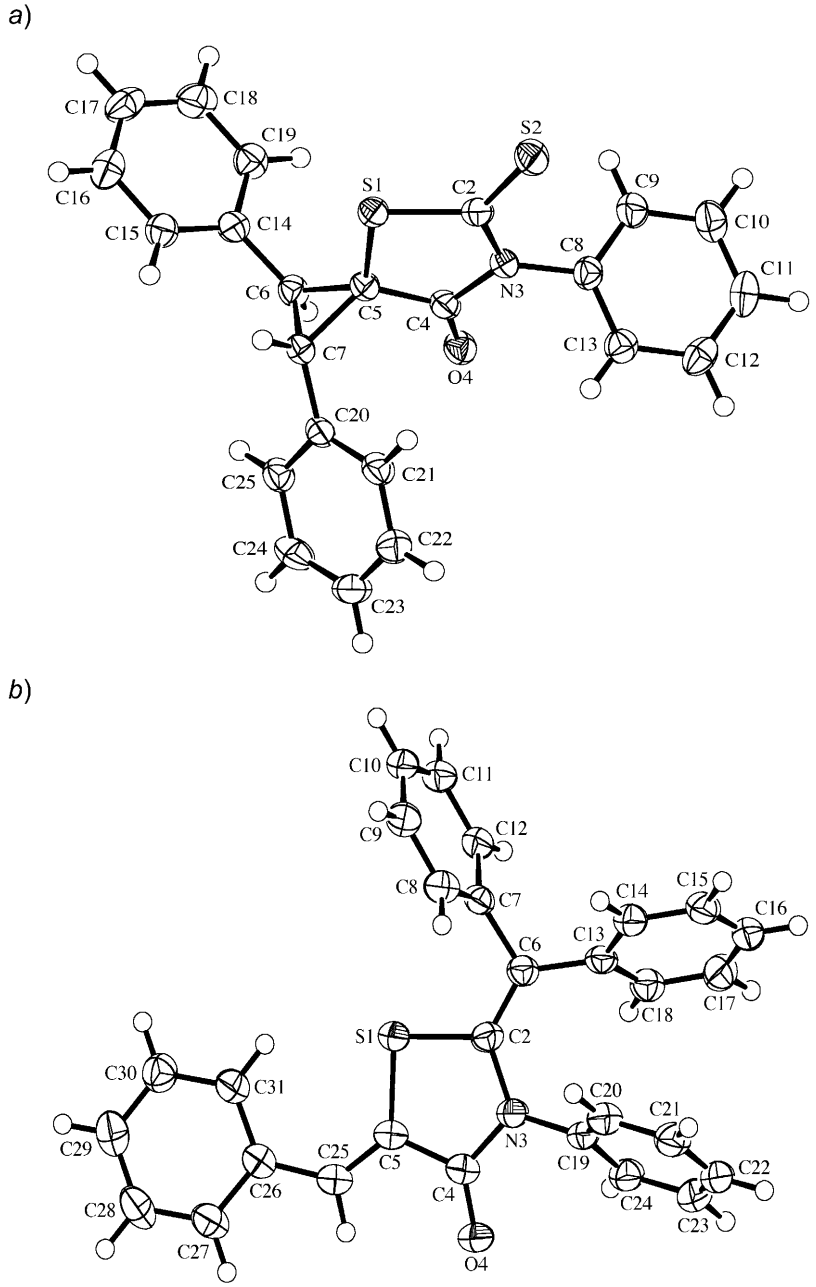
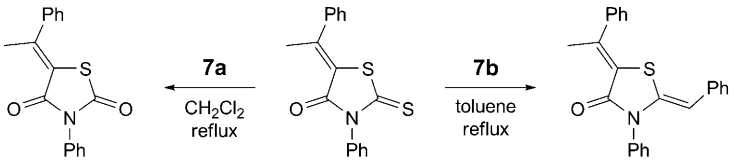


Fig. 3. *ORTEP Plots* [26] *of the molecular structures of* a) **9b** *and* b) **11** (arbitrary numbering of the atoms; 50% probability ellipsoids)

cyclization then yields the spirocyclic cyclopropane **9a**, whereas the formation of **8** can be rationalized by a 1,2-H shift in the intermediate **13**. Alternatively, the diazo compound could react with the benzylidene group of **2** in a *Michael*-type reaction to give **14**. Elimination of N_2 could also lead to the intermediate **13** or directly to **8** and **9a**.

2.2. *Reactions of* **8**, **9b**, *and* **11** *with Diazomethanes.* The major product of the reaction of **2** with **7a**, (*Z*)-**8**[4]), which still offers three π-bonds as dipolarophiles, was dissolved in CH_2Cl_2, and a 0.5M solution of **7a** in Et_2O (20 equiv.) was added portionwise under reflux under Ar. After stirring for 24 h, chromatographic workup gave, in addition to recovered (*Z*)-**8**, the corresponding crude 1,3-thiazolidine-2,4-dione (*Z*)-**15**, but no cycloadduct could be detected (*Scheme 3*). After recrystallization from EtOH, 34% of (*Z*)-**15**[5]) was isolated.

Scheme 3



(*Z*)-**15**[a]) (*Z*)-**8**[a]) (*Z*,*Z*)-**16**[b])

[a]) Major isomer; *ca.* 3:1 mixture of (*Z*)- and (*E*)-isomer.

[b]) Major isomer; *ca.* 100:30:15:10 mixture of (*Z*,*Z*)-, (*E*,*Z*)-, (*Z*,*E*)-, and (*E*,*E*)-isomer.

The analogous treatment of a solution of (*Z*)-**8**[4]) in boiling toluene with an excess of **7b** for 6 h led to a mixture of the starting material (*Z*)-**8** (34%) and the 2-benzylidene derivative (*Z*,*Z*)-**16** as the major product (38%, *Scheme 3*). The ^{1}H-NMR spectrum of the product indicated the presence of four isomeric compounds, the ratio of which was determined by GC/MS as 100 : 30 : 15 : 10. Tentatively, we propose that the major isomer is (*Z*,*Z*)-**16**.

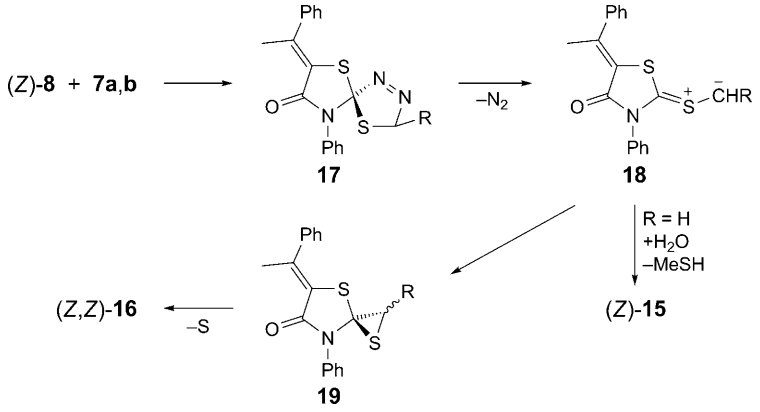
Obviously, both products (*Z*)-**15** and (*Z*,*Z*)-**16** were formed *via* the reaction of the diazo compound with the C=S group of (*Z*)-**8**. The change in the reactivity from **2** to **8** can be rationalized by a steric effect, *i.e.*, the addition onto the exocyclic C=C bond of **8** is less favored because of the presence of an additional Me group. On the other hand, the C=C bond of **8** is less electrophilic, *i.e.*, the LUMO is lying higher, and the reaction with the diazoalkane as an electron-rich 1,3-dipole [3d] is slower. Therefore, we propose that **7a** and **7b** reacted with the C=S group of (*Z*)-**8** in a [2 + 3] cycloaddition to give **17**. In the case of R = Ph, 'two-fold extrusion' of N_2 and S yielded (*Z*,*Z*)-**16** as the final product (*Scheme 4*). The intermediate thiirane **19** seems not to be stable under the reaction conditions (boiling toluene). The formation of (*Z*)-**15** is the result of the initial capture of H_2O by the thiocarbonyl ylide **18** and subsequent elimination of MeSH.

In an additional series of experiments, the reactions of **9b** with **7a**–**7c** were studied with the expectation that additions at the C=S bond will occur. The reaction with **7a** (4 equiv.) was carried out at room temperature in the presence of $[Rh_2(OAc)_4]$ and

4) The used material was a mixture of (*Z*)-**8** and *ca.* 25% of the (*E*)-isomer (see *Footnote 2*).

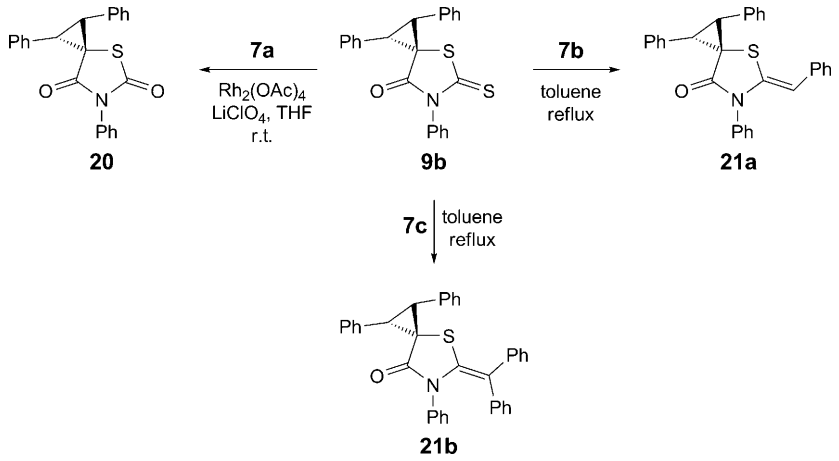
5) According to the ^{1}H-NMR spectrum, the product was also a *ca.* 3:1 mixture of (*Z*)- and (*E*)-**15**.

Scheme 4



$LiClO_4$ in THF. Chromatographic workup after 24 h gave the spirocyclic-1,3-thiazolidine-2,4-dione **20** (22%, *Scheme 5*) and 46% of the starting material. On the other hand, the reactions of **9b** with **7b** and **7c** in boiling toluene gave the expected 2-methylidene derivatives **21a** and **21b** in 53 and 82% yield, respectively.

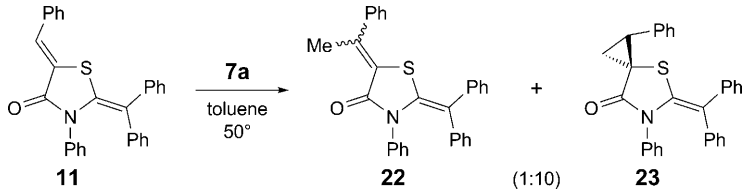
Scheme 5



The structures of **21a** and **21b** were deduced from their MS and ^{13}C-NMR data and, in the case of **21b**, also from elemental analysis, which all indicated the absence of the C=S group. The proposed (*Z*)-configuration of the benzylidene group of **21a** could not be confirmed unambiguously by the NOE experiment: the benzylidene H-atom showed a NOE with an aromatic H-atom, but the latter could not be assigned with certainty to a specific Ph group.

Finally, the reaction of **11** with **7a** in toluene at 50° yielded a mixture of the *C*-methylated product (*Z*)-**22**[6]) and the spirocyclopropane derivative **23** in a ratio of *ca.* 1:10 besides 39% of unchanged starting material (*Scheme 6*). The (*Z*)-configuration of the major isomer of **22** was assigned in analogy to (*Z*)-**8**, and the structure of **23** was established unambiguously by X-ray crystallography (*Fig. 4*).

Scheme 6



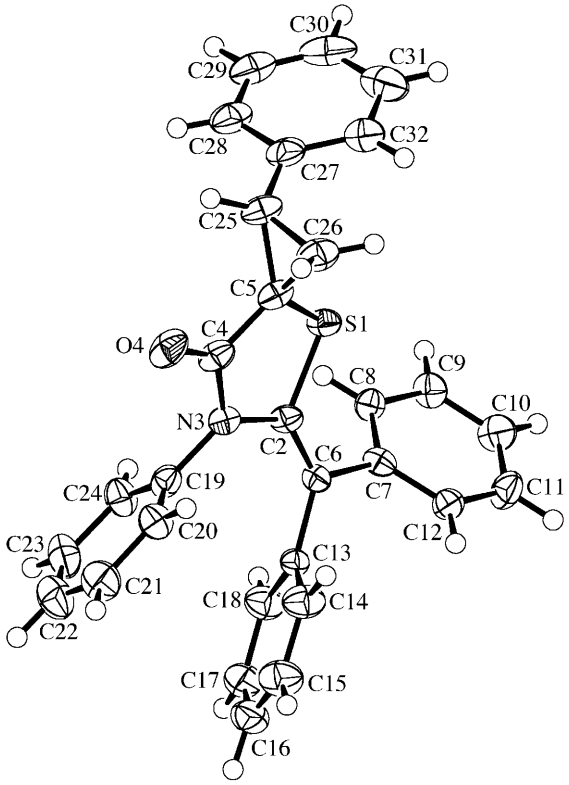


Fig. 4. *ORTEP Plot* [26] *of the molecular structure of one of the two symmetry-independent molecules of* **23** (arbitrary numbering of the atoms; 50% probability ellipsoids)

---

[6]) Mixture of two isomers.

3. Conclusions. – The presented results of the reactions of CH_2N_2 (**7a**), $PhCHN_2$ (**7b**), and Ph_2CN_2 (**7c**) with 5-benzylidene rhodanine **2**, which possesses C=S, C=C, and C=O groups as potential dipolarophiles, show that the reactivities of the C=S and the C=C group are quite similar, *i.e.*, the C=S group of **2** shows no 'superdipolarophilic' character. An analogous observation has been reported earlier for the C=S group of an α,β-unsaturated thioamide [24]. The preferred dipolarophile in the reactions with **7a** and **7b** is the conjugated benzylidene group. Surprisingly, a *C*-methylation leading to **8** competes with the cyclopropanation to give **9**. On the other hand, **7c** reacts chemoselectively with the C=S group of **2** yielding the 2-methylidene derivative **11** *via* [2 + 3] cycloaddition and a subsequent 'two-fold extrusion reaction'. This result indicates comparable dipolarophilicities of the C=S and C=C bonds of **2**, and, accordingly, the chemoselectivity of the reaction depends on the diazo compound. It is most likely that steric as well as electronic effects play a role. This is also reflected in the reactions of **7a** and **7b** with (*Z*)-**8**, which still possesses C=S, C=C, and C=O groups, the only difference to **2** being the additional Me group at the benzylidene C=C bond. In this case, both diazo compounds reacted with the C=S group, leading to the 2-benzylidene-1,3-thiazolidin-4-one (*Z*,*Z*)-**16** in the reaction with **7b**. With **7a**, only the product of the hydrolysis of an intermediate – most likely the thiocarbonyl ylide **18** – was obtained. In the reactions with **9b**, the C=S group is the most reactive dipolarophile for all three diazo compounds **7a**, **7b**, and **7c**.

In comparison with thioketones, the C=S groups of **2**, **8**, and **9b**, which may be classified as dithiocarbamates, are much less reactive, and relatively harsh conditions are necessary for the reaction with diazo compounds. As a result, the initially formed [2 + 3] cycloadduct could not be isolated in any of the experiments.

We thank the analytical sections of our institute for spectra and analyses, and *F. Hoffmann-La Roche AG*, Basel, for financial support.

Experimental Part

1. *General*. TLC: *Merck 60 F_{254}* SiO_2-coated Al-plates, 0.2 mm; detection of the substances on the TLC plates under UV light (λ 254 nm) or with $KMnO_4$ soln. Column chromatography (CC): SiO_2 60, 43 – 63 μm (*ZEOCHEM*, *Chemie Uetikon*). HPLC: *Varian 2510* pump and a UV detector *Varian 2550*; *CC 250/4.6 Nucleosil 100-7* column (*Macherey-Nagel*); indicated are the retention time and the rel. intensity. M.p.: *Olympus* microscope with *TECON-Controller Series 150* instrument; uncorrected. IR Spectra: *Perkin-Elmer 1600 FT-IR* spectrophotometer; in KBr. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AVX-300* or *Bruker ARX-300* instrument (300 and 75.5 MHz, resp.), in $CDCl_3$; multiplicity of C-atoms from DEPT spectra. MS: *Finnigan MAT-95* (EI, 70 eV, or CI (NH_3)) or *FinniganTSQ-700* (ESI) instrument. GC/MS: *Hewlett-Packard 5890 Series II* instrument. Elemental analyses were performed by the Mikroanalytisches Laboratorium des Organisch-Chemischen Instituts der Universität Zürich (*Elementar Vario EL* instrument).

2. *Starting Materials.* CH_2N_2 (**7a**) was prepared from *N*-nitrosomethylurea according to [31], $PhCHN_2$ (**7b**) from benzaldehyde tosylhydrazone according to [32], and Ph_2CN_2 (**7c**) from benzophenone hydrazone according to [33]. The *5-benzylidene-3-phenyl-2-thioxo-1,3-thiazolidin-4-one* (**2**) was prepared from phenylisothiocyanate and thioglycolic acid, followed by condensation with benzaldehyde according to [34] (see also [20b][21]): M.p.: 190 – 194° (EtOH). IR: 3057*w*, 3023*w*, 1717v*s*, 1603*m*, 1594*s*, 1572*w*, 1492*m*, 1453*w*, 1446*m*, 1357*s*, 1316*w*, 1285*w*, 1251v*s*, 1185*w*, 1174*s*, 1156*s*, 1070*w*, 1036*w*, 1025*w*, 933*w*, 824*w*, 758*m*, 732*m*, 691*m*, 681*s*, 632*w*. ^{1}H-NMR: 7.80 (*s*, =CH); 7.59 – 7.47 (*m*, 8 arom. H); 7.31 – 7.27 (*m*, 2 arom. H). ^{13}C-NMR: 193.3 (*s*, C=S); 167.5 (*s*, C=O); 134.8, 133.3 (2*s*, 2 arom. C); 133.3, 130.7, 130.6, 129.6, 129.5, 129.3, 128.3 (7*d*, 10 arom. CH, =CH); 123.3 (*s*, C(5)).

3. *Reactions of* **2** *with* **7a**–**7c**. 3.1. *Reaction with* **7a**. To a stirred soln. of **2** (0.149 g, 0.501 mmol) in abs. THF (*ca.* 6 ml) at −20° under Ar was added dropwise 2 ml of a 0.5M soln. of **7a** in Et_2O. Control by TLC showed that **2** was completely consumed, and an unstable product was formed, which, on warming the mixture to r.t., reacted further to give two new products. The mixture was adsorbed on SiO_2, and CC (hexane/AcOEt 15:1) gave 0.102 g (65%) of *5-[(methyl)(phenyl)methylidene]-2-thioxo-1,3-thiazolidin-4-one* (**8**) and 54 mg (35%) of cis-*1,6-diphenyl-5-thioxo-4-thia-6-azaspiro[2.4]heptan-7-one* (**9a**). The products were purified by recrystallization from EtOH and hexane, resp.

Data of **8** (mixture of isomers). Yellow crystals. M.p. 165–167°. R_f (hexane/AcOEt 5:1): 0.44. HPLC (hexane/EtOH 30:1): 5.16 (100, (*Z*)-**8**), 5.37 (33, (*E*)-**8**). IR: 1708*s*, 1589*m*, 1569*w*, 1496*s*, 1488*m*, 1443*w*, 1348*s*, 1318*w*, 1291*w*, 1235v*s*, 1177*s*, 1168*s*, 1074*w*, 1061*w*, 1026*w*, 983*w*, 865*w*, 762*w*, 727*s*, 698*m*, 688*m*, 639*w*. ^{1}H-NMR: 7.55–7.27 (*m*, 10 arom. H); 2.76 (*s*, Me, (*Z*)-**8**); 2.35 (*s*, Me, (*E*)-**8**). ^{13}C-NMR: 194.2 (*s*, C=S); 165.8 (*s*, C=O); 150.9 (*s*, Ph(Me)*C*); 142.0, 135.2 (2*s*, 2 arom. C); 129.7, 129.5, 129.4, 129.3, 129.0, 128.3, 128.0, 127.3, 126.6 (9*d*, 10 arom. C, (*Z*)- and (*E*)-**8**); 123.1 (*s*, C(5)); 21.8 (*q*, Me). EI-MS: 313 (7), 312 (13), 311 (65, M^+), 295 (9), 176 (6, $[M-CSNPh]^+$), 149 (13), 148 (100, $[M-CONPhCS]^+$), 147 (18), 135 (9), 115 (11), 104 (8), 103 (9), 77 (11, Ph^+). Anal. calc. for $C_{17}H_{13}NOS_2$ (311.43): C 65.56, H 4.21, N 4.50, S 20.59; found: C 65.43, H 4.13, N 4.41, S 20.46.

Suitable crystals of (*Z*)-**8** for the X-ray crystal-structure determination were obtained by isothermal distillation of pentane into a soln. of **8** in AcOEt.

Data of **9a**. Colorless crystals. M.p. 140–142°. R_f (hexane/AcOEt 5:1): 0.38. IR: 1721v*s*, 1593*w*, 1497*m*, 1455*w*, 1424*w*, 1372*m*, 1351*s*, 1318*w*, 1241v*s*, 1178*m*, 1154*w*, 1129*m*, 1073*w*, 1055*w*, 1046*w*, 1030*w*, 976*m*, 834*w*, 777*w*, 757*w*, 728v*s*, 708*w*, 696*m*, 688*m*, 629*w*. ^{1}H-NMR: 7.55–7.47, 7.42–7.33, 7.28–7.25, 7.25–7.17 (4*m*, 10 arom. H); 3.37 (*dd*, $^3J(cis) = 9.7$, $^3J(trans) = 8.1$, PhC*H*); 2.42 (*dd*, $^2J = 5.9$, $^3J(cis) = 9.7$, 1 H of CH_2); 2.08 (*dd*, $^2J = 5.9$, $^3J(trans) = 8.1$, 1 H of CH_2). ^{13}C-NMR: 199.5 (*s*, C=S); 175.3 (*s*, C=O); 135.2, 134.3 (2*s*, 2 arom. C); 129.6, 129.5, 129.0, 128.4, 128.3, 127.9 (6*d*, 10 arom. C); 41.4 (*s*, spiro-C); 34.9 (*d*, Ph*C*H); 22.7 (*t*, CH_2). EI-MS: 313 (11), 312 (21), 311 (100, M^+), 295 (16), 176 (35), 148 (28, $[M-CONPhCS]^+$), 147 (26), 136 (10), 135 (13), 115 (47, $[M-CONPhCSS]^+$), 104 (13, $[PhCHCH_2]^+$), 91 (9, $[PhCH_2]^+$), 77 (14, Ph^+). Anal. calc. for $C_{17}H_{13}NOS_2$ (311.43): C 65.56, H 4.21, N 4.50, S 20.59; found: C 65.66, H 4.16, N 4.47, S 20.35.

Suitable crystals of **9a** for the X-ray crystal-structure determination were obtained by isothermal distillation of pentane into a soln. of **9a** in 1,2-dimethoxyethane.

3.2. *Reaction with* **7b**. To a stirred suspension of **2** (0.595 g, 2.001 mmol) in toluene (*ca.* 10 ml) at 0° under Ar were added 80 ml of a 30 mM soln. of **7b** (1.2 equiv.) in toluene. After 48 h at r.t., **2** was completely consumed (TLC). The solvent was evaporated, and the residue was crystallized from EtOH, yielding 0.703 g (91%) of trans-*1,2,6-triphenyl-5-thioxo-4-thia-6-azaspiro[2.4]heptan-7-one* (**9b**). Pale yellow crystals. M.p. 222–225°. R_f (hexane/AcOEt 5:1): 0.31. IR: 3057*w*, 1731v*s*, 1593*w*, 1495*s*, 1446*w*, 1339v*s*, 1316*m*, 1279*w*, 1226v*s*, 1197*s*, 1180*m*, 1145*m*, 1115*m*, 1075*w*, 1027*w*, 980*m*, 954*w*, 816*w*, 758*w*, 748*m*, 737*s*, 697*s*, 632*w*. ^{1}H-NMR: 7.47–7.26 (*m*, 13 arom. H); 7.13–7.10 (*m*, 2 arom. H); 4.03 (*d*, $^3J = 8.9$, PhC*H*); 3.68 (*d*, $^3J = 8.9$, PhC*H*). ^{13}C-NMR: 198.6 (*s*, C=S); 171.6 (*s*, C=O); 134.9, 134.2, 132.0 (3*s*, 3 arom. C); 129.4, 129.3, 129.02, 128.99, 128.4, 128.3, 128.2, 128.0 (8*d*, 15 arom. C); 46.7 (*s*, spiro-C); 41.3, 37.7 (2*d*, 2 Ph*C*H). EI-MS: 389 (12), 388 (26), 387 (100, M^+), 252 (14), 251 (11), 224 (11), 223 (13, $[M-CONPhCS]^+$), 218 (11), 192 (15), 191 (34, $[M-CONPhCSS]^+$), 178 (8), 165 (7), 147 (5), 135 (8), 91 (7, $[PhCH_2]^+$), 77 (7, Ph^+). Anal. calc. for $C_{23}H_{17}NOS_2$ (387.53): C 71.29, H 4.42, N 3.61, S 16.65; found: C 17.15, H 4.46, N 3.56, S 16.64.

Suitable crystals of **9b** for the X-ray crystal-structure determination were obtained by isothermal distillation of pentane into a soln. of **9b** in 1,2-dimethoxyethane.

3.3. *Reaction with* **7c**. To a stirred suspension of **2** (0.155 g, 0.521 mmol) in toluene (*ca.* 5 ml) at r.t. under Ar were added 8 ml of a 0.1M soln. of **7c** (1.3 equiv.) in benzene. After heating to reflux overnight, the solvent was evaporated, and the residue was washed with boiling hexane to remove starting material and side products. Yield of *(Z)-5-benzylidene-2-(diphenylmethylidene)-3-phenyl-1,3-thiazolidin-4-one* (**11**): 0.210 g (93%). Yellow crystals. M.p. 255–258°. R_f (hexane/AcOEt 5:1): 0.41. IR: 3046*w*, 2924*w*, 2852*w*, 1696v*s*, 1604v*s*, 1491v*s*, 1455*w*, 1442*s*, 1353v*s*, 1309*w*, 1287*m*, 1247v*s*, 1209*w*, 1175*s*, 1164*m*, 1130*m*, 1071*m*, 1051*m*, 1026*m*, 876*w*, 837*w*, 777*w*, 761*s*, 750*m*, 733*m*, 694v*s*, 643*m*, 606*m*. ^{1}H-NMR: 7.61 (*s*, =CH); 7.49–7.28 (*m*, 10 arom. H); 7.12–6.98 (*m*, 5 arom. H); 6.86–6.81 (*m*, 3 arom. H); 6.75–6.72 (*m*, 2 arom.

H). ^{13}C-NMR: 167.6 (*s*, C=O); 141.5, 138.8, 136.8, 134.7, 130.9 (5*s*, 4 arom. C, Ph_2C); 130.4, 130.1, 129.7, 128.7, 128.6, 128.2, 127.8, 127.5, 127.2, 127.1, 126.5, 126.3 (12*d*, 20 arom. CH, =CH); 123.5, 119.7 (2*s*, C(2), C(5)). CI-MS (NH_3): 449 (21, $[M+NH_4]^+$), 434 (16), 433 (34), 432 (100, $[M+H]^+$). Anal. calc. for $C_{29}H_{21}NOS$ (431.55): C 80.71, H 4.90, N 3.25, S 7.43; found: C 80.58, H 5.08, N 3.15, S 7.34.

Suitable crystals of **11** for the X-ray crystal-structure determination were obtained by isothermal distillation of pentane into a soln. of **11** in 1,2-dimethoxyethane.

4. *Synthesis of Benzophenonazine* (**10**). 4.1. *Synthesis from* Ph_2CN_2 (**7c**). According to [27c], to a soln. of $[Rh_2(OAc)_4]$ (4.3 mg, 9.0 μmol) in abs. THF (8 ml) at 55° were added 7.5 ml of the 0.1M soln. of **7c** (0.75 mmol). The mixture was filtered through SiO_2 and recrystallized from EtOH: 159 mg (59%) of **10**. M.p. and the UV spectrum are in accordance with reported data [34]. M.p. 168–169°. R_f (hexane/AcOEt 5:1): 0.53. IR: 3083*w*, 3056*w*, 3022*w*, 2926*w*, 1587*m*, 1564*m*, 1488*m*, 1443*s*, 1320*s*, 1294*w*, 1177*w*, 1159*w*, 1076*w*, 1027*w*, 999*w*, 983*w*, 956*s*, 910*w*, 774*s*, 764*s*, 692v*s*, 667*m*, 655*s*, 613*w*. ^{1}H-NMR: 7.50–7.24 (*m*, 20 arom. H). ^{13}C-NMR: 159.1 (*s*, 2 =CN–); 138.0, 135.4 (2*s*, 4 arom. C); 129.6, 129.2, 128.6, 127.9, 127.8 (5*d*, 20 arom. CH). EI-MS: 361 (21), 360 (76, M^+), 359 (35), 284 (21), 283 (100, $[M-Ph]^+$), 257 (14), 256 (13), 180 (29), 165 (25), 77 (13).

4.2. *Synthesis from Benzophenone.* According to [29], to a soln. of benzophenone (1.094 g, 6.003 mmol) in EtOH (*ca.* 15 ml), $NH_2NH_2 \cdot H_2O$ (80%, 0.180 g, 2.87 mmol) and 3 drops of AcOH were added. The mixture was heated to 160° for 5 h in an autoclave. Evaporation to dryness and crystallization from EtOH gave 0.203 g (20%) of **10**.

5. *Reaction of Some 1:1 Adducts with an Additional Diazo Component.* 5.1. *Reaction of* **8** *with* **7a**. A stirred soln. of **8**[7]) (0.157 g, 0.504 mmol) in CH_2Cl_2 (*ca.* 10 ml) under Ar was heated to reflux. Within 24 h, 20 ml of the *ca.* 0.5M soln. of **7a** (10 mmol, 20 equiv.) were added portionwise. Then, the solvent was evaporated, the residue adsorbed on SiO_2 and separated by CC (hexane/AcOEt 20:1) to yield **8** (28%) and crude *5-[(methyl)(phenyl)methylidene]-3-phenyl-1,3-thiazolidin-2,4-dione* (**15**; 62 mg, 42%)[8]). Crystallization from EtOH gave 34% of **15**, which was still contaminated with traces of **8**.

Data of **15**[8]). Colorless crystals. M.p. 117–127°. R_f (hexane/AcOEt 5:1): 0.41. ^{1}H-NMR: 7.48–7.25 (*m*, 10 arom. H); 2.69 (*s*, Me, (*Z*)-**15**, major product); 2.25 (*s*, Me, (*E*)-**15**, minor product). ^{13}C-NMR (signals of the major product (*Z*)-**15**): 163.7 (*s*, C=O(amide)); 151.0 (*s*, C=O(thiocarbamate)); 141.2, 139.4, 131.9 (3*s*, 2 arom. C, Ph(Me)*C*); 128.5, 128.3, 128.1, 128.0, 127.9, 127.5, 127.4, 127.3, 126.5, 125.7 (10*d*, 10 arom. CH); 115.1 (*s*, C(5)); 28.7 (*q*, Me). ESI-MS (MeOH + NaI): 334 (20, $[M(\mathbf{8})+Na]^+$), 318 (100, $[M(\mathbf{15})+Na]^+$).

5.2. *Reaction of* **8** *with* **7b**. A soln. of **8**[7]) (0.160 g, 0.515 mmol) in toluene (40 ml) under Ar was heated to reflux, and 80 ml of the *ca.* 30 mM soln. of **7b** (2.4 mmol, 4.8 equiv.) was added in 4 portions within 6 h. After cooling to r.t., the solvent was evaporated, the residue was adsorbed on SiO_2 and separated by CC (hexane/AcOEt 20:1). In addition to **8** (55 mg, 34%), crude **16** (73 mg, 38%) was obtained, which was crystallized from CH_2Cl_2/hexane to give a mixture of diastereoisomers of *2-benzylidene-5-[(methyl)(phenyl)methylidene]-3-phenyl-1,3-thiazolidin-4-one* (**16**). Colorless crystals. M.p. 84–87°. R_f (hexane/AcOEt 5:1): 0.41. HPLC (hexane/EtOH 25:1): 5.27 (major product, (*Z*,*Z*)-**16**), 4.82, 5.78, and 7.05 ((*E*,*Z*)-, (*Z*,*E*)-, and (*E*,*E*)-**16**, resp.). IR: 3059*m*, 2924*s*, 2853*m*, 1736v*s*, 1677v*s*, 1592v*s*, 1571*s*, 1492v*s*, 1454*s*, 1441*s*, 1348v*s*, 1290*m*, 1239v*s*, 1195v*s*, 1157v*s*, 1072*m*, 1028*s*, 1002*m*, 985*s*, 915*w*, 868*w*, 843*m*, 814*w*, 762*s*, 737*s*, 728*s*, 692v*s*, 664*w*, 655*w*, 638*m*, 619*w*, 603*w*. ^{1}H-NMR: 7.58–7.14 (*m*, 15 arom. H); 2.78 (*s*, Me, (*Z*,*Z*)-**16**, major product); 2.71, 2.35, and 2.17 (3*s*, Me of (*Z*,*E*)-, (*E*,*Z*)-, and *E*,*E*)-**16**, resp.). ^{13}C-NMR: 164.6 (*s*, C=O); 152.0, 143.5, 142.2, 135.3, 134.6, 132.8 (6*s*, 3 arom. C, Ph(Me)*C*); 129.8, 129.7, 129.4, 129.2, 129.0, 128.9, 128.9, 128.7, 128.4, 128.2, 127.6, 127.4, 126.7, 126.5, 125.7 (15*d*, 15 arom. C); 125.7 (*s*, C(5)); 120.5 (*s*, C(2)); 103.1 (*d*, =CH); 22.6, 20.7 (2*q*, Me). ESI-MS (MeOH + NaI): 410 (10), 392 (100, $[M+Na]^+$). GC/EI-MS: 14.1–14.4 min (10): 295 (4), 281 (14), 207 (100, $[M-CO-SCCHPh]^+$), 191 (9), 148 (97, $[M-CONPhCCHPh]^+$), 133 (12), 114 (12), 103 (16), 96 (14), 91 (12), 77 (17, Ph^+); 14.4–14.8 min (100): 295 (15), 281 (3), 207 (31), 191 (3), 148 (100), 133 (6), 114 (15), 103 (17), 96 (4), 91 (10), 77 (19); 15.3–15.5 min (15): 281 (17), 256 (22), 253 (25), 207 (100), 201 (20), 198 (10), 174 (16), 159 (14), 148 (5), 133 (17), 104 (25), 91 (18), 77 (22); 15.6–15.8 min (30): 281 (17), 255 (55),

---

[7]) Mixture of (*Z*)- and (*E*)-**8** (*ca.* 3:1).

[8]) Mixture of (*Z*)- and (*E*)-**15** (*ca.* 3:1) and contaminated with some starting material.

253 (62), 207 (100), 199 (47), 191 (8), 185 (8), 174 (39), 159 (39), 148 (9), 133 (17), 121 (10), 104 (55), 91 (63), 77 (40).

5.3. *Reaction of* **9b** *with* **7a**. To a mixture of **9b** (0.0965 g, 0.249 mmol), 2 mg [$Rh_2(OAc)_4 \cdot H_2O$] (4 μmol, 0.2 equiv.), and 35 mg $LiClO_4$ (0.329 mmol, 1.3 equiv.) in THF (5 ml) under Ar was added 1 ml of the *ca.* 0.5M soln. of **7a** (2 mmol, 4 equiv.). After 4 h, the addition was repeated, and, after stirring for 24 h at r.t., the mixture was filtered through cotton, the solvent was evaporated, and the residue was adsorbed on SiO_2 and separated by CC (hexane/AcOEt 15:1). Besides **9b** (44 mg, 46%), trans-*1,2,6-triphenyl-4-thia-6-azaspiro[2.4]heptane-5,7-dione* (**20**, 20 mg, 22%) was obtained and recrystallized from CH_2Cl_2/hexane. Colorless crystals. M.p. 159–160°. R_f (hexane/AcOEt 5:1): 0.31. IR: 3063*w*, 3038*w*, 1747*s*, 1722v*s*, 1699v*s*, 1602*m*, 1593*m*, 1493*s*, 1448*m*, 1424*w*, 1368v*s*, 1291*w*, 1245v*s*, 1199*m*, 1162v*s*, 1146*s*, 1131*m*, 1073*w*, 1026*w*, 1005*w*, 991*w*, 955*w*, 849*m*, 753v*s*, 737*s*, 694v*s*, 657*w*, 630*w*, 607*w*. ^{1}H-NMR: 7.46–7.26 (*m*, 13 arom. H); 7.21–7.09 (*m*, 2 arom. H); 3.97 (*d*, ^3J = 8.9, PhC*H*); 3.56 (*d*, ^3J = 8.9, PhC*H*). ^{13}C-NMR: 170.1, 169.6 (2*s*, 2 C=O); 134.4, 132.7, 132.6 (3*s*, 3 arom. C); 129.3, 129.01, 128.99, 128.9, 128.4, 128.3, 128.0, 127.9, 127.1 (9*d*, 15 arom. C); 44.1 (*s*, spiro-C); 40.2, 35.9 (2*d*, 2 Ph*C*H). ESI-MS (CH_2Cl_2/MeCN 1:1 + NaI): 410 (10, [*M*(**9a**) + Na]$^+$), 394 (100, [*M*(**20**) + Na]$^+$).

5.4. *Reaction of* **9b** *with* **7b**. A soln. of **9b** (0.101 g, 0.260 mmol) in toluene (5 ml) under Ar was heated to reflux, and 40 ml of the *ca.* 30 mM soln. of **7b** (1.2 mmol, 4.8 equiv.) were added portionwise during 7 h. After cooling to r.t., the solvent was evaporated, and the residue was adsorbed on SiO_2 and separated by CC (hexane/AcOEt 15:1). Besides **9b** (37 mg, 32%), trans-*(Z)-5-benzylidene-1,2,6-triphenyl-4-thia-6-azaspiro[2.4]heptan-7-one* (**21a**, 61 mg, 53%) was obtained, which was recrystallized from $CHCl_3$/hexane. Colorless crystals. M.p. 224–228°. R_f (hexane/AcOEt 5:1): 0.31. IR: 3059*w*, 3030*w*, 2923*w*, 1753*w*, 1706v*s*, 1620v*s*, 1572*s*, 1495v*s*, 1446*s*, 1377v*s*, 1282*w*, 1233*s*, 1201*s*, 1180*s*, 1156*m*, 1120*w*, 1070*w*, 1027*m*, 1005*w*, 989*w*, 796*m*, 750*s*, 734*s*, 695v*s*, 630*w*, 616*w*. ^{1}H-NMR: 7.49–7.07 (*m*, 20 arom. H); 5.73 (*s*, =CH); 3.82 (*d*, ^3J = 8.6, PhC*H*); 3.31 (*d*, ^3J = 8.6, PhC*H*). ^{13}C-NMR: 168.6 (*s*, C=O); 136.4, 135.8, 135.5, 135.2, 133.8 (5*s*, 4 arom. C, C(5)); 129.7, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 127.7, 127.4, 127.1, 125.7 (12*d*, 20 arom. C); 104.6 (*d*, =CH); 43.1 (*s*, spiro-C); 40.5, 34.8 (2*d*, 2 Ph*C*H). ESI-MS (MeOH/CH_2Cl_2 3:1 + NaI): 468 (100, [*M* + Na]$^+$), 446 (12, *M*$^+$).

5.5. *Reaction of* **9b** *with* **7c**. To a soln. of **9b** (0.197 g, 0.509 mmol) in toluene (25 ml) under Ar was added 10 ml of the *ca.* 0.1M soln. of **7c** (1.0 mmol, 2 equiv.), and the mixture was heated to reflux. After 2 h, an additional 15 ml of the soln. of **7c** (1.5 mmol, 3 equiv.) were added, and heating was continued for 2 h. Then, the mixture was cooled to r.t., the solvent was evaporated, and the residue adsorbed on SiO_2. CC gave 219 mg (82%) of trans-*5-(diphenylmethylidene)-1,2,6-triphenyl-4-thia-6-azaspiro[2.4]heptan-7-one* (**21b**), which was recrystallized from CH_2Cl_2/hexane. Colorless crystals. M.p. 223–225°. R_f (hexane/AcOEt 5:1): 0.41. IR: 3060*w*, 3029*m*, 1705v*s*, 1597v*s*, 1494v*s*, 1452*m*, 1442*s*, 1340v*s*, 1309*m*, 1289*s*, 1247*m*, 1224v*s*, 1196*w*, 1180*w*, 1154*m*, 1127*m*, 1073*m*, 1030*m*, 1002*w*, 982*w*, 758v*s*, 730*m*, 698v*s*, 647*m*, 604*m*. ^{1}H-NMR: 7.48–7.46 (*m*, 2 arom. H); 7.40–7.19 (*m*, 13 arom. H); 6.94–6.81 (*m*, 8 arom. H); 6.79–6.69 (*m*, 2 arom. H); 3.76 (*d*, ^3J = 8.4, PhC*H*); 3.28 (*d*, ^3J = 8.4, PhC*H*). ^{13}C-NMR: 170.7 (*s*, C=O); 141.7, 139.2, 137.0, 135.2, 134.5, 132.0 (6*s*, 5 arom. C, Ph_2C); 130.3, 129.9, 128.9, 128.6, 128.43, 128.38, 128.2, 127.9, 127.5, 127.2, 126.9, 126.5, 126.1 (13*d*, 25 arom. C); 121.4 (*s*, C(5)); 43.8 (*s*, spiro-C); 40.7, 33.9 (2*d*, 2 Ph*C*H). CI-MS (NH_3): 539 (15, [*M* + NH_4]$^+$), 522 (100, [*M* + H]$^+$). Anal. calc. for $C_{36}H_{27}NOS$ (521.67): C 82.88, H 5.22, N 2.68, S 6.15; found: C 82.70, H 4.99, N 2.65, S 6.02.

5.6. *Reaction of* **11** *with* **7a**. A soln. of **11** (0.217 g, 0.503 mmol) in toluene (60 ml) under Ar was heated to 50°, and 16 ml of the *ca.* 0.5M soln. of **7a** (2 mmol, 4 equiv.) were added portionwise within 24 h. After evaporation of the solvent, the residue was extracted with boiling hexane, and 85 mg (39%) of **11** were recovered. The hexane fraction was evaporated, and the residue was adsorbed on SiO_2 and separated by CC (hexane/AcOEt 20:1): 8 mg (4%) of *5-[(methyl)(phenyl)methylidene]-2-(diphenylmethylidene)-3-phenyl-1,3-thiazolidin-4-one* (**22**) and 97 mg (43%) of cis-*5-(diphenylmethylidene)-1,6-diphenyl-6-aza-4-thiaspiro[2.4]heptan-7-one* (**23**). The latter was recrystallized from CH_2Cl_2/hexane.

Data of **22** (impure). Colorless crystals. M.p. 160–195°. R_f (hexane/AcOEt 5:1): 0.47. ^{1}H-NMR: 7.45–7.15 (*m*, 10 arom. H); 7.10–6.89 (*m*, 5 arom. H); 6.83–6.80 (*m*, 3 arom. H); 6.73–6.67 (*m*, 2 arom. H); 2.66 (*s*, Me, (*Z*)-**22**, major product); 2.17 (*s*, Me, (*E*)-**22**, minor product). ^{13}C-NMR (signals of the major product): 166.8 (*s*, C=O); 143.6, 142.1, 141.6, 139.3, 137.4, 131.3 (6*s*, 4 arom. C, Ph(Me)*C*, Ph_2C); 130.9, 130.5, 128.8, 128.5, 128.3, 127.8, 127.7, 127.6, 127.2, 126.2, 126.8, 126.0 (12*d*, 20 arom. C, =CH); 122.1,

Table. *Crystallographic Data for Compounds (Z)*-**8**, **9a**, **9b**, **11**, *and* **23**

	(*Z*)-**8**	**9a**	**9b**	**11**	**23**
Crystallized from	AcOEt/pentane	DME/pentane	toluene/DME/pentane	DME/pentane	CH_2Cl_2/hexane
Empirical formula	$C_{17}H_{13}NOS_2$	$C_{17}H_{13}NOS_2$	$C_{23}H_{17}NOS_2$	$C_{29}H_{21}NOS$	$C_{30}H_{23}NOS \cdot 0.85\ CH_2Cl_2$
M_r	311.42	311.42	387.51	431.55	517.77
Crystal color, habit	yellow, prism	colorless, prism	yellow, prism	yellow, prism	colorless, prism
Crystal dimensions [mm]	$0.07 \times 0.10 \times 0.25$	$0.05 \times 0.10 \times 0.17$	$0.15 \times 0.18 \times 0.20$	$0.15 \times 0.25 \times 0.30$	$0.15 \times 0.17 \times 0.32$
Temp. [K]	160(1)	160(1)	160(1)	160(1)	160(1)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P\bar{1}$	Pn
Z	8	4	8	2	4
Reflections for cell determination	93969	27659	58836	32571	123238
2θ Range for cell determination [°]	4–55	4–60	4–50	4–50	4–55
Unit cell parameters					
a [Å]	9.9462(4)	13.4766(3)	27.1347(8)	9.5724(6)	16.8631(3)
b [Å]	8.4913(4)	5.1922(1)	8.9893(3)	10.1289(5)	6.2540(1)
c [Å]	35.564(1)	21.5970(5)	20.6284(7)	12.5773(7)	25.6343(4)
α [°]	90	90	90	74.792(3)	90
β [°]	94.755(2)	95.839(1)	129.874(1)	71.200(4)	102.6264(8)
γ [°]	90	90	90	76.689(4)	90
V [Å^3]	2993.3(2)	1503.37(6)	3861.6(2)	1099.7(1)	2638.06(8)
D_x [g cm^{-3}]	1.382	1.376	1.333	1.303	1.304
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.353	0.351	0.288	0.169	0.319
Scan type	ϕ and ω	ϕ and ω	ω	ω	ϕ and ω
$2\theta_{(\max)}$ [°]	55	60	50	50	55
Transmission factors [min; max]	0.761; 0.985	0.837; 0.996	0.801; 0.958	0.866; 0.980	0.808; 0.988
Total reflections measured	36896	39804	27602	15203	58386
Symmetry-independent reflections	6741	4399	3403	3840	11058
Reflections with $I > 2\sigma(I)$	3904	3012	2627	3192	9476
Reflections used in refinement	6739	4399	3402	3840	11058
Parameters refined; restraints	381; 0	190; 0	244; 0	289; 0	635; 2
Final $R(F)$ ($I > 2\sigma(I)$ reflections)	0.0595	0.0453	0.0406	0.0409	0.0895
$wR(F^2)$ (all data)	0.1421	0.1141	0.1042	0.1039	0.2612
Weighting parameters [a; b][a])	0.0492; 2.2856	0.0438; 0.7983	0.0471; 4.1059	0.0424; 0.4405	0.1364; 7.9962
Goodness-of-fit	1.025	1.030	1.054	1.073	1.052
Secondary extinction coefficient	–	–	–	–	0.019(3)
Final $\Delta_{\max}/\sigma$	0.001	0.001	0.001	0.001	0.001
$\Delta\rho$(max; min) [e Å^{-3}]	0.32; −0.38	0.35; −0.44	0.23; −0.27	0.18; −0.29	1.23; −0.53

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

117.5 (2*s*, C(2), C(5)); 21.0 (*q*, Me). ESI-MS (MeOH + NaI): 528 (30), 500 (13, $[M+Na+MeOH]^+$), 484 (18, $[M+K]^+$), 468 (100, $[M+Na]^+$).

Data of **23**. Colorless crystals. M.p. 170–171°. R_f (hexane/AcOEt 5:1): 0.41. IR: 3053*w*, 2924*w*, 1708v*s*, 1596*s*, 1492*s*, 1454*m*, 1442*m*, 1345v*s*, 1310*w*, 1287*m*, 1253*s*, 1227*s*, 1202*w*, 1178*w*, 1142*m*, 1073*m*, 1029*w*, 976*w*, 776*w*, 759*m*, 725*m*, 697v*s*, 643*m*, 605*m*, 589v*s*. ^{1}H-NMR: 7.35–6.93 (*m*, 15 arom. H); 6.85–6.77 (*m*, 3 arom. H); 6.75–6.68 (*m*, 2 arom. H); 3.09 (*dd*, $^3J(cis) = 9.7$, $^3J(trans) = 7.7$, PhC*H*); 2.13 (*dd*, $^2J = 5.5$, $^3J(cis) = 9.7$, 1 H of CH_2); 1.63 (*dd*, $^2J = 5.5$, $^3J(trans) = 7.7$, 1 H of CH_2). ^{13}C-NMR: 174.2 (*s*, C=O); 141.8, 139.2, 137.1; 135.5 (4*s*, 4 arom. C); 132.2, 119.7 (*s*, Ph_2C, C(2)); 130.2, 130.0, 128.5, 128.4, 128.1, 128.0, 127.3, 127.2, 127.14, 127.12, 126.8, 125.9 (12*d*, 20 arom. C); 37.7 (*s*, spiro-C); 31.6 (*d*, PhC*H*); 22.1 (*t*, CH_2). CI-MS (isobutane): 447 (31), 446 (100, $[M+H]^+$), 445 (32), 365 (15), 326 (10), 312 (22), 296 (24), 282 (10), 85 (18).

Suitable crystals of **23** for the X-ray crystal-structure determination were obtained by crystallization from CH_2Cl_2/hexane at −20°.

6. *X-Ray Crystal-Structure Determination of* (Z)-**8**, **9a**, **9b**, **11**, *and* **23** (*Table* and *Figs. 2–4*)[9]. All measurements were performed on a *Nonius KappaCCD* diffractometer [35] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 2–4*. Data reduction was performed with *HKL Denzo* and *Scalepack* [36]. The intensities were corrected for *Lorentz* and polarization effects, and absorption corrections based on the multi-scan method [37] were applied. Equivalent reflections were merged. Each structure was solved by direct methods using SIR92 [38], which revealed the positions of all non-H-atoms. In the case of (*Z*)-**8**, the asymmetric unit contains two symmetry-independent molecules. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher-symmetry space group using the program PLATON [39], but none could be found. In the case of **23**, only low-quality crystals could be obtained. The asymmetric unit contains two molecules of **23** plus two partially occupied sites for CH_2Cl_2 molecules. The occupation factors of these sites refined to 0.865(9) and 0.827(9). The non-H-atoms were refined anisotropically. 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 group in (*Z*)-**8a**). The refinement of each structure 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 case of **21**. In the cases of (*Z*)-**8** and **9b**, two and one reflection, resp., whose intensities were considered to be extreme outliers, were omitted from the final refinement. Refinement of the absolute structure parameter [40] of **23** yielded a value of 0.02(11), which suggests that the refined coordinates represent the true absolute structure, although the precision on this parameter is low. Neutral atom-scattering factors for non-H-atoms were taken from [41a], and the scattering factors for H-atoms were taken from [42]. Anomalous dispersion effects were included in F_c [43]; the values for f' and f'' were those of [41b]. The values of the mass attenuation coefficients are those of [41c]. All calculations were performed using the SHELXL97 [44] program.

REFERENCES

[1] R. Huisgen, *Angew. Chem., Int. Ed.* **1963**, *2*, 565; R. Huisgen, *Angew. Chem., Int. Ed.* **1963**, *2*, 633; R. Huisgen, in '1,3-Dipolar Cycloaddition Chemistry', Ed. A. Padwa, Wiley-Interscience, New York, 1984, Vol. 1, p. 1; R. Huisgen, *Adv. Cycloadd.* **1988**, *1*, 1; R. Sustmann, *Heterocycles* **1995**, *40*, 1.

[2] '1,3-Dipolar Cycloaddition Chemistry', Vol. 1 and 2, Ed. A. Padwa, Wiley-Interscience, New York, 1984; W. Carruthers, 'Cycloaddition Reactions in Organic Synthesis', Pergamon, Oxford, 1990; A. Padwa, in 'Comprehensive Organic Synthesis', Eds. B. M. Trost, I. Fleming, Pergamon, Oxford,

---

[9] CCDC-730139–730143 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.cam.ac.uk/data_request/cif.

1991, Vol. 4, p. 1085; P. A. Wade, in 'Comprehensive Organic Synthesis', Eds. B. M. Trost, I. Fleming, Pergamon, Oxford, 1991, Vol. 4, p. 1134; 'Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products', in 'The Chemistry of Heterocyclic Compounds', Eds. A. Padwa, W. H. Pearson, Vol. 59, J. Wiley & Sons, New York, 2002.

[3] a) R. Hoffmann, R. B. Woodward, *Acc. Chem. Res.* **1968**, *1*, 17; b) R. B. Woodward, R. Hoffmann, *Angew. Chem., Int. Ed.* **1969**, *8*, 781 – 853; c) K. N. Houk, J. Sims, C. R. Watts, L. J. Luskus, *J. Am. Chem. Soc.* **1973**, *95*, 7301; d) R. Sustmann, *Pure Appl. Chem.* **1974**, *40*, 569; e) K. N. Houk, *Acc. Chem. Res.* **1975**, *8*, 361; f) K. N. Houk, K. Yamaguchi, in '1,3-Dipolar Cycloaddition Chemistry', Ed. A. Padwa, Wiley-Interscience, New York, 1984, Vol. 2, p. 407; g) I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions', J. Wiley & Sons, New York, 1976; h) I. Fleming, 'Pericyclic Reactions', Oxford University Press, Oxford, 1999; i) D. H. Ess, K. N. Houk, *J. Am. Chem. Soc.* **2008**, *130*, 10187.

[4] C. DiValentin, M. Freccero, R. Gandolfi, A. Rastelli, *J. Org. Chem.* **2000**, *65*, 6112; S. Vivanco, B. Lecea, A. Arrieta, P. Prieto, I. Morao, A. Linden, F. P. Cossio, *J. Am. Chem. Soc.* **2000**, *122*, 6078; K. Kaitha, P. Venuvanalingam, *J. Chem. Soc., Perkin Trans. 2* **2002**, 2130; K. Kaitha, P. Venuvanalingam, *Int. J. Quant. Chem.* **2005**, *104*, 64.

[5] a) R. A. Firestone, *J. Org. Chem.* **1968**, *33*, 2285; b) R. A. Firestone, *J. Org. Chem.* **1972**, *37*, 2181; c) A. Padwa, P. H. J. Carlsen, *J. Am. Chem. Soc.* **1977**, *99*, 1514; d) R. Sustmann, W. Sicking, R. Huisgen, *J. Am. Chem. Soc.* **2003**, *125*, 14425.

[6] R. Huisgen, G. Mlostoń, E. Langhals, *J. Org. Chem*. **1986**, *51*, 4087; R. Huisgen, G. Mlostoń, E. Langhals, *Helv. Chim. Acta* **2001**, *84*, 1805; R. Huisgen, E. Langhals, G. Mlostoń, O. Oshima, *Heterocycles* **1989**, *29*, 2069; R. Huisgen, E. Langhals, G. Mlostoń, O. Oshima, *Helv. Chim. Acta* **2002**, *85*, 2668; R. Huisgen, N. H. Langhals, *J. Org. Chem.* **1990**, *55*, 1412; G. Mlostoń, R. Huisgen, H. Giera, *Tetrahedron* **2002**, *58*, 4185; V. V. Rostovtsev, L. G. Green, V. V. Vokin, K. B. Sharpless, *Angew. Chem., Int. Ed.* **2001**, *41*, 2596; L. R. Domingo, M. T. Picher, *Tetrahedron* **2004**, *60*, 5053.

[7] L. Fišera, R. Huisgen, I. Kalwinsch, E. Langhals, X. Li, G. Mlostoń, K. Polborn, J. Rapp, W. Sicking, R. Sustmann, *Pure Appl. Chem.* **1996**, *68*, 789; R. Huisgen. G. Mlostoń, in 'Modern Problems of Organic Chemistry', Eds. A. A. Potekhin, R. R. Kostikov, M. S. Baird, St. Petersburg University Press, St. Petersburg 2004, Vol. 14, pp. 23 – 45.

[8] R. Huisgen, L. Fišera, H. Giera, R. Sustmann, *J. Am. Chem. Soc.* **1995**, *117*, 9671; R. Sustmann, W. Sicking, R. Huisgen, *J. Am. Chem. Soc.* **1995**, *117*, 9679.

[9] R. Huisgen, E. Langhals, *Tetrahedron Lett.* **1989**, *30*, 5369; R. Huisgen, E. Langhals, *Heteroat. Chem.* **2006**, *17*, 433.

[10] R. Huisgen, G. Mlostoń, K. Polborn, R. Sustmann, W. Sicking, *Liebigs Ann./Recl.* **1997**, 179.

[11] R. N. Butler, A. G. Coyne, P. McArdle, L. M. Sibley, L. A. Burke, *Tetrahedron Lett.* **2007**, *48*, 6687.

[12] T. Büchel, R. Prewo, J. H. Bieri, H. Heimgartner, *Helv. Chim. Acta* **1984**, *67*, 534.

[13] P. Wipf, H. Heimgartner, *Chimia* **1984**, *38*, 357; P. Wipf, R. Prewo, J. H. Bieri, G. Germain, H. Heimgartner, *Helv. Chim. Acta* **1988**, *71*, 1177; N. Bojkova, H. Heimgartner, *Heterocycles* **1998**, *47*, 781.

[14] G. Mlostoń, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1991**, *74*, 1386.

[15] K.-R. Meier, A. Linden, G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **1997**, *80*, 1190.

[16] G. Mlostoń, A. Linden, H. Heimgartner, *Pol. J. Chem.* **1997**, *71*, 32; G. Mlostoń, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1998**, *81*, 558; A. Gebert, A. Linden, G. Mlostoń, H. Heimgartner, *Heterocycles* **2002**, *56*, 393; A. Gebert, H. Heimgartner, *Helv. Chim. Acta* **2002**, *85*, 2073; A. Gebert, A. Linden, G. Mlostoń, H. Heimgartner, *Pol. J. Chem.* **2003**, *77*, 157; A. Gebert, A. Linden, G. Mlostoń, H. Heimgartner, *Pol. J. Chem.* **2003**, *77*, 867.

[17] a) G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **1992**, *75*, 1825; b) M. Kägi, A. Linden, H. Heimgartner, G. Mlostoń, *Helv. Chim. Acta* **1993**, *76*, 1715; c) G. Mlostoń, M. Petit, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1994**, *77*, 435; d) M. Petit, A. Linden, G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **1994**, *77*, 1076; e) M. Kägi, G. Mlostoń, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1994**, *77*, 1299; f) M. Kägi, A. Linden, G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **1996**, *79*, 855; g) M. Kägi, A. Linden, G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **1998**, *81*, 285.

[18] S. Pekcan, H. Heimgartner, *Helv. Chim. Acta* **1988**, *71*, 1673; G. Mlostoń, J. Romański, H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 1067; G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 1298.
[19] H. Heimgartner, *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *58*, 281.
[20] a) H. M. Hassaneen, A. S. Shawali, D. S. Farag, E. M. Ahmed, *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *113*, 53; b) A. Linden, E. M. A. H. Awad, H. Heimgartner, *Acta Crystallogr., Sect. C* **1999**, *55*, 1877.
[21] M. S. Seyfried, A. Linden, G. Mlostoń, H. Heimgartner, *Pol. J. Chem.* **2006**, *80*, 1363.
[22] C. Fu, M. V. Thrane, A. Linden, H. Heimgartner, *Tetrahedron* **2004**, *60*, 5407.
[23] D. H. Egli, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **2006**, *89*, 3041.
[24] D. H. Egli, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **2006**, *89*, 2815.
[25] L. Fišera, L. Jarošková, I. Matejková, H. Heimgartner, *Heterocycles* **1995**, *40*, 271.
[26] C. K. Johnson, 'ORTEP II', Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
[27] a) P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100; b) H. Werner, P. Schwab, E. Bleuel, N. Mahr, P. Steinert, J. Wolf, *Chem. – Eur. J.* **1997**, *3*, 1375; c) H. Werner, P. Schwab, E. Bleuel, N. Mahr, B. Windmüller, J. Wolf, *Chem. – Eur. J.* **2000**, *6*, 4461.
[28] K. C. Nicolaou, C. J. N. Mathison, T. Montagnon, *J. Am. Chem. Soc.* **2004**, *126*, 5192.
[29] E. R. Blout, V. W. Eager, R. M. Golfstein, *J. Am. Chem. Soc.* **1946**, *68*, 1983.
[30] D. H. R. Barton, B. J. Willis, *J. Chem. Soc., Chem. Commun.* **1970**, 1225; J. Buter, S. Wassenaar, R. M. Kellogg, *J. Org. Chem.* **1972**, *37*, 4045; R. M. Kellogg, *Tetrahedron* **1976**, *32*, 2165; F. S. Guziek Jr., L. J. Sanfilippo, *Tetrahedron* **1988**, *44*, 6241.
[31] W. E. Bachmann, W. S. Struve, *Org. React.* **1942**, *1*, 38.
[32] D. S. Wulfman, S. Yousefian, J. M. White, *Synth. Commun.* **1988**, *18*, 2349.
[33] H. Staudinger, O. Kupfer, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 2197.
[34] R. Andreasch, A. Zipser, *Monatsh. Chem.* **1903**, *24*, 499.
[35] R. Hooft, KappaCCD Collect Software, Nonius BV, Delft, The Netherlands, 1999.
[36] 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.
[37] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
[38] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *SIR92*, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[39] A. L. Spek, PLATON, Program for the Analysis of Molecular Geometry, University of Utrecht, The Netherlands, 2004.
[40] H. D. Flack, G. Bernardinelli, *Acta Crystallogr., Sect. A* **1999**, *55*, 908; H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **2000**, *33*, 1143.
[41] 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.
[42] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[43] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[44] G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

Received April 30, 2009