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

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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 CH₂Cl₂ and in THF at room temperature in the presence of [Rh₂(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. twostep 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].

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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.



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 , PhCHN₂, and Ph₂CN₂.

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(4H)-thione (1) [17b–d], we chose CH₂N₂ (**7a**), PhCHN₂ (**7b**), and Ph₂CN₂ (**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 N₂ 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 2diazopropane [17a] or (*t*-Bu)₂CN₂ [17c].



The reaction of 2 with 7a was started by dropwise addition of a 5M solution of 7a in Et₂O 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 CH₂ adducts of 2. Furthermore, the ¹³C-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 (¹H) and 21.8 (¹³C)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 ¹H-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 ¹H-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–CH₂ 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*.



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 LiClO₄ 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 LiClO₄ by ¹³C-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 ¹³C-NMR, elemental-analysis, and MS data, and was established by X-ray crystallog-raphy (*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].



Whereas the transformation $2 + 7c \rightarrow 11$ 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 N₂, could lead to 13 (*Scheme 2*). Ring closure *via* 1,3-

³) The formation of **10** from **7c** in the presence of [Rh₂(OAc)₄] has been described repeatedly [27]. Because the ¹³C-NMR data of our compound did not correspond to those described in the literature [28], we synthesized **10** independently from benzophenone and NH₂NH₂·H₂O in EtOH at 160° according to [29] and from **7c** according to the procedure described in [27b]. The ¹³C-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 N₂ 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)-8⁴), which still offers three π -bonds as dipolarophiles, was dissolved in CH₂Cl₂, and a 0.5M solution of 7a in Et₂O (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)-15⁵) was isolated.



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

The analogous treatment of a solution of (Z)-8⁴) 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 ¹H-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 N₂ 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 H₂O 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

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

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

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



LiClO₄ 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.



The structures of **21a** and **21b** were deduced from their MS and ¹³C-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*).



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), PhCHN₂ (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 Cmethylation 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=Cbond. In this case, both diazo compounds reacted with the C=S group, leading to the 2benzylidene-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.

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Experimental Part

1. General. TLC: Merck 60 F_{254} SiO₂-coated Al-plates, 0.2 mm; detection of the substances on the TLC plates under UV light (λ 254 nm) or with KMnO₄ soln. Column chromatography (CC): SiO₂ 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. ¹H- and ¹³C-NMR Spectra: Bruker AVX-300 or Bruker ARX-300 instrument (300 and 75.5 MHz, resp.), in CDCl₃; multiplicity of C-atoms from DEPT spectra. MS: Finnigan MAT-95 (EI, 70 eV, or CI (NH₃)) 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], PhCHN₂ (7b) from benzaldehyde tosylhydrazone according to [32], and Ph₂CN₂ (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: 3057w, 3023w, 1717vs, 1603m, 1594s, 1572w, 1492m, 1453w, 1446m, 1357s, 1316w, 1285w, 1251vs, 1185w, 1174s, 1156s, 1070w, 1036w, 1025w, 933w, 824w, 758m, 732m, 691m, 681s, 632w. ¹H-NMR: 7.80 (*s*, =CH); 7.59–7.47 (*m*, 8 arom. H); 7.31–7.27 (*m*, 2 arom. H). ¹³C-NMR: 193.3 (*s*, C=S); 167.5 (*s*, C=O); 134.8, 133.3 (*z*, 2 arom. C); 133.3, 130.7, 130.6, 129.6, 129.5, 129.3, 128.3 (7d, 10 arom. CH, =CH); 123.3 (*s*, C(5)).

3. Reactions of **2** with $7\mathbf{a} - 7\mathbf{c}$. 3.1. Reaction with $7\mathbf{a}$. 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 $7\mathbf{a}$ in Et₂O. 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 SiO₂, 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. $165-167^{\circ}$. $R_{\rm f}$ (hexane/AcOEt 5:1): 0.44. HPLC (hexane/EtOH 30:1): 5.16 (100, (*Z*)-**8**), 5.37 (33, (*E*)-**8**). IR: 1708s, 1589m, 1569w, 1496s, 1488m, 1443w, 1348s, 1318w, 1291w, 1235vs, 1177s, 1168s, 1074w, 1061w, 1026w, 983w, 865w, 762w, 727s, 698m, 688m, 639w. ¹H-NMR: 7.55-7.27 (*m*, 10 arom. H); 2.76 (*s*, Me, (*Z*)-**8**); 2.35 (*s*, Me, (*E*)-**8**). ¹³C-NMR: 194.2 (*s*, C=S); 165.8 (*s*, C=O); 150.9 (*s*, Ph(Me)*C*); 142.0, 135.2 (*2s*, 2 arom. C); 129.7, 129.5, 129.4, 129.3, 129.0, 128.3, 128.0, 127.3, 126.6 (9d, 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 C₁₇H₁₃NOS₂ (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: 1721vs, 1593w, 1497m, 1455w, 1424w, 1372m, 1351s, 1318w, 1241vs, 1178m, 1154w, 1129m, 1073w, 1055w, 1046w, 1030w, 976m, 834w, 777w, 757w, 728vs, 708w, 696m, 688m, 629w. ¹H-NMR: 7.55–7.47, 7.42–7.33, 7.28–7.25, 7.25–7.17 (4m, 10 arom. H); 3.37 (dd, ³*J*(*cis*) = 9.7, ³*J*(*trans*) = 8.1, PhC*H*); 2.42 (dd, ²*J* = 5.9, ³*J*(*cis*) = 9.7, 1 H of CH₂): ¹³C-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 (6d, 10 arom. C); 41.4 (*s*, spiro-C); 34.9 (*d*, PhCH); 22.7 (*t*, CH₂). 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, [PhCHCH₂]⁺), 91 (9, [PhCH₂]⁺), 77 (14, Ph⁺). Anal. calc. for C₁₇H₁₃NOS₂ (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°. $R_{\rm f}$ (hexane/AcOEt 5 : 1): 0.31. IR: 3057*w*, 1731*vs*, 1593*w*, 1495*s*, 1446*w*, 1339*vs*, 1316*m*, 1279*w*, 1226*vs*, 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*. ¹H-NMR: 7.47–7.26 (*m*, 13 arom. H); 7.13–7.10 (*m*, 2 arom. H); 4.03 (*d*, ³*J*=8.9, PhCH); 3.68 (*d*, ³*J*=8.9, PhCH). ¹³C-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 PhCH). EI-MS: 389 (12), 388 (26), 387 (100, *M*⁺), 252 (14), 251 (11), 224 (11), 223 (13, [*M* – CONPhCS]⁺), 178 (8), 165 (7), 147 (5), 135 (8), 91 (7, [PhCH₂]⁺), 77 (7, Ph⁺). Anal. calc. for C₂₃H₁₇NOS₂ (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. $255-258^{\circ}$. $R_{\rm f}$ (hexane/AcOEt 5:1): 0.41. IR: 3046w, 2924w, 2852w, 1696vs, 1604vs, 1491vs, 1455w, 1442s, 1353vs, 1309w, 1287m, 1247vs, 1209w, 1175s, 1164m, 1130m, 1071m, 1051m, 1026m, 876w, 837w, 777w, 761s, 750m, 733m, 694vs, 643m, 606m. ¹H-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). ¹³C-NMR: 167.6 (*s*, C=O); 141.5, 138.8, 136.8, 134.7, 130.9 (5*s*, 4 arom. C, Ph₂C); 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 (NH₃): 449 (21, $[M + NH_4]^+$), 434 (16), 433 (34), 432 (100, $[M + H]^+$). Anal. calc. for C₂₉H₂₁NOS (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 SiO₂ 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_t (hexane/AcOEt 5:1): 0.53. IR: 3083w, 3056w, 3022w, 2926w, 1587m, 1564m, 1488m, 1443s, 1320s, 1294w, 1177w, 1159w, 1076w, 1027w, 999w, 983w, 956s, 910w, 774s, 764s, 692vs, 667m, 655s, 613w. ¹H-NMR: 7.50–7.24 (*m*, 20 arom. H). ¹³C-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 CH₂Cl₂ (*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 SiO₂ 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. ¹H-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). ¹³C-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*(**8**) + Na]⁺), 318 (100, [*M*(**15**) + Na]⁺).

5.2. Reaction of 8 with 7b. A soln. of 87) (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 SiO₂ 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 CH₂Cl₂/hexane to give a mixture of diastereoisomers of 2benzylidene-5-[(methyl)(phenyl)methylidene]-3-phenyl-1,3-thiazolidin-4-one (16). Colorless crystals. M.p. $84-87^\circ$. $R_{\rm f}$ (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: 3059m, 2924s, 2853m, 1736vs, 1677vs, 1592vs, 1571s, 1492vs, 1454s, 1441s, 1348vs, 1290m, 1239vs, 1195vs, 1157vs, 1072m, 1028s, 1002m, 985s, 915w, 868w, 843m, 814w, 762s, 737s, 728s, 692vs, 664w, 655w, 638m, 619w, 603w. ¹H-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 (3s, Me of (Z,E)-, (E,Z)-, and E,E)-**16**, resp.). ¹³C-NMR: 164.6 (s, C=O); 152.0, 143.5, 142.2, 135.3, 134.6, 132.8 (6s, 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 (15d, 15 arom. C); 125.7 (s, C(5)); 120.5 (s, C(2)); 103.1 (d, =CH); 22.6, 20.7 (2q, 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 LiClO₄ (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 SiO₂ 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 CH₂Cl₂/hexane. Colorless crystals. M.p. 159–160°. R_f (hexane/AcOEt 5:1): 0.31. IR: 3063w, 3038w, 1747s, 1722vs, 1699vs, 1602m, 1593m, 1493s, 1448m, 1424w, 1368vs, 1291w, 1245vs, 1199m, 1162vs, 1146s, 1131m, 1073w, 1026w, 1005w, 991w, 955w, 849m, 753vs, 737s, 694vs, 657w, 630w, 607w. ¹H-NMR: 7.46–7.26 (*m*, 13 arom. H); 7.21–7.09 (*m*, 2 arom. H); 3.97 (*d*, ³*J* = 8.9, PhCH); 3.56 (*d*, ³*J* = 8.9, PhCH). ¹³C-NMR: 170.1, 169.6 (2s, 2 C=O); 134.4, 132.7, 132.6 (3s, 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 PhCH). ESI-MS (CH₂Cl₂/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 SiO₂ 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 CHCl₃/hexane. Colorless crystals. M.p. 224–228°. *R*_f (hexane/AcOEt 5:1): 0.31. IR: 3059*w*, 3030*w*, 2923*w*, 1753*w*, 1706*vs*, 1620*vs*, 1572*s*, 1495*vs*, 1446*s*, 1377*vs*, 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*, 695*vs*, 630*w*, 616*w*. ¹H-NMR: 7.49–7.07 (*m*, 20 arom. H); 5.73 (*s*, =CH); 3.82 (*d*, ³*J* = 8.6, PhC*H*); 3.31 (*d*, ³*J* = 8.6, PhC*H*). ¹³C-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 PhCH). ESI-MS (MeOH/CH₂Cl₂ 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 SiO₂. 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 CH₂Cl₂/hexane. Colorless crystals. M.p. 223 – 225°. *R*_f (hexane/AcOEt 5 : 1): 0.41. IR: 3060w, 3029m, 1705vs, 1597vs, 1494vs, 1452m, 1442s, 1340vs, 1309m, 1289s, 1247m, 1224vs, 1196w, 1180w, 1154m, 1127m, 1073m, 1030m, 1002w, 982w, 758vs, 730m, 698vs, 647m, 604m. ¹H-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*, ³*J* = 8.4, PhC*H*); 3.28 (*d*, ³*J* = 8.4, PhC*H*). ¹³C-NMR: 170.7 (*s*, C=O); 141.7, 139.2, 137.0, 135.2, 134.5, 132.0 (6s, 5 arom. C, Ph₂C); 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 (13d, 25 arom. C); 121.4 (*s*, C(5)); 43.8 (*s*, spiro-C); 40.7, 33.9 (2*d*, 2 PhCH). CI-MS (NH₃): 539 (15, [*M*+NH₄]⁺), 522 (100, [*M*+H]⁺). Anal. calc. for C₃₆H₂₇NOS (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 SiO₂ and separated by CC (hexane/AcOEt 20:1): 8 mg (4%) of 5-[(methyl)(phenyl)methylidene]-2-(diphenyl-methylidene)-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 CH₂Cl₂/hexane.

Data of **22** (impure). Colorless crystals. M.p. $160-195^{\circ}$. $R_{\rm f}$ (hexane/AcOEt 5:1): 0.47. ¹H-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). ¹³C-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, Ph₂C); 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. Crystallogr	aphic Data for Com	pounds (Z)- 8, 9a, 9b, 11 , a	md 23	
	8 -(<i>Z</i>)	9a	96	11	23
Crystallized from Empirical formula M	AcOEt/pentane C ₁₇ H ₁₃ NOS ₂ 311 42	DME/pentane C ₁₇ H ₁₃ NOS ₂ 311.42	toluene/DME/pentane C ₂₃ H ₁₇ NOS ₂ 387 51	DME/pentane C ₂₉ H ₂₁ NOS 43155	CH ₂ Cl ₂ /hexane C ₃₀ H ₂₃ NOS · 0.85 CH ₂ Cl ₂ 517 77
Crystal color, habit Crystal dimensions [mm]	yellow, prism $0.07 \times 0.10 \times 0.25$	colorless, prism $0.05 \times 0.10 \times 0.17$	yellow, prism $0.15 \times 0.18 \times 0.20$	yellow, prism $0.15 \times 0.25 \times 0.30$	colorless, prism $0.15 \times 0.17 \times 0.32$
Temp. [K]	160(1)	160(1)	160(1)	160(1)	160(1)
Crystal system Space group	P2 ₄ /c	monoclinic P2./n	monoclinic C2/c	triclinic <i>P</i> Ţ	monoclinic
	8	4	8	2	4
Reflections for cell determination 2θ Range for cell determination [°]	93969 4 - 55	27659 4-60	58836 4-50	32571 4-50	123238 4-55
Umt cell parameters					16 8631637
	9.9402(4) 8 4012(4)	(c)00(1).	2/.1.54/(8) 8.0803/3)	(0)47/C.6 (2)00CL01	(c)10.8051(c)
	35 564(1)	21 5970(5)	(c)ccoc.o 20.6284(7)	12 5773(7)	0.2240(1) 25 6343(4)
α []	90	90 00	90	74.792(3)	90
β [°]	94.755(2)	95.839(1)	129.874(1)	71.200(4)	102.6264(8)
√ [∘]	90	90	90	76.689(4)	90
$V[\dot{A}^3]$	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
$\mu(MoK_a) \ [mm^{-1}]$	0.353	0.351	0.288	0.169	0.319
Scan type	ϕ and ω	ϕ and ω	(i) 20	8	ϕ and ω
Zo _(max) [] Transmission factors [min . mov]	0.761 · 0.005	00 0.827+0.006	JU 0 201 - 0 05 2	00 0 866 : 0 080	7.2 0 202 - 0 022
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	I	I	I	I	0.019(3)
Final Δ_{\max}/σ	0.001	0.001	0.001	0.001	0.001
$\Delta \rho(\max; \min) [e \ \text{\AA}^{-3}]$	0.32; -0.38	0.35; -0.44	0.23; -0.27	0.18; -0.29	1.23; -0.53
a) $w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$ where P .	$=(F_{ m o}^{2}+2F_{ m c}^{2})/3$				

Helvetica Chimica Acta – Vol. 92 (2009)

117.5 (2s, 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. $170-171^{\circ}$. R_t (hexane/AcOEt 5:1): 0.41. IR: 3053w, 2924w, 1708vs, 1596s, 1492s, 1454m, 1442m, 1345vs, 1310w, 1287m, 1253s, 1227s, 1202w, 1178w, 1142m, 1073m, 1029w, 976w, 776w, 759m, 725m, 697vs, 643m, 605m, 589vs. ¹H-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*, ${}^{3}J(cis) = 9.7$, ${}^{3}J(trans) = 7.7$, PhCH); 2.13 (*dd*, ${}^{2}J = 5.5$, ${}^{3}J(cis) = 9.7$, 1 H of CH₂); 1.63 (*dd*, ${}^{2}J = 5.5$, ${}^{3}J(trans) = 7.7$, 1 H of CH₂). ¹³C-NMR: 174.2 (*s*, C=O); 141.8, 139.2, 137.1; 135.5 (4*s*, 4 arom. C); 132.2, 119.7 (*s*, Ph₂C, C(2)); 130.2, 130.0, 128.5, 128.4, 128.0, 127.3, 127.2, 127.14, 127.12, 126.8, 125.9 (12d, 20 arom. C); 37.7 (*s*, spiro-C); 31.6 (*d*, PhCH); 2.1 (*t*, CH₂). 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_a 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 CH₂Cl₂ 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.

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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.

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