1,5-Dipolar Electrocyclizations of Thiocarbonyl Ylides Bearing C=N Groups: Reactions of *N*-[(Dimethylamino)methylene]thiobenzamide and 2-(Dimethylhydrazono)-1-phenylethane-1-thione with Diazo Compounds

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The reactions of thiobenzamide **8** with diazo compounds proceeded *via* reactive thiocarbonyl ylides as intermediates, which underwent either a 1,5-dipolar electrocyclization to give the corresponding five membered heterocycles, *i.e.*, 4-amino-4,5-dihydro-1,3-thiazole derivatives (*i.e.*, **10a**, **10b**, **10c**, *cis*-**10d**, and *trans*-**10d**) or a 1,3-dipolar electrocyclization to give the corresponding thiiranes as intermediates, which underwent a S_Ni'-like ring opening and subsequent 5-*exo-trig* cyclization to yield the isomeric 2-amino-2,5-dihydro-1,3-thiazole derivatives (*i.e.*, **11a**, **11b**, **11c**, *cis*-**11d**, and *trans*-**11d**). In general, isomer **10** was formed in higher yield than isomer **11**. In the case of the reaction of **8** with diazo(phenyl)methane (**3d**), a mixture of two pairs of diastereoisomers was formed, of which two, namely *cis*-**10d** and *trans*-**10d**, could be isolated as pure compounds. The isomers *cis*-**11d** and *trans*-**11d** remained as a mixture. In the reactions of the thioxohydrazone **9** with diazo compounds **3b** and **3d**, the main products were the alkenes **18** and **23**, respectively. Their formation was rationalized by a 1,3-dipolar electrocyclization of the corresponding thiocarbonyl ylide and subsequent desulfurization of the intermediate thiiran. As minor products, 2,5-dihydro-1,3-thiazol-5-amines **21** and **24** were obtained, which have been formed by 1,5-dipolar electrocyclization of the thiocarbonyl ylide, followed by a 1,3-shift of the dimethylamino group.

1. Introduction. – The concept of the 1,5-dipolar electrocyclization as a tool for the synthesis of five-membered heterocycles has been proposed 25 years ago [1][2]. Since, we have shown that thiocarbonyl ylides, which bear a C=O group at the C(α)-atom, undergo this cyclization to give 1,3-oxathioles [3][4] (see also [5][6]). These thiocarbonyl ylides were generated *in situ* by the reaction of thiocarbonyl derivatives with α-diazo carbonyl compounds. Very recently, we reported on the reaction of α-thioxocarbonyl derivatives with diazo compounds [7]. We were mostly interested in systems, in which the conjugated π-system consisted of a C=O or a C=S group, *i.e.*, in reactions of α-thioxo ketone **1** and α-thioxo thioamide **2** (*Scheme 1*).

The reactions with diazo compounds **3** all followed the same pathway: 1,3-dipolar cycloaddition to give a 2,5-dihydro-1,3,4-thiadiazole, N_2 elimination by cycloreversion to produce thiocarbonyl ylides **4**, and 1,5-dipolar electrocyclization. The resulting products are either 1,3-oxathioles **5** or 1,3-dithioles **6**, respectively. Some thiirane side products, which were formed by a competing 1,3-dipolar electrocyclization, were unstable, and elimination of sulfur led to the corresponding alkenes, *e.g.*, **7**.

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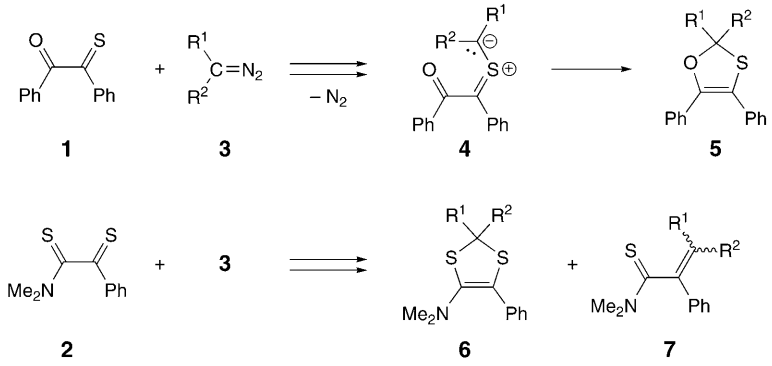
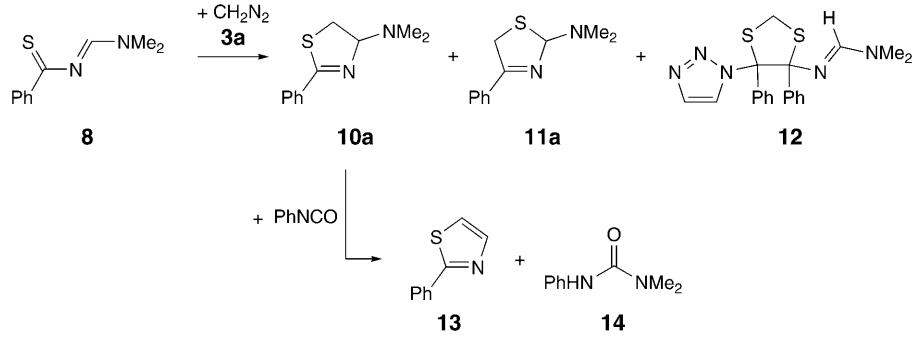
Scheme 1



With the aim of extending the scope of this reaction, we used thiocarbonyl compounds that possess a conjugated system containing a N-atom. Since *N*-[(dimethylamino)methylidene]thiobenzamide (**8**; *cf. Scheme 2*) is not only readily available, but also stable, and thus allows for a precise calculation of the yield[2]), we used it as a starting material in the present work. Because we were interested in systems with the N-atom in different positions, reactions of 2-(dimethylhydrazono)-1-phenylethane-1-thione (**9**; *cf. Scheme 7*) were also investigated. Although **9** showed a few drawbacks concerning stability and yield calculation, we used it because of the relatively simple four-step synthesis. The results of the reactions with **8** and **9** are presented below.

2. Results and Discussion. – 2.1. *Reactions with* N-*[(Dimethylamino)methylidene]-thiobenzamide* (**8**). In 1989, *Danion-Bougot et al.* [8a] showed that the reaction of **8** with diazomethane (**3a**) in Et_2O in the dark led to three products, **10a**, **11a**, and **12** (*Scheme 2*; see also [8b]). The correlation of the spectroscopic data with the corresponding structures was supported by the conversion of **10a** with phenyl isothiocyanate in refluxing benzene to give the known 1,3-thiazole **13** and *N*,*N*-dimethyl-*N*′-phenylurea **14** (*Scheme 2*).

Scheme 2



[2]) Because of unstable starting materials, it was a problem to calculate correct yields for the reactions described in [7].

On closer inspection of this result, we became convinced that the correlation of the structures and data requires verification, because an additional structure also corresponds to the given data. Instead of **11a**, the isomeric structure **10a**′ (*Fig. 1*) could be generated by a 1,3-H shift in **10a**. The corresponding data of **10a**′ and **11a** are expected to be quite similar, but the results of NOE experiments by irradiation of the Me_2N group would be distinctive. Whereas **10a** and **11a** should show a positive NOE, no NOE would be observed in the case of **10a**′ (*Fig. 1*).

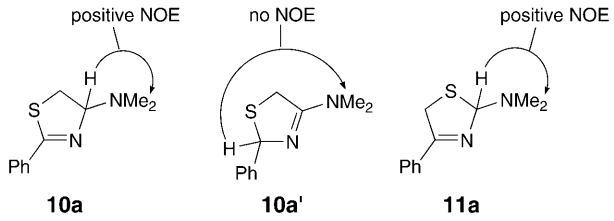
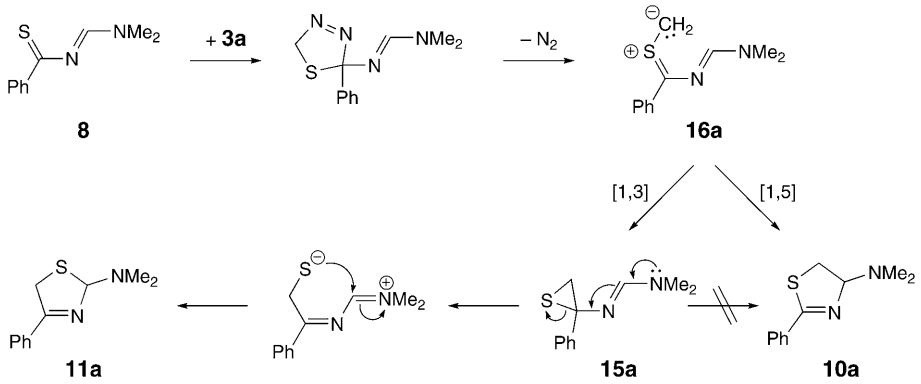


Fig. 1. *NOE Signals of* **10a**, **10a**′, *and* **11a**

Therefore, we repeated the experiment with **8** and **3a** in Et_2O and obtained two isomeric dihydro-1,3-thiazoles in accordance with [8a] (ratio *ca.* 1:1). Both products showed a positive NOE of the methine H-atom on irradiation of Me_2N, *i.e.*, both molecules contain the structure fragment $CH-NMe_2$, and, therefore, the assignment made by *Danion-Bougot et al.* is correct indeed. The formation of **10a**′ can be excluded.

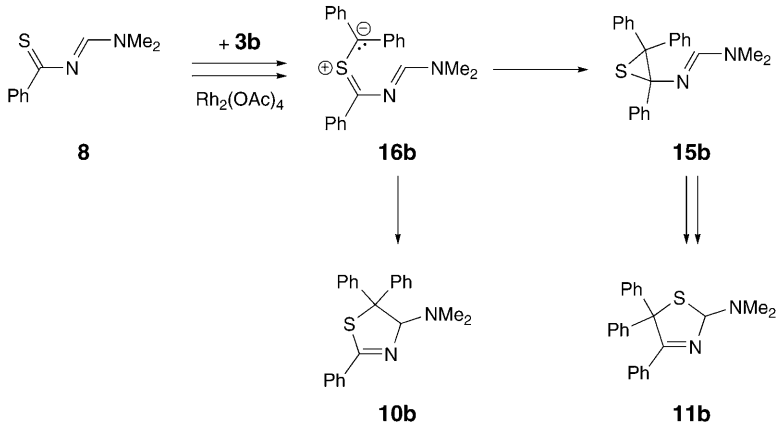
However, the reaction pathway proposed by *Danion-Bougot et al.*, in which **10a** and **11a** are formed *via* an intermediate thiirane **15a**, is not in accordance with the general experience for such reactions. We assume that the intermediate thiocarbonyl ylide **16a** is the origin of both compounds **10a** and **11a** (*Scheme 3*). Whereas the formation of **11a** can be explained *via* a 1,3-dipolar electrocyclization to give **15a**, followed by a S_Ni'-like ring opening and subsequent 5-*exo-trig* cyclization, as proposed by *Danion-Bougot et al.*, **10a** is formed *via* a 1,5-dipolar electrocyclization of **16a**. This pathway seems to be much more reliable, as there is no C–C-bond cleavage of the thiirane ring known to give thiocarbonyl ylides. Rather, thiocarbonyl ylides are the usual intermediates of reactions of thioketones with diazo compounds [5][6].

Scheme 3



The reaction of **8** with diazo(diphenyl)methane (**3b**) was carried out in CH_2Cl_2 at room temperature in the presence of a catalytic amount of $Rh_2(OAc)_4$ and yielded two products. Based on previous experiences from experiments with thiocarbonyl ylides [7], we assumed that the reaction would lead to an intermediate thiocarbonyl ylide **16b**, which would undergo either a 1,3-dipolar electrocyclization to give the thiirane **15b** and, by subsequent S_Ni' ring opening and 1,5-cyclization, the 2,5-dihydro-1,3-thiazole **11b**, or a 1,5-dipolar electrocyclization to yield the corresponding 4,5-dihydro-1,3-thiazole **10b** (*Scheme 4*).

Scheme 4

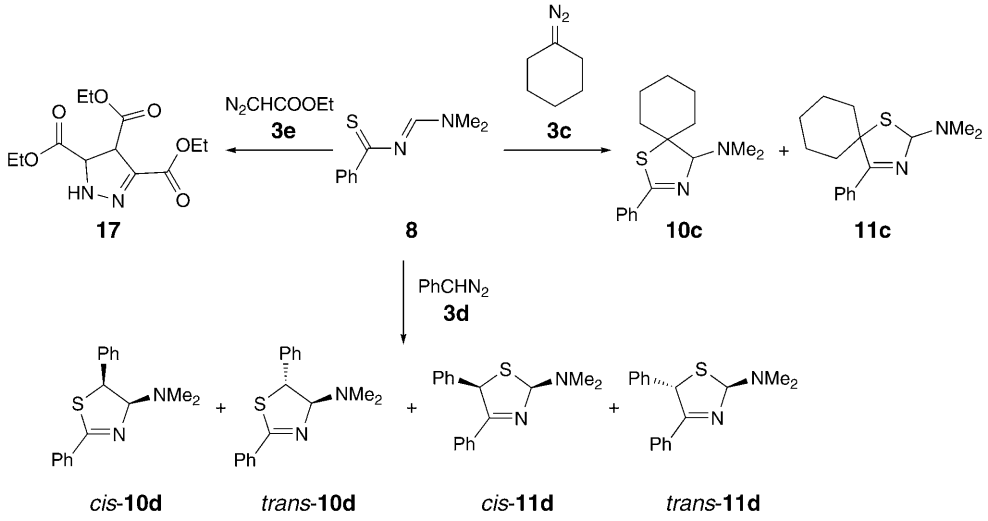


The ^{13}C-NMR spectra of the two isolated products showed that we could exclude structure **15b**, because the expected *d* for the amidine C-atom at *ca.* 155 ppm was missing (see *Exper. Part*). The spectra of both compounds again were very similar with only small deviations of 5–10 ppm for some signals. The NOE experiment showed that the Me_2N group in **10b** has to be close to the H-atom, which absorbed at 6.84 ppm. In the case of **11b**, the NOE experiment showed the analogous response of an H-atom bonded to the heterocycle, therefore, an isomer of type **10a**′ (*Fig. 1*) can be excluded. By 'inadequate-NMR measurements' of **10b**, it has been shown that $CHNMe_2$ is connected directly to another C-atom of the ring. In compound **11b**, no such coupling would be observed. Unfortunately, it was not possible to crystallize the two products, as they remained as oily substances. Obviously, the 1,5-dipolar electrocyclization is preferred to a 1,3-dipolar electrocyclization, since the yield of **10b** (49%) is significantly higher than that of **11b** (30%).

Similar to the reaction of **8** with **3b**, treatment with diazocyclohexane (**3c**) led to two products **10c** and **11c** (*Scheme 5*). The latter proved to be unstable and could not be isolated in pure form. In contrast to the previous experiments, the reaction takes place spontaneously, and, therefore, there was no need of Rh catalyst. In the crude NMR spectrum, the products showed the already known pattern of the **10a**/**11a** mixture, but the ratio of **10c** to **11c** rose to 3 : 1 (*Scheme 5*).

The next diazo compound selected for the reaction with **8** was diazo(phenyl)methane (**3d**). In Et_2O/toluene at room temperature, a spontaneous reaction occurred, which, after 5 d, led to a mixture of four isomeric products, but only three of them,

Scheme 5



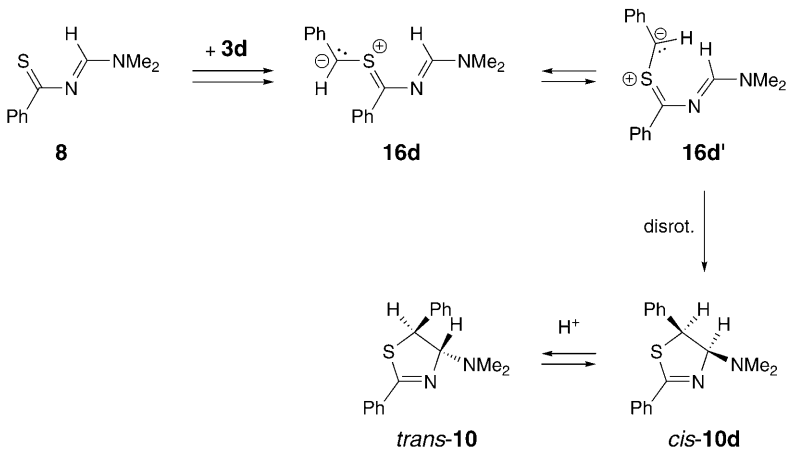
namely *cis*-**10d**, *cis*-**11d**, and *trans*-**11d**, could be isolated after chromatographic workup (SiO_2; hexane/AcOEt/Et_3N; *Scheme 5*). The analogous reaction of **8** with **3d** in THF, catalyzed by $Rh_2(OAc)_4$, and workup without using Et_3N as an additive led only to one product, namely the fourth isomer, *i.e.*, *trans*-**10d**, of the reaction described above (see *Exper. Part*). The reasons for the different results are not clear. A possible explanation could be that, under acidic workup conditions (SiO_2 without Et_3N), the isomers *cis*-**11d** and *trans*-**11d** decomposed, and *cis*-**10d** isomerized to *trans*-**10d**. With respect to the thermodynamic stability, the *trans*-product should be more stable than the *cis*-isomer.

The assignment of the structures of the four isomers was achieved on the basis of the following data. First, 2D-NMR studies (HMBC) have shown a coupling between Me_2N and both H-atoms of the heterocycle, namely H–C(4) and H–C(5), of *trans*-**10d**. On the other hand, only one coupling (Me_2N, H–C(2)) was observed in *cis*-**11d** and *trans*-**11d**. Second, the *cis*- and *trans*-isomers could be distinguished on the basis of their H,H-coupling constants. As a rule, the *cis* coupling in five-membered heterocycles is larger than the *trans* coupling [9]. Therefore, the smaller $J(4,5)$ value of 4.4 Hz of *trans*-**10d** (*cis*-**10d**, 7.6 Hz) indicates the *trans*-configuration.

An explanation of the formation of the thermodynamically less favored *cis*-**10d** is based on the selectivity rules for pericyclic reactions (see, *e.g.*, [10][11]). For steric reasons, the preferred structure of the thiocarbonyl ylide formed from **8** and **3d** should be **16d**, which is in equilibrium with **16d′** (*Scheme 6*). The disrotatory ring closure of the latter then yields *cis*-**10d**. The more stable *trans*-**10d** could be formed under the conditions of the acidic workup *via* a reversible 1,3-H shift.

Surprisingly, the reaction of ethyl diazoacetate (**3e**) with **8** did not lead to the expected thiazole derivative. The only product, which could be isolated in traces, was **17**, the 'trimer' of the starting diazo compound (*Scheme 5*). Its structure was established by X-ray crystallography (*Fig. 2*). In the crystal structure, the two ester groups at the

Scheme 6



adjacent stereogenic centres have the *trans*-configuration. The NH group forms an intermolecular H-bond with one of the ester carbonyl O-atoms of an adjacent molecule and thereby links the molecules into extended chains, which run parallel to the [100] direction and can be described by a graph set motif [12] of C(6).

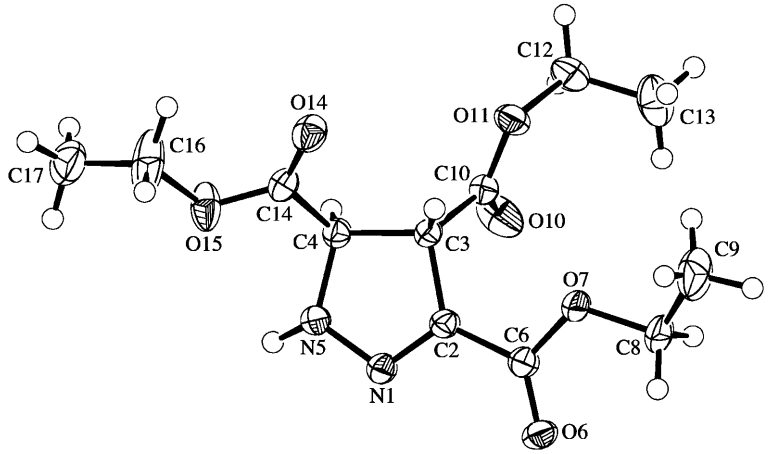
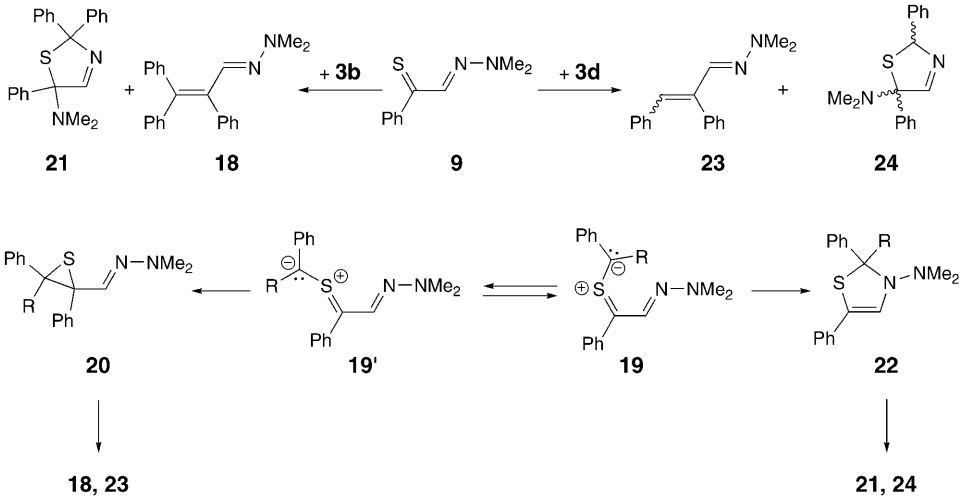


Fig. 2. *ORTEP Plot* [13] *of the molecular structure of* **17** (50% probability ellipsoids, arbitrary numbering of atoms)

The described results obtained with **8** show that this starting material is relatively unreactive, and, therefore, the reaction with less reactive diazo compounds has to be catalyzed by $Rh_2(OAc)_4$, or the reaction time has to be increased. Whereas, in the reaction of **8** with **3a**, 46% of the products (**10a** + **11a**) could be isolated, no reaction took place with **3b** without addition of catalyst. In the case of **3e**, no formation of a thiocarbonyl ylide was observed. Instead, dimerization of the generated carbenoid yielded diethyl fumarate [14], which underwent a 1,3-dipolar cycloaddition with **3e** to give **17**.

2.2. *Reactions with 2-(Dimethylhydrazono)-1-phenylethane-1-thione* (**9**). The reaction of **9** with **3b** in benzene at room temperature gave two products. The first one was identified as *N*,*N*-dimethyl-*N*′-(2,3,3-triphenylprop-2-enylidene)hydrazine (**18**; *Scheme 7*). The reaction mechanism of its formation, in analogy with previous cases, is proposed as follows: 1,3-dipolar cycloaddition and elimination of N_2 yields the thiocarbonyl ylide of type **19**′, which undergoes a 1,3-dipolar electrocyclization to give the corresponding thiirane **20**. Finally, desulfurization of the latter leads to **18** (*cf.* [7]). The second product was isolated in small yields and turned out, surprisingly, to be 2,5-dihydro-*N*,*N*-dimethyl-2,2,5-triphenylthiazol-5-amine (**21**). It apparently results from a rearrangement of the primarily formed intermediate 1,3-thiazol-3-amine **22** (R = Ph). In this case, unlike in the reactions with **8**, the Me_2N group is bound to the N(3)-atom. A 1,3-shift of the amino substituent then leads to the 2,5-dihydro-1,3-thiazole **21** (*Scheme 7*).

Scheme 7



The structures of **18** and **21** have been established by X-ray crystallography (*Fig. 3*). The conjugated π-system in **18** from C(1) to N(4), including N(5), C(7), C(13), and C(19) is almost planar. All Ph substituents in compound **18** are twisted out of this plane because of steric reasons (torsion angles C(2)–C(1)–C(7)–C(8) 52.7(2)°, C(2)–C(1)–C(13)–C(18) 44.0°, and C(1)–C(2)–C(19)–C(20) 55.1(2)°). In the case of **21**, the asymmetric unit contains two symmetry-independent molecules, each of which is disordered by inversion of the entire molecule about its centre of gravity. The ratio of the major orientation of each molecule to the minor orientation is *ca.* 93 : 7. The crystals are also inversion twins.

The analogous reaction of **9** with **3d** gave a complex mixture of products, which consisted of two pairs of diastereoisomers at least. The (*E*/*Z*)-isomers of *N*,*N*-dimethyl-*N*′-(2,3-diphenylprop-2-enylidene)hydrazine (**23**) and the *cis*/*trans*-isomers of 2,5-dihydro-*N*,*N*-dimethyl-2,5-diphenylthiazol-5-amine (**24a** and **24b**) are the likely products, which could be separated partially by CC and MPLC. The structures were elucidated on the

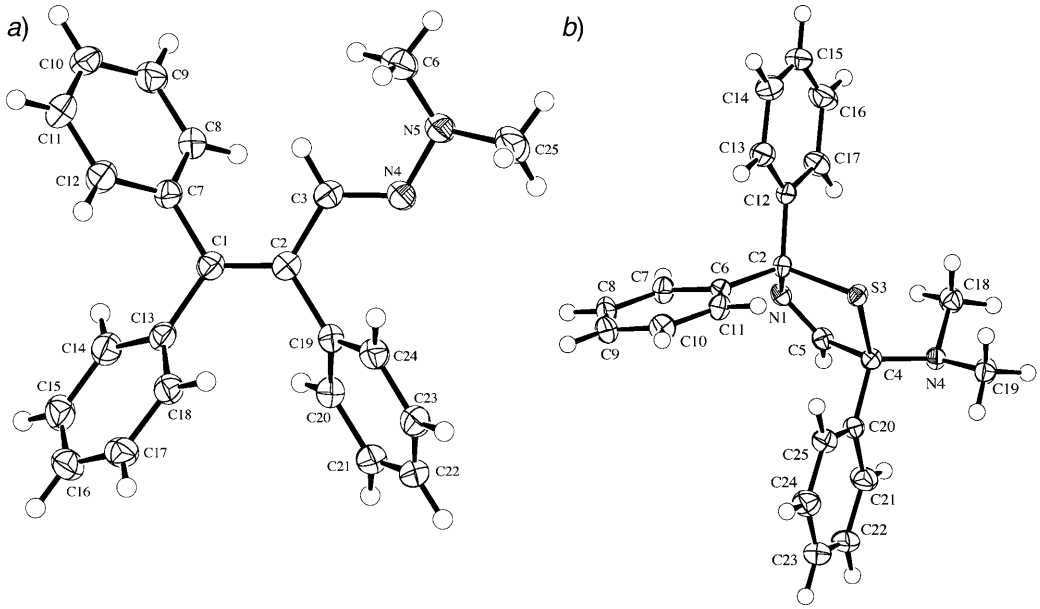


Fig. 3. *ORTEP Plot* [13] *of the molecular structure of* a) **18** *and* b) *one of the independent molecules of* **21** (50% probability ellipsoids, arbitrary numbering of atoms)

basis of the NMR and mass spectra. Furthermore, one of the diastereoisomers of **24**, *i.e.*, *trans*-**24**, could be crystallized, and the X-ray crystal structure was determined successfully (*Fig. 4*). In the crystal, the heterocyclic ring has a shallow envelope conformation with S(3) as the envelope flap. The Ph substituents are *cis*-oriented.

The reactions of **9** with **3b** and **3d**, respectively, showed that the intermediate thiocarbonyl ylide **19** reacts only to a minor extent to the five-membered ring. The preferred reaction of **19** is the 1,3-dipolar electrocyclization, which leads to an intermediate thiirane **20**, and subsequent desulfurization yields the alkenes.

3. Conclusions. – The presented results show that the two thiocarbonyl compounds **8** and **9** with a conjugated C=N group react with diazo compounds **3** to give the corresponding thiocarbonyl ylides of type **16** and **19**, respectively, with an extended π-system. In the case of **8** and the less reactive **3b**, the reaction has to be catalyzed by $Rh_2(OAc)_4$. Whereas, in the non-catalyzed reaction, a 1,3-dipolar cycloaddition to give the corresponding 2,5-dihydro-1,3,4-thiadiazole and subsequent N_2 elimination is the likely reaction mechanism of the formation of the thiocarbonyl ylide, an initial Rh-catalyzed N_2 elimination to give a carbenoid, which adds to the C=S group, leads to the intermediate 1,3-dipoles in the catalyzed reactions [5][6]. The thiocarbonyl ylides of type **16**, which have been generated from **8**, undergo competitive 1,5- and 1,3-dipolar electrocyclizations, and yield dihydrothiazole and thiirane derivatives, respectively. On the other hand, the main reaction of the isomeric thiocarbonyl ylides **19** is the 1,3-dipolar electrocyclization, which leads to thiiranes **20**.

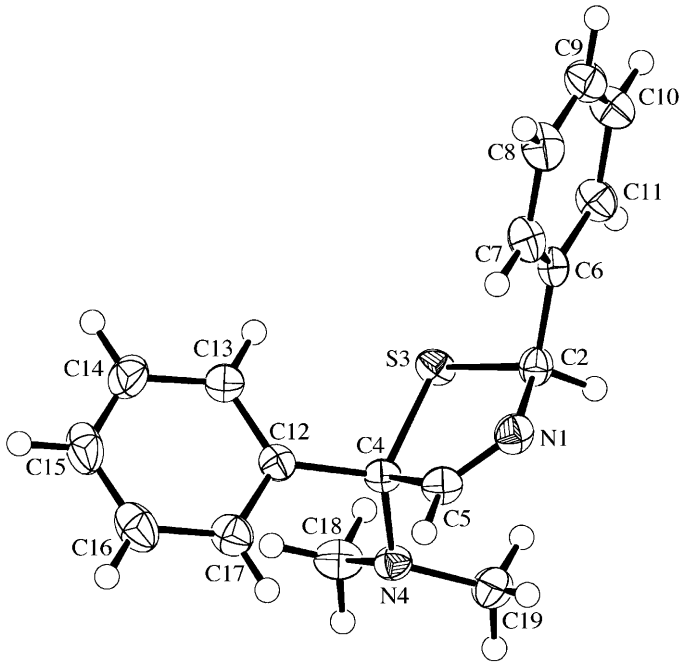


Fig. 4. *ORTEP Plot* [13] *of the molecular structure of* trans-**24** (50% probability ellipsoids, arbitrary numbering of atoms)

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

Experimental Part

1. *General.* See [7]. M.p.: *Büchi B-540*. IR Spectra: in KBr unless otherwise stated. ^{1}H- and ^{13}C-NMR Spectra: *Avance DRX-500* (500 and 125 MHz, resp.), and *Avance DRX-600* (600 and 150 MHz, resp.).

2. *Starting Materials.* All thiocarbonyl derivatives and their precursors, and all diazo compounds were prepared according to known protocols: *diazomethane* (**3a**) [15], *diazo(diphenyl)methane* (**3b**) [16], *diazocyclohexane* (**3c**) [17], *diazo(phenyl)methane* (**3d**) [18], N-*[(dimethylamino)methylidene]thiobenzamide* (**8**) [19], *2-(dimethylhydrazono)-1-phenylethane-1-thione* (**9**) [20][21]. All other reagents are commercially available.

3. *Yields.* As **9** and almost all diazo compounds are only stable in soln., and the diazo compounds were often used in excess, the yields of the corresponding reactions were approximated. They are based on experience [7] or on the volume of N_2 evolved.

4. *General Procedure A* (*GP A*). To a soln. of a thiocarbonyl compound (1.8–5.2 mmol) in CH_2Cl_2, Et_2O, or THF (20–100 ml), the diazo compound (3–8 mmol) in toluene, benzene, or Et_2O (30–150 ml) was added in several portions by means of a dropping funnel, or, in the case of **3a**, by means of a *Pasteur* pipette. After total conversion of the thiocarbonyl compound, monitored either by TLC (treated during 20 s with a soln. of Et_2O and 1% of Et_3N), color change or evolution of N_2[3]), the solvent was evaporated, and the mixture was analyzed and purified by chromatography using silica gel, which had been treated with 3% Et_3N. Furthermore, the solvent was doped with 1% of Et_3N.

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

5. *Reaction of* **8** *with Diazoalkanes.* 5.1. *4,5-Dihydro*-N,N-*dimethyl-2-phenyl-1,3-thiazol-4-amine* (**10a**) *and 2,5-Dihydro*-N,N-*dimethyl-4-phenyl-1,3-thiazol-2-amine* (**11a**). According to *GP A*, a soln. of **8** (772 mg, 4 mmol) in Et_2O (30 ml) and **3a** (*ca.* 6 mmol) in Et_2O (30 ml) were used. After 3 d at r.t. in the dark, the mixture was separated by CC (hexane/AcOEt 5:1) to give 173 mg (*ca.* 21%) of **10a** and 206 mg (*ca.* 25%) of **11a**.

Data of **10a**. Yellowish oil. IR (neat): 3081*w*, 3060*m*, 3028*m*, 2970v*s*, 2939v*s*, 2864v*s*, 2829v*s*, 2784*s*, 1688*w*, 1607v*s*, 1578*s*, 1490*s*, 1473*s*, 1448v*s*, 1358v*s*, 1297v*s*, 1272v*s*, 1233v*s*, 1196*s*, 1177*m*, 1156*m*, 1119*s*, 1073v*s*, 1042v*s*, 999v*s*, 949v*s*, 766v*s*, 690v*s*, 624*s*. ^{1}H-NMR: 7.88–7.85 (*d*-like, 2 arom. H); 7.47–7.38 (*m*, 3 arom. H); 5.56 (*dd*, J = 6.7, 2.4, H–C(4)); 3.51 (*dd*, J = 9.1, 2.7, 1 H of CH_2); 3.28 (*dd*, J = 6.7, 5.1, 1 H of CH_2); 2.44 (*s*, Me_2N). ^{13}C-NMR: 167.0 (*s*, C(2)); 133.1 (*s*, 1 arom. C); 131.2, 128.3, 128.3 (3*d*, 5 arom. CH); 97.3 (*d*, C(4)); 40.4 (*t*, CH_2); 34.5 (*q*, Me_2N). CI-MS (NH_3): 207 (100, $[M+1]^+$), 162 (36, $[M-Me_2NH]^+$), 104 (17).

Data of **11a**. Yellowish crystals. M.p. 64–67°. IR: 3126*w*, 3058*m*, 3032*w*, 2922*m*, 2805*w*, 1726*m*, 1683*m*, 1644v*s*, 1579*m*, 1489*s*, 1445*s*, 1414*s*, 1354*m*, 1274*m*, 1254*m*, 1226*m*, 1185*m*, 1159*w*, 1116*m*, 1061*s*, 1042*s*, 1030*s*, 1009*m*, 775*s*, 746*s*, 732*s*, 696*s*. ^{1}H-NMR: 7.95–7.92 (*d*-like, 2 arom. H); 7.49–7.40 (*m*, 3 arom. H); 7.08 (*dd*, J = 5.2, 1.9, H–C(4)); 4.34 (*dd*, J = 16.3, 1.9, 1 H of CH_2); 4.22 (*dd*, J = 16.3, 5.2, 1 H of CH_2); 2.25 (*s*, Me_2N). ^{13}C-NMR: 168.9 (*s*, C(2)); 133.1 (*s*, 1 arom. C); 131.4, 128.5, 128.5 (3*d*, 5 arom. CH); 107.3 (*d*, C(4)); 41.3 (*t*, CH_2); 39.0 (*q*, Me_2N). CI-MS (NH_3): 206 (18, M^+), 174 (100, $[M-S]^+$), 161 (94, $[M-Me_2N]^+$), 134 (82, $[M-NHCHNMe_2]^+$), 103 (58, $PhCN^+$).

When the chromatographic workup was carried out without addition of Et_3N as described in [8], only **11a** was isolated.

5.2. *4,5-Dihydro*-N,N-*dimethyl-2,5,5-triphenyl-1,3-thiazol-4-amine* (**10b**) *and 2,5-Dihydro*-N,N-*dimethyl-4,5,5-triphenyl-1,3-thiazol-2-amine* (**11b**). According to *GP A*, a suspension of **8** (360 mg, 1.87 mmol) in CH_2Cl_2 (20 ml) and a soln. of **3b** (*ca.* 2.5 mmol) in benzene (20 ml) were used. To the stirred mixture at r.t., a cat. amount (20 mg) of $Rh_2(OAc)_4$ was added. After *ca.* 16 h, the mixture was separated by CC (hexane/AcOEt 20:1 to 5:1): 328 mg (0.92 mmol, 49%) of **10b** and 200 mg (0.56 mmol, 30%) of **11b**.

Data of **10b**. Yellowish oil. R_f (hexane/AcOEt 8:1) 0.5. IR: 3057*m*, 3027*m*, 2935*s*, 2865*s*, 2831*s*, 2786*m*, 1805*w*, 1733*w*, 1596*s*, 1575*s*, 1491v*s*, 1472*m*, 1445v*s*, 1311*m*, 1275*s*, 1227*s*, 1176*m*, 1156*m*, 1083*s*, 1062v*s*, 1040v*s*, 994v*s*, 944v*s*, 920*m*, 901*m*, 888*m*, 828*m*, 765v*s*, 752v*s*, 723v*s*, 694v*s*, 632*m*, 623*s*. ^{1}H-NMR: 7.87–7.84 (*q*-like, 2 arom. CH); 7.43–7.07 (*m*, 13 arom. CH); 6.01 (*s*, H–C(2)); 2.19 (*s*, Me_2N). ^{13}C-NMR: 166.1 (*s*, C(4)); 149.1, 140.1, 133.2 (3*s*, 3 arom. C); 131.4, 129.9, 128.5, 128.3, 128.3, 127.3, 126.9, 126.9, 126.4 (9*d*, 15 arom. CH); 100.9 (*d*, C(2)); 74.4 (*s*, C(5)); 41.3 (*q*, Me_2N). CI-MS (NH_3): 359 (100, $[M+1]^+$), 314 (39, $[M-Me_2NH]^+$), 224 (37).

Data of **11b**. Yellowish oil. R_f (hexane/AcOEt 8:1) 0.3. IR: 3056*m*, 3028*w*, 2977*m*, 2942*m*, 2860*m*, 2825*m*, 2779*m*, 1807*w*, 1734*w*, 1680*w*, 1624*s*, 1599*s*, 1545*m*, 1489*s*, 1470*s*, 1445v*s*, 1352*s*, 1289*m*, 1257*s*, 1205*m*, 1179*s*, 1152*m*, 1081*s*, 1067*s*, 1043*s*, 1023v*s*, 1002*s*, 932*m*, 908*w*, 852*s*, 824*w*, 772*s*, 758*s*, 742v*s*, 695v*s*, 639*m*. ^{1}H-NMR: 7.52–7.49 (*d*-like, 2 arom. H); 7.40–7.35 (*t*-like, 4 arom. H); 7.21–7.00 (*m*, 9 arom. H); 6.84 (*s*, H–C(4)); 2.27 (*s*, Me_2N). ^{13}C-NMR: 171.2 (*s*, C(2)); 143.1, 142.8, 133.2 (3*s*, 3 arom. C); 130.5, 130.2, 129.4, 129.0, 128.0, 127.8, 127.7, 127.0, 126.9 (9*d*, 15 arom. CH); 101.5 (*d*, C(4)); 78.3 (*s*, C(5)); 39.8 (*q*, Me_2N). CI-MS (NH_3): 359 (10, $[M+1]^+$), 327 (100, $[M-S+1]^+$), 314 (5 $[M-Me_2NH]^+$), 193 (22).

5.3. N,N-*Dimethyl-2-phenyl-1-thia-3-azaspiro[4.5]dec-2-en-4-amine* (**10c**). According to *GP A*, a suspension of **8** (384 mg, 2 mmol) in CH_2Cl_2 (10 ml) and a soln. of **3c** (*ca.* 2.5 mmol) in CH_2Cl_2 (40 ml) were used. After 1 d at r.t., the mixture was separated by CC (hexane/AcOEt 10:1 to 5:1): 360 mg (67%) of **10c**, and 120 mg (22%) of a mixture of **10c** and N,N-*dimethyl-4-phenyl-1-thia-3-azaspiro[4.5]dec-3-en-2-amine* (**11c**)[4]).

Data of **10c**. Yellowish oil. IR (neat): 3061*m*, 3027*w*, 2930v*s*, 2855v*s*, 2833v*s*, 2790*s*, 2669*w*, 1808*w*, 1756*w*, 1688*w*, 1595v*s*, 1577*s*, 1491*m*, 1473*s*, 1447v*s*, 1404*w*, 1377*m*, 1295*s*, 1266v*s*, 1246v*s*, 1229*s*, 1212*m*, 1176*m*, 1156*m*, 1135*m*, 1091*s*, 1074*s*, 1042v*s*, 1025v*s*, 993v*s*, 958*s*, 940*s*, 909*m*, 858*s*, 766v*s*, 690v*s*, 625*m*.

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[4]) It was not possible to isolate **11c** in pure state.

^{1}H-NMR: 7.91–7.88 (*d*-like, 2 arom. H); 7.45–7.36 (*m*, 3 arom. H); 4.92 (*s*, H–C(4)); 2.48 (*s*, Me_2N); 2.04–1.32 (*m*, 10 H, cyclohexane). ^{13}C-NMR: 167.4 (*s*, C(2)); 133.8 (*s*, 1 arom. C); 131.0, 128.3, 128.1 (3*d*, 5 arom. CH); 101.5 (*d*, C(4)); 66.6 (*s*, C(5)); 42.3 (br. *q*, Me_2N); 40.9, 32.2, 26.3, 25.5, 24.2 (5*t*, 5 CH_2, cyclohexane). EI-MS: 275 (10), 274 (47, M^+), 230 (7, $[M-Me_2N]^+$), 171 (28), 160 (100, $[M-C_6H_{10}S]^+$), 138 (18), 121 (11), 103 (24), 57 (84).

Data of **11c** (from a *ca.* 1:3 mixture of **10c**/**11c**). ^{1}H-NMR: 7.48–7.38 (*m*, 5 arom. H); 6.76 (*s*, H–C(2)); 2.31 (*s*, Me_2N); 1.93–1.59 (*m*, 10 H, cyclohexane). ^{13}C-NMR: 176.8 (*s*, C(4)); 135.0 (*s*, 1 arom. C); 129.0, 128.2, 127.9 (3*d*, 5 arom. CH); 100.3 (*d*, C(2)); 72.7 (*s*, C(5)); 39.3 (*s*, Me_2N); 38.1, 36.9, 25.2, 25.0, 24.5 (5*t*, 5 CH_2, cyclohexane).

5.4. cis-*4,5-Dihydro*-N,N-*dimethyl-2,5-diphenyl-1,3-thiazol-4-amine* (*cis*-**10d**) *and* cis/trans-*2,5-Dihydro*-N,N-*dimethyl-4,5-diphenyl-1,3-thiazol-2-amine* (*cis*-**11d** and *cis*/*trans*-**11d**). According to *GP A*, a soln. of **8** (1 g, 5.2 mmol) in dry Et_2O (30 ml) and **3d** (*ca.* 8 mmol) in toluene (150 ml) were used. After 4 d at r.t. in the dark, the mixture was separated by CC (hexane/AcOEt 3:1) and MPLC (Et_2O/hexane 1:5): 362 mg (*ca.* 24%) of *cis*-**10d** (colorless oil), and 616 mg (*ca.* 43%) of a mixture of *cis*- and *trans*-**11d** (yellowish oil).

Data of cis-**10d**. IR (neat): 3061*m*, 3028*m*, 2941*s*, 2866*s*, 2833*m*, 2786*m*, 2771*m*, 1680*w*, 1600*s*, 1577*s*, 1531*m*, 1493*s*, 1471*m*, 1447v*s*, 1420*m*, 1366*m*, 1312*s*, 1269*s*, 1226*m*, 1177*m*, 1155*m*, 1068*s*, 1040*s*, 988*s*, 943*m*, 910*m*, 896*m*, 765v*s*, 731*s*, 694v*s*. ^{1}H-NMR: 7.96–7.93 (*d*-like, 2 arom. H); 7.49–7.23 (*m*, 8 arom. H); 5.20 (*d*, $J=7.6$, H–C(4)); 5.05 (*d*, $J=7.6$, H–C(5)); 2.30 (*s*, Me_2N). ^{13}C-NMR: 166.2 (*s*, C(2)); 137.5, 133.4 (2*s*, 2 arom. C); 131.4, 128.5, 128.4, 128.3, 128.2, 127.6 (6*d*, 10 arom. CH); 99.2 (*d*, C(4)); 57.4 (*d*, C(5)); 42.8 (*q*, Me_2N). CI-MS (NH_3): 281 (8), 238 (100, $[M-Me_2NH+1]^+$), 148 (20).

Data of the Mixture of cis-**11d** *and* trans-**11d**[5]: IR (neat): 3060*m*, 3027*m*, 2978*m*, 2944*s*, 2862*s*, 2825*s*, 2779*m*, 1635v*s*, 1599*m*, 1577*m*, 1494*s*, 1471*s*, 1448v*s*, 1355*s*, 1337*m*, 1317*m*, 1279v*s*, 1213*m*, 1177*s*, 1067v*s*, 1046v*s*, 1037v*s*, 1024v*s*, 1001*m*, 886*s*, 853*s*, 763v*s*, 729v*s*, 693v*s*, 630*s*, 585*m*, 546*s*. ^{1}H-NMR (*cis*-**11d**): 7.82–7.74 (*m*, 2 arom. H); 7.35–7.15 (*m*, 8 arom. H, H–C(4)); 5.88 (*d*, $J=4.8$, H–C(5)); 2.32 (*s*, Me_2N). ^{13}C-NMR (*cis*-**11d**): 169.7 or 169.2 (*s*, C(2)); 141.7, 132.7 or 132.4 (2*s*, 2 arom. C); 130.9, 130.8, 129.7, 129.5, 129.4, 129.1, 128.9, 128.3, 128.0, 127.5, 127.4, 127.2 (12*d*, 10 arom. CH); 105.7 (*d*, C(4)); 61.6 (*d*, C(5)); 39.3 (*q*, Me_2N). ^{1}H-NMR (*trans*-**11d**): 7.82–7.74 (*m*, 2 arom. H); 7.35–7.15 (*m*, 8 arom. H); 7.10 (*d*, $J=2.6$, H–C(4)); 5.97 (*d*, $J=2.6$, H–C(5)); 2.38 (*s*, Me_2N). ^{13}C-NMR (*trans*-**11d**): 169.7 or 169.2 (*s*, C(2)); 141.8, 132.7 or 132.4 (2*s*, 2 arom. C); 130.9, 130.8, 129.7, 129.5, 129.4, 129.1, 128.9, 128.3, 128.0, 127.5, 127.4, 127.2 (12*d*, 10 arom. CH); 105.2 (*d*, C(4)); 60.8 (*d*, C(5)); 39.8 (*q*, Me_2N). CI-MS (NH_3): 281 (6), 251 (100, $[M-S+1]^+$), 238 (70, $[M-Me_2NH+1]^+$), 148 (29).

5.5. trans-*4,5-Dihydro*-N,N-*dimethyl-2,5-diphenyl-1,3-thiazol-4-amine* (*trans*-**10d**). According to *GP A*, a soln. of **8** (592 mg, 3 mmol) in dry THF (20 ml) and **3d** (*ca.* 4 mmol) in toluene (80 ml) were used. To the stirred mixture at r.t., a cat. amount (20 mg) of $Rh_2(OAc)_4$ was added. After 4 d, the mixture was separated by CC (hexane/AcOEt 4:1 to 1:4)[6]): 258 mg (*ca.* 41%[7])) of *trans*-**10d**. Yellowish-oily crystals. M.p. could not be determined. IR (neat): 3083*m*, 3061*s*, 3028*s*, 2972*s*, 2940v*s*, 2866*s*, 2833*s*, 2788*s*, 1808*w*, 1754*w*, 1716*w*, 1687*w*, 1608v*s*, 1600v*s*, 1579*s*, 1492v*s*, 1473*s*, 1449v*s*, 1361*s*, 1293*s*, 1272*s*, 1253*s*, 1228*s*, 1177*m*, 1158*s*, 1075*s*, 1040v*s*, 997v*s*, 960*s*, 936*s*, 865*m*, 766v*s*, 751*m*, 690v*s*. ^{1}H-NMR: 7.95–7.92 (*d*-like, 2 arom. H); 7.52–7.40 (*m*, 3 arom. H); 7.32–7.23 (*m*, 5 arom. H); 5.53 (*d*, $J=4.4$, H–C(4)); 4.80 (*d*, $J=4.4$, H–C(5)); 2.45 (*s*, Me_2N). ^{13}C-NMR: 167.3 (*s*, C(2)); 142.7, 131.5 (2*s*, 2 arom. C); 133.1, 128.9, 128.6[8]), 127.6, 127.4 (5*d*, 10 arom. CH); 106.2 (*d*, C(4)); 55.7 (*d*, C(5)); 40.5 (*q*, Me_2N). CI-MS (NH_3): 284 (21), 283 (100, $[M+1]^+$), 238 (45, $[M-Me_2NH+1]^+$), 148 (21).

5.6. *Experiment with Ethyl Diazoacetate* (**3e**). According to *GP A*, a suspension of **8** (380 mg, 2 mmol) in THF (20 ml) and a soln. of **3e** (*ca.* 4 mmol) in CH_2Cl_2 (40 ml) were used. To the stirred mixture,

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5) On the basis of 2D-NMR experiments (HMBC), some signals could be assigned to the structures of *cis*-**11d** and *trans*-**11d**. The signals of the aromatic C-atoms and the quaternary C-atoms could not be correlated.

6) In the workup procedure, no Et_3N was used.

7) *Ca.* 160 mg of the starting material **8** were recovered.

8) The intensity of this signal indicates absorption of 4 arom. CH.

a cat. amount (*ca.* 20 mg) of $Rh_2(OAc)_4$ was added. After 10 d at r.t., the mixture was separated by CC (hexane/AcOEt 4:1): 450 mg of a complex mixture of products resulting from decomposition and *ca.* 15 mg of *triethyl* trans-*4,5-dihydro-1*H-*pyrazole-3,4,5-tricarboxylate* (**17**).

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

6. *Reactions of* **9** *with Diazoalkanes.* 6.1. N,N-*Dimethyl*-N′-*(2,3,3-triphenylprop-2-enylidene)hydrazine* (**18**) *and 2,5-Dihydro*-N,N-*dimethyl-2,2,5-triphenyl-1,3-thiazol-5-amine* (**21**). To a soln. of freshly prepared **9** (*ca.* 1.6 mmol) in benzene (10 ml), a purple soln. of **3b** (*ca.* 2.5 mmol) in benzene (20 ml) was added dropwise. After stirring for 1 h at r.t., purification of the crude mixture by CC (hexane/AcOEt 15:1) and MPLC (hexane/MeOH 90:5) afforded a mixture of two products, which were separated by crystallization from hexane/AcOEt/Et_2O affording 234 mg of **18** (30%) and 60 mg (7%) of **21**.

Data of **18**. Pale-brownish crystals. M.p. 176–177°. IR: 3056*w*, 3027*w*, 2992*w*, 2970*w*, 2947*m*, 2867*m*, 2828*m*, 2783*w*, 1805*w*, 1664*m*, 1596*w*, 1580*w*, 1558*w*, 1488*s*, 1467*m*, 1445v*s*, 1175*m*, 1082*m*, 1073*m*, 1033*m*, 1009v*s*, 932*m*, 923*m*, 902*s*, 873*m*, 758v*s*, 697v*s*, 648*s*, 637*s*. ^{1}H-NMR: 7.36–6.85 (*m*, 15 arom. H, and 1 =CH); 2.72 (*s*, Me_2N). ^{13}C-NMR: 142.8, 142.4, 139.5 (3*s*, 3 arom. C); 137.8 (*s*, 1 =C); 136.5 (br. *s*, 1 =C, 1 =CH); 131.7, 131.0, 130.9, 127.9, 127.2, 127.1, 126.2, 126.0 (8*d*, 15 arom. CH); 42.6 (*q*, Me_2N). CI-MS (NH_3): 327 (100, $[M+1]^+$), 284 (16, $[M-Me_2N+1]^+$), 203 (12), 178 (19), 160 (15), 158 (13).

Crystals suitable for the X-ray crystal-structure determination were grown from hexane/AcOEt/Et_2O by slow evaporation of the solvent.

Data of **21**. Colorless crystals. M.p. 135–137°. IR: 3063*w*, 3026*w*, 2992*w*, 2970*m*, 2946*m*, 2868*m*, 2828*m*, 2783*w*, 1956*w*, 1804*w*, 1664*m*, 1595*m*, 1580*w*, 1487*s*, 1467*s*, 1445v*s*, 1031*m*, 1009v*s*, 932*m*, 923*m*, 901v*s*, 873*m*, 757v*s*, 697v*s*, 661*m*, 648*s*, 637*s*, 615*m*. ^{1}H-NMR: 7.75 (*d*-like, 2 arom. H); 7.68–7.64 (*d*-like, 2 arom. H); 7.35–7.15 (*m*, 11 arom. H, H–C(4)); 2.09 (*s*, Me_2N). ^{13}C-NMR: 162.7 (*d*, H–C(4)); 146.2, 145.2, 139.8 (3*s*, 3 arom. C); 128.7, 128.5, 128.3, 127.9, 127.1, 127.1, 126.9, 126.5 (8*d*, 15 arom. CH); 106.7 (*s*, C(2)); 97.5 (*s*, C(5)); 41.2, 41.1 (2*q*, Me_2N). CI-MS (NH_3): 358 (5, M^+), 327 (10, $[M-Me_2N+NH_4]^+$), 314 (28, $[M-Me_2N]^+$), 178 (100).

Crystals suitable for the X-ray crystal-structure determination were grown from $CDCl_3$ by slow evaporation of the solvent.

6.2. *(*E*/*Z*)*-N,N-*Dimethyl*-N′-*(2,3-diphenylprop-2-enylidene)hydrazine* (**23**) *and 2,5-Dihydro*-N,N-*dimethyl-2,5-diphenyl-1,3-thiazol-5-amine* (**24**). To a soln. of freshly prepared **9** (*ca.* 5 mmol) in a mixture of hexane and AcOEt (300 ml, 10:1), a soln. of **3d** (*ca.* 6 mmol) in toluene (150 ml) was slowly added at r.t. Purification of the crude mixture after 1 h by CC (hexane/AcOEt 10:1 to 3:1) and MPLC (hexane/AcOEt 90:5) afforded 3 almost pure compounds: 163 and 54 mg, resp., of the (*E*)- and (*Z*)-isomer of **23** (*i.e.*, **23a** and **23b**)[9]), and 75 mg of one of the diastereoisomers of **24**.

Data of **23a**. Yellowish oil. IR: 3019*m*, 2950*m*, 2851*m*, 2824*m*, 2786*m*, 1626*m*, 1593*m*, 1551*s*, 1491*s*, 1469*s*, 1446*s*, 1266*s*, 1129*m*, 1077*m*, 1043v*s*, 896*m*, 862*m*, 760*s*, 750*s*, 698v*s*, 607*m*. ^{1}H-NMR: 7.96 (*s*, CH=N); 7.88–7.59 (*m*, 10 arom. H); 7.06 (*s*, CH=C); 3.24 (*s*, Me_2N). ^{13}C-NMR: 161.9 (*d*, CH=N); 141.2, 139.6, 137.5 (3*s*, 2 arom. C, 1 =C); 132.1, 130.2, 129.3, 127.8, 127.6, 127.2, 126.9 (7*d*, 10 arom. CH, 1 =CH); 42.6 (*q*, Me_2N). CI-MS (NH_3): 252 (20), 251 (100, $[M+1]^+$), 210 (16, $[M-Me_2N_2+NH_4]^+$), 209 (99, $[M-Me_2N_2+NH_3]^+$).

Data of **23b**: Colorless oil. IR: 3055*m*, 3022*m*, 2951*m*, 2854*m*, 2784*m*, 1595*m*, 1553*s*, 1444*s*, 1361*m*, 1272*s*, 1133*s*, 1040v*s*, 918*m*, 897*m*, 849*m*, 778*m*, 756v*s*, 703v*s*, 632*m*, 601*s*. ^{1}H-NMR: 7.70–7.54 (*m*, 5 arom. H); 7.53 (*s*, CH=N); 7.46–7.39 (*m*, 3 arom. H); 7.29–7.26 (*m*, 2 arom. H); 7.06 (*s*, CH=C); 3.21 (*s*, Me_2N). ^{13}C-NMR: 140.2, 139.1, 138.1 (3*s*, 2 arom. C, 1 =C); 137.0 (*d*, CH=N); 129.9, 129.8, 129.4, 128.2, 127.8, 127.0, 126.5 (7*d*, 10 arom. CH, 1 =CH); 42.7 (*q*, Me_2N). CI-MS (NH_3): 252 (19), 251 (100, $[M+1]^+$), 223 (11, $[M-Me_2N+NH_4]^+$).

Data of trans-**24**. Colorless crystals. M.p. 86–88°. IR: 3080*w*, 3058*m*, 3024*m*, 2986*m*, 2959*m*, 2897*w*, 2843*w*, 2816*s*, 2772*s*, 1655*s*, 1595*w*, 1580*w*, 1488*s*, 1469*m*, 1451v*s*, 1427*m*, 1253*m*, 1235*s*, 1154*m*, 1095*m*, 1082*m*, 1064*s*, 1042*m*, 1028*m*, 996v*s*, 979*s*, 943*m*, 923*s*, 911*s*, 857*m*, 844*s*, 780*w*, 754v*s*, 732v*s*, 695v*s*, 633v*s*, 613*s*. ^{1}H-NMR: 8.02–8.00 (*d*-like, 2 arom. H); 7.99–7.50 (*m*, 6 arom. H); 7.49 (*d*, $J=2.9$, H–

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[9]) It was not possible to assign the spectra to (*E*)- and (*Z*)-**23** on the basis of the present information.

C(4)); 7.48–7.37 (*m*, 2 arom. H); 6.79 (*d*, *J* = 2.9, H–C(2)); 2.39 (*s*, Me_2N). ^{13}C-NMR: 165.7 (*d*, C(4)); 141.0, 140.4 (2*s*, 2 arom. C); 128.7, 128.5, 128.5, 128.2, 127.9, 126.7 (6*d*, 10 arom. CH); 106.7 (*s*, C(5)); 83.5 (*d*, H–C(2)); 40.6 (*q*, Me_2N). CI-MS (NH_3): 283 (10, $[M+1]^+$), 251 (12, $[M-S+1]^+$), 238 (100, $[M-Me_2N]^+$), 178 (88, $[M-PhCN]^+$).

Table. *Crystallographic Data of Compounds* **17**, **18**, **21**, *and* trans-**24**

		17	**18**	**21**	trans-**24**
Crystallized from		CH_2Cl_2/pentane	hexane/AcOEt/Et_2O	$CDCl_3$	CH_2Cl_2/hexane
Empirical formula		$C_{12}H_{18}N_2O_6$	$C_{23}H_{22}N_2$	$C_{23}H_{22}N_2S$	$C_{17}H_{18}N_2S$
Formula weight [g mol^{-1}]		286.28	326.44	358.50	282.40
Crystal color, habit		colorless, prism	colorless, prism	colorless, prism	colorless, prism
Crystal dimensions [mm]		0.22×0.25×0.32	0.10×0.15×0.22	0.10×0.15×0.25	0.20×0.22×0.30
Temp. [K]		160(1)	160(1)	160(1)	160(1)
Crystal system		orthorhombic	triclinic	monoclinic	monoclinic
Space group		$P2_12_12_1$	$P\bar{1}$	Cc	$P2_1/n$
Z		4	2	8	4
Reflections for cell determination		14502	4028	5653	34463
2θ Range for cell determination [°]		4–55	4–55	4–60	4–60
Unit cell parameters	a [Å]	7.8473(2)	9.9323(3)	12.9159(1)	10.9672(2)
	b [Å]	10.3424(2)	9.9977(3)	15.0573(2)	6.0702(1)
	c [Å]	17.3424(5)	10.4338(3)	20.1476(2)	22.4345(4)
	α [Å]	90	62.635(2)	90	90
	β [°]	90	84.408(1)	106.6416(6)	91.248(1)
	γ [Å]	90	78.997(1)	90	90
	V [Å^3]	1407.51(6)	903.16(5)	3754.16(7)	1493.18(5)
D_x [g cm^{-3}]		1.351	1.200	1.268	1.256
μ(MoK$_\alpha$) [mm^{-1}]		0.109	0.0703	0.181	0.208
Scan type		ϕ and ω	ϕ and ω	ω	ϕ and ω
2θ_{max} [°]		55	55	60	60
Transmission factors (min; max)		0.816; 0.925	–	–	0.870; 0.961
Total reflections measured		20739	21209	52142	38665
Symmetry-independent reflections		1867	4105	10265	4378
Reflections with $I > 2\sigma(I)$		1679	2953	8259	3218
Reflections used in refinement		1866	4102	10257	4376
Parameters refined; restraints		189; 0	229; 0	684; 1266	184; 0
R (on F; $I > 2\sigma(I)$ reflections)		0.0390	0.0483	0.0421	0.0449
wR (on F^2; all indept. reflections)		0.1050	0.1375	0.1000	0.1166
Weighting parameters [a, b][a]):		0.0578; 0.3696	0.0785; 0.0696	0.0506; 0.966	0.0533; 0.4053
Goodness-of-fit		1.066	1.045	1.024	1.062
Secondary extinction coefficient		0.032(6)	0.040(8)	–	0.069(4)
Final Δ_{max}/σ		0.001	0.001	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]		0.28; −0.24	0.25; −0.22	0.24; −0.27	0.30; −0.27

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

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

7. *X-Ray Crystal-Structure Determination of* **17**, **18**, **21**, *and* trans-**24** (*Table* and *Figs. 1–3*)[10]. All measurements were performed on a *Nonius KappaCCD* diffractometer [22] 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. 1–3*. Data reduction was performed with *HKL Denzo* and *Scalepack* [23]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [24] was applied in the cases of **17** and *trans*-**24**. Equivalent reflections were merged with the exception of the *Friedel* pairs of **21**. The structures were solved by direct methods using SHELXS97 [25] (for **17**) and SIR92 [26] (for **18**, **21**, and *trans*-**24**), which revealed the positions of all non-H-atoms. In the case of **21**, there are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the program PLATON [27], but none could be found. In addition, both molecules are disordered by inversion of each entire molecule about its center of gravity. Refinement of constrained site occupation factors for the two orientations of each molecule yielded values of 0.934(1) and 0.935(1) for the major conformation of molecules A and B, resp. An extensive series of similarity restraints was applied in order to keep the chemically equivalent bond lengths and angles about all atoms in the minor components to be similar to those of the major components. Furthermore, neighboring atoms within and between each disordered orientation were restrained to have similar atomic displacement parameters. The non-H-atoms of the major orientations were refined anisotropically, while those of the minor orientations were refined isotropically. The non-H-atoms of **17**, **18**, and *trans*-**24** were refined anisotropically. The amine H-atom of **17** was placed in the position indicated by a difference electron density map, and its position was allowed to refine together with an isotropic displacement parameter. All remaining H-atoms of **17** and all of the H-atoms of **18**, **21**, and *trans*-**24** 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 any Me group). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied, except in the case of **18**. In **17**, **18**, **21**, and *trans*-**24**, 1, 3, 8, and 2 reflections, resp., whose intensities were considered as extreme outliers, were omitted from the final refinement. Refinement of the absolute structure parameter [28] for **21** yielded a value of 0.45(4), which indicates that the structure is an inversion twin. For **17**, the space group permits the compound to be enantiomerically pure, but the absolute configuration could not be determined. The enantiomer used in the refinement model was chosen arbitrarily. Neutral atom scattering factors for non-H-atoms were taken from [29a], and the scattering factors for H-atoms were taken from [30]. Anomalous dispersion effects were included in F_c [31]; the values for f' and f'' were those of [29b]. The values of the mass attenuation coefficients are those of [29c]. All calculations were performed using the SHELXL97 [32] program.

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