# [2+3] Cycloadditions of 'Thiocarbonyl Ylides' (= (Alkylidenesulfonio)methanides) and Diazoalkanes with N,N'-(Thiocarbonyl)diimidazole (= 1,1'-(Carbonothioyl)bis[1H-imidazole])<sup>1</sup>)

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Dedicated to Professor Romuald Bartnik (University of Łódź) on the occasion of his 60th birthday

Heating of a mixture of N,N'-(thiocarbonyl)diimidazole (= 1,1'-(carbonothioyl)bis[1*H*-imidazole]; 1) and 2,5-dihydro-1,3,4-thiadiazole **2a** or **2b** gave the 1,3-dithiolanes **4a** and **4b**, respectively, *via* a regiospecific 1,3-dipolar cycloaddition of the corresponding 'thiocarbonyl methanides' **3a**,**b** onto the C=S group of 1 (*Schemes 1* and 2). The adamantane derivative **4b** was not stable in the presence of 1*H*-imidazole and during chromatographic workup. The isolated 1,3-dithiole **5** is the product of a base-catalyzed elimination of 1*H*-imidazole from the initial cycloadduct **4b**. The formation of the S,N-acetal **6** can be rationalized by a protonation of the 'thiocarbonyl ylide' **3b** followed by a nucleophilic addition of 1*H*-imidazole. With the diazo compounds **8a**-e (*Scheme 3*), 1 underwent a regiospecific 1,3-dipolar cycloadditon to give the corresponding 2,5-dihydro-1,3,4-thiadiazoles 10. The structures of **10a** and **10d** were established by X-ray crystallography. In the case of diazodiphenylmethane (**8**), the initial cycloadduct **9f** decomposed *via* a 'twofold extrusion' of N<sub>2</sub> and S to give 1,1'-(2,2-diphenylethenylidene)bis[1*H*-imidazole] (**11**; *Scheme 3*).

Introduction. – In a series of our recent papers, 1,3-dipolar cycloadditions of thiocarbonyl compounds with diazo compounds [1-3], azides [4], 'carbonyl ylides' [5], 'azomethine ylides' [6], and S-centered 1,3-dipoles [7-9] have been described. The thiocarbonyl compounds involved in these studies were aromatic and cycloaliphatic thioketones, 1,3-thiazole-5(4*H*)-thiones, thio- and dithioesters, as well as some of their derivatives, *e.g.*, 'sulfines' (thiocarbonyl *S*-oxides). In addition to the expected [2 + 3] cycloadducts, we isolated from some of the reaction mixtures other products resulting from prototropic shifts, N<sub>2</sub>- and S-extrusion, as well as rearrangements. These results clearly showed that thiocarbonyl compounds may be considered as useful building blocks for the preparation of S-containing compounds, especially three- and five-membered heterocycles.

N,N'-(Thiocarbonyl)diimidazole (= 1,1'-(carbonothioyl)bis[1*H*-imidazole]; 1) is a well known reagent which reacts with nucleophiles like amines or alcohols to form thiourea derivatives and thiocarbonates, respectively (*cf.* [10][11])<sup>2</sup>). Although aromatic thioketones were frequently used as dipolarophiles in 1,3-dipolar cycloadditions [13], similar

<sup>&</sup>lt;sup>1</sup>) Part of the planned Ph.D. Thesis of T.G., University of Łódź.

applications for 1 are very scarcely described. The first paper dealing with reactions of 1 and diazo compounds was published by *Martvoń et al.* [14]. In the case of ethyl diazoacetate in the presence of  $Et_3N$ , they obtained ethyl 5-(1*H*-imidazol-1-yl)-1,3,4-thiadiazole-2-carboxylate. A plausible explanation for its formation is a 1,3-dipolar cycloaddition followed by elimination of 1*H*-imidazole. In contrast to similar reactions with aromatic thioketones and diazo compounds, no N<sub>2</sub> elimination was observed. Some years after the first report, *Harpp et al.* described the crystalline product of the analogous reaction of 1 and ethyl diazoacetate in benzene as ethyl 5-(1*H*-imidazol-1-yl)-1,2,3-thiadiazole-4-carboxylate [15]. They deduced the structure from NMR experiments; in particular, the C,C connectivity was established using a 2D-inadequate pulse sequence (CCC2D).

Apart from diazo compounds, only aldonitrones were reported to undergo 1,3dipolar cycloadditions with 1 to yield thioamides *via* an addition/elimination process [16].

The aim of the studies described in the present paper was to use 1 as a C,S-dipolarophile in reactions with 'thiocarbonyl ylides', diazo compounds, and other 1,3-dipoles.

**Results and Discussion.** – 'Thiocarbonyl ylides' of type **3** are known to undergo 1,3-dipolar cycloadditions with aromatic thioketones to give a mixture of regioisomeric cycloadducts [17]. Heating a THF solution of the 2,5-dihydro-1,3,4-thiadiazole derivative **2a**, which is a precursor of 'thiocarbonyl ylide' **3a**, in the presence of a slight excess of **1**, resulted in the evolution of an equimolar amount of  $N_2$  and the formation of only one cycloadduct **4a** (*Scheme 1*). Compound **4a** was stable enough to be isolated and purified by crystallization without decomposition. Its structure follows from the spectral data.



<sup>&</sup>lt;sup>2</sup>) Therefore, **1** is called a 'thiocarbonyl-transfer reagent' which found many applications for mild transformations in peptide, carbohydrate, and other natural-product chemistry (cf. [12]).

The <sup>1</sup>H-NMR spectrum of **4a** shows a characteristic signal at 3.92 ppm (*s*) for the CH<sub>2</sub> group and a broad *s* at 1.18 ppm for four Me groups. The <sup>13</sup>C-NMR spectrum reveals the presence of a CH<sub>2</sub> group (*t* at 49.9 ppm) which corresponds well with the structure **4a**. The regioisomeric structure **A** was excluded on the basis of the chemical shift of the CH<sub>2</sub> group, which in **A** is expected to be at *ca*. 20–30 ppm (*cf*. [18]).

Similar treatment of freshly purified 1 (which was free of 1*H*-imidazole formed by hydrolysis during storage) with the precursor 2b of adamantanethione-derived S-methanide **3b** resulted also in the evolution of an equimolar amount of  $N_2$ . After crystallization from benzene, the expected spirocyclic 1,3-dithiolane 4b was isolated in satisfactory yield (Scheme 2). A different result was obtained when the reaction was carried out with an old sample of 1 containing ca. 10% of 1*H*-imidazole. In this case, the examination of the crude reaction mixture by <sup>1</sup>H-NMR spectroscopy showed the presence of the cycloadduct 4b (s at 4.10 ppm,  $CH_2S$ ) besides two new compounds 5 (s at 6.05 ppm, =CHS) and **6** (s at 1.62 ppm, MeS). After chromatographic workup (SiO<sub>2</sub>), only the two products 5 and 6 were isolated. The initially formed cycloadduct 4b could not be obtained. The structure of the major product 5 and the minor product 6 was shown to be a 1,3-dithiole derivative and a S,N-acetal, respectively. The formation of 5 is the result of the elimination of 1H-imidazole from the primary cycloadduct **4b**. We propose that the first step in the conversion  $4b \rightarrow 6$  is the deprotonation of 4b by the basic and nucleophilic ylide **3b** [19][20], followed by elimination of imidazolide. This anion is then trapped by the sulfonium ion 7 to yield the N,S-acetal 6. The amount of 4b detected in the crude reaction mixture obviously was converted into 5 during workup, probably catalyzed by  $SiO_2^3$ ).

In an attempted addition of thiobenzophenone-derived S-methanide (=[(diphenyl-methylidene)sulfonio]methanide) with 1, the only products isolated were the known 2,2-



<sup>3</sup>) In another experiment, **2b** was heated in THF in the presence of equimolar amounts of 1*H*-imidazole. In this case, the S,N-acetal **6** was the only product [21].

diphenylthiirane and 2,2,3,3-tetraphenyl-1,4-dithiane. According to *Huisgen* and coworkers, these compounds are formed by 1,3-dipolar electrocyclization and dimerization, respectively, of the starting methanide (*cf.* [22]). The reason for the absence of a product of an intermolecular reaction of **1** with this methanide is most likely the insolubility of **1** in THF at  $-30^{\circ}$ , at which temperature the relatively instable methanide has to be generated.

Contradictory results for the reaction of 1 with diazoacetates [14][15] (cf. Introduction) prompted us to re-examine this conversion. In our experiments, ethyl diazoacetate (8a) and 1 were dissolved in  $CH_2Cl_2$  at room temperature. Under these mild conditions, the reaction was complete within a few hours without any evolution of N<sub>2</sub>. The crystalline compound **10a**, isolated after chromatographic workup, showed the same physical and spectroscopic properties as the product described in [14] and [15] (Scheme 3). The arguments of Martvoń et al. [14] for the assignment of the 1,3,4-thiadiazole structure to the adduct (prepared in CHCl<sub>3</sub> in the presence of Et<sub>3</sub>N) originated from the structure of the product isolated from the reaction of 1 with  $CH_2N_2$ . Ten years later, Harpp et al. proposed the 1,2,3-thiadiazole structure for the product they obtained from 1 and 8a in benzene [15], without referring to the previous paper. Both proposals had to be evaluated carefully, since studies of the reactions of diazo compounds with thiocarbonyl derivatives showed that in some cases the cycloaddition occurs with low regioselectivity [23-26]. The regioselectivity depends on both substitution pattern and polarity of the solvent [23][24]. Therefore, the regioselectivity of the cycloaddition of 1 on  $CH_2N_2$  does not necessarily correspond to that obtained with diazoacetates.



The final proof of the 1,3,4-thiadiazole structure of the product 10a that we obtained from 1 and  $8a^4$ ) was given by the X-ray crystal-structure determination of crystals grown from benzene (*Fig.*). Analogously, the reaction of 1 and methyl diazoacetate (**8b**) yielded 10b.

<sup>&</sup>lt;sup>4</sup>) Repeating the reaction of 1 and 8a under the conditions of [14] or [15], we obtained in both cases the same product 10a (m.p., IR, and NMR).



Figure. ORTEP Plots [27] of the molecular structures of 1,3,4-thiadiazole derivatives: a) 10a (two crystallographically independent molecules A and B) and b) 10d. With 50% probability ellipsoids; arbitrary numbering of the atoms.

The ease of the elimination of 1*H*-imidazole from the initially formed cycloadduct 9  $(\mathbb{R}^1 = \mathbb{H})$  should depend on the electron-withdrawing properties of the substituent  $\mathbb{R}^2$ . For instance, the adducts of **8a** with 1,3-thiazole-5(4*H*)-thiones underwent a spontaneous rearrangement induced by a deprotonation [3b], whereas the analogous conversion of the corresponding diazo(phenyl)methane adduct occurred only after treatment with a base [2b]. Therefore, we reacted 1 with diazo(phenyl)methane (**8c**), diazoethane (**8d**), and diazomethane (**8e**) instead of **8a, b**. The yellow color of the Et<sub>2</sub>O solutions

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of 1 disappeared immediately without  $N_2$  evolution. The precipitated products were purified chromatographically and/or by crystallization and identified as 2-(1*H*-imidazol-1-yl)-5-phenyl- (10c), 2-(1*H*-imidazol-1-yl)-5-methyl- (10d), and 2-(1*H*-imidazol-1-yl)-1,3,4-thiadiazole (10e), respectively. The structure of 10d was determined unambiguously by means of X-ray crystallography (*Fig.*). Very similar chemical shifts for the C and CH atoms in the <sup>13</sup>C-NMR spectra supported analogous structures for 10c-e. These experiments show that the elimination of 1*H*-imidazole from 9c-e also occurs spontaneously<sup>5</sup>). Furthermore, the structures of the products confirm that the cycloadditions of 1 with 8c-e proceeded with the same regioselectivity as found when the diazoacetates 8a,b were used.

Finally, we used diazodiphenylmethane (8f) in the cycloaddition with 1. Under similar conditions to those described above, an equimolar amount of  $N_2$  evolved and, after chromatographic workup, product 11 (Scheme 3) was isolated in high yield. Its formation can be explained by a 'twofold extrusion' of  $N_2$  and S from the initial cycloadduct of type 9 ( $R^1 = R^2 = Ph$ ). The alternative structure **B** of the primary cycloadduct of 1 and 8f cannot be excluded with certainty; the spontaneous N<sub>2</sub> elimination, however, is in better agreement with the less stable 2,5-dihydro-1,3,4-thiadiazole structure<sup>6</sup>). On the other hand, the elimination of  $N_2$  from 9 should lead to the formation of a thiirane via an intermediate 'thiocarbonyl ylide' (cf. [30]). Furthermore, tetraarylthiiranes are, in general, fairly stable compounds and do not eliminate S spontaneously; therefore, one should be able to isolate them. In the case of **B** ( $R^1 = R^2 = Ph$ ) as the initial cycloadduct, a 'twofold extrusion' of N<sub>2</sub> and S via an open-chain, biradical intermediate can be postulated (cf. [24][26][31]). Regardless of the mechanism leading to 11, the results described in this paper show once more that certain tetrasubstituted ethylene derivatives can be obtained in a one-pot procedure via the reaction of thiocarbonyl compounds with suitably substituted diazomethanes under very mild conditions (cf. also [2][3c][30][32-34]).

In conclusion, all of the investigated 1,3-dipolar cycloadditions of 'thiocarbonyl ylides' 3a, b and diazo compounds 8a-e with 1 occur with high regioselectivity<sup>7</sup>). It is especially worth mentioning that diazo compounds with an electron-withdrawing group (esters 8a, b), with a conjugating Ph group (8c), or with an electron-donating Me group (8d) cycloadd with the same regioselectivity to give 2,5-dihydro-1,3,4-thiadiazole derivatives, and, *via* elimination of 1*H*-imidazole, aromatization yields 1,3,4-thiadiazoles.

The reaction of diazo compounds with suitable C=S compounds, *e.g.*, thioacyl chlorides, thio- and dithioesters, chlorodithioformates, thiophosgene, carbondisulfide, thioketenes, and isothiocyanates has recently been reviewed as a method for the prepa-

<sup>&</sup>lt;sup>5</sup>) Probably, the presence of 1*H*-imidazole is responsible for the ease of the base-catalyzed elimination.

<sup>&</sup>lt;sup>6</sup>) Generally, elimination of N<sub>2</sub> occurs more easily from 2,5-dihydro-1,3,4-thiadiazoles (type 9) than from 4,5-dihydro-1,2,3-thiadiazoles (type B) [24][26] (*cf.* also [28][29]). Whereas, in the first case, the thermal decomposition often takes place around room temperature, it requires temperatures of *ca.* 100° in the latter case.

<sup>&</sup>lt;sup>7</sup>) We also attempted to react 1 with a thermally generated 'azomethine ylide'. For this reason, *cis*-1-methyl-2,3diphenylaziridine was heated with an equimolar amount of 1 in boiling toluene according to the procedure described in [6]. After 3 h, the initially yellow solution was black, and after evaporation of the solvent, examination of the tary residue by <sup>1</sup>H-NMR indicated total decomposition of starting materials without formation of any stable product.



ration of 1,2,3- as well as for 1,3,4-thiadiazoles [28][29][35], because in several studies both isomers **E** and **F** (*Scheme 4*) have been isolated<sup>8</sup>). In these cases, a non-regioselective 1,3-dipolar cycloaddition to the 4,5-dihydro-1,2,3- and 2,5-dihydro-1,3,4-thiadiazoles **C** and **D**, respectively, can be proposed as the first step of the transformation. Aromatization by elimination of HX then leads to the corresponding thiadiazoles. A reaction *via* initial formation of an  $\alpha$ -diazo(thiocarbonyl) intermediate of type **G** followed by a 1,5-dipolar electrocyclization has also been discussed for the formation of the 1,2,3-thiadiazoles [35].

The low regional region region X = X = X and X = X. was the reason for some confusion with respect to the structure of the aromatized product. In 1896, Pechmann and Nold published the synthesis of N-phenyl-1,2,3-thiadiazol-5-amine from phenyl isothiocyanate and  $CH_2N_2$  [36]. Some years later, *Staudinger* and Siegwart described the reaction of 8a and thiobenzoyl chloride yielding ethyl 5-phenyl-1,3,4-thiadiazole-2-carboxylate [37]. In the sixties, the reaction of thiophosgene (CSCl<sub>2</sub>) and diazo ketones was studied by *Ried* and *Beck* [38] who proposed the 1,2,3thiadiazole structure for the products, as well as by Bacchetti et al. [39] who proved that the products are 1,3,4-thiadiazole derivatives. Mixtures of 1,2,3- and 1,3,4-thiadiazoles were formed in the reactions of CH<sub>2</sub>N<sub>2</sub> with N,N-dimethyl-C-(methylsulfonyl)thioformamide (12,  $R^1 = Me_2N$ ,  $X = MeSO_2$ ) and ethyl chlorodithioformate (12,  $R^1 = EtS$ , X = Cl [40], respectively, as well as in those of several  $\alpha$ -diazo carbonyl compounds and  $CSCl_2$ . For instance, 4-chloro- $\alpha$ -diazoacetophenone (13,  $R^2 = 4-ClC_6H_4CO$ ) and  $CSCl_2$ in benzene gave the corresponding 1,2,3- and 1,3,4-thiadiazoles E and F in 13 and 47% yield, respectively<sup>9</sup>). The same products were obtained from an analogous reaction in the presence of Et<sub>3</sub>N (4 and 25% yield) and from bis(4-chloro- $\alpha$ -diazophenacyl)mercury and CSCl<sub>2</sub> in MeCN (5 and 20% yield; ratio determined by NMR 1:6). On the other hand, treatment of 13 ( $R^2 = 4$ -ClC<sub>6</sub>H<sub>4</sub>CO) with 12 ( $R^1 = EtS, X = Cl$ ) in MeCN/Et<sub>3</sub>N yielded

<sup>&</sup>lt;sup>8</sup>) Thioketenes, isothiocyanates, and some thioesters react in a regiospecific way to give 1,2,3-thiadiazole derivatives (cf. refs. cited in [28][29][35]).

<sup>&</sup>lt;sup>9</sup>) The ratio in the crude mixture was 2:3, as determined by NMR.

only 2-(4-chlorobenzoyl)-5-(ethylthio)-1,3,4-thiadiazole (type F), whereas with bis(4chloro- $\alpha$ -diazophenacyl)mercury in MeCN the isomeric 4-(4-chlorobenzoyl)-5-(ethylthio)-1,2,3-thiadiazole (type E) was formed exclusively [41]. In a similar reaction, 2-(methoxycarbonyl)ethyl chlorodithioformate and CH<sub>2</sub>N<sub>2</sub> in Et<sub>2</sub>O at 0° gave a 1:2 mixture of the corresponding 1,2,3- and 1,3,4-thiadiazoles [42], and CH<sub>2</sub>N<sub>2</sub> and methyl dithioacetate at  $-70^{\circ}$  yielded 5-methyl-1,2,3- and 2-methyl-1,3,4-thiadiazole together with 2-methyl-2-(methylthio)thiirane (20, 45, and 22% yield, resp.) [43]. Most likely, the latter is formed from 2,5-dihydro-2-methyl-2-(methylthio)-1,3,4-thiadiazole, one of the two regioisomeric cycloadducts, by elimination of N<sub>2</sub> and 1,3-dipolar electrocyclization of the formed 'thiocarbonyl ylide'. Elimination of MeSH from the same intermediate leads to 2-methyl-1,3,4-thiadiazole. The regioselectivity of the 1,3-dipolar cycloaddition is, therefore, *ca.* 1:4.

In several papers, selective syntheses of 1,2,3-thiadiazoles *via* reaction of diazo compounds with *O*-alkyl thioesters [43–45] and CS<sub>2</sub> [46] have been described. Because of the big difference in the thermal stability of 4,5-dihydro-1,2,3- and 2,5-dihydro-1,3,4-thiadiazoles (**C** and **D** in *Scheme 4*) [24][26][43], which can be considered as the initially formed intermediates, the exclusive isolation of 1,2,3-thiadiazoles of type **E** does not prove a regioselective 1,3-dipolar cycloaddition. Selective preparation of 1,2,3-thiadiazoles is reported to occur when *O*-alkyl thioesters or dithioesters are treated with lithium diazo(trimethylsilyl)methane [47]. The reactions of diazo compounds with isothiocyanates yield 5-amino-1,2,3-thiadiazole derivatives as the only products (*cf.* [28]). Diazomethane readily adds to bis(trifluoromethyl)thioketene to form almost equal amounts of both regioisomeric dihydrothiadiazoles without loss of N<sub>2</sub>; spontaneous H-shifts convert the primary cycloadducts into the aromatic 1,3,4- and 1,2,3-thiadiazoles [48]. Other electrondeficient thioketenes react with diazomethane or diazo(phenyl)methane to give mesoionic and non-mesoionic derivatives of 1,2,3-thiadiazoles exclusively [49].

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### **Experimental Part**

1. General. M.p.s: Mel-Temp. II apparatus (Aldrich); in capillary; uncorrected. IR Spectra: Specord-71-IR spectrometer; in KBr;  $\tilde{v}$  in cm<sup>-1</sup>. NMR Spectra: Tesla-BS-476 (60 MHz (<sup>1</sup>H)) or Bruker-AC-300 (300 (<sup>1</sup>H) or 76.5 MHz (<sup>13</sup>C)) instrument; CDCl<sub>3</sub> solns.; chemical shifts  $\delta$  in ppm rel. to SiMe<sub>4</sub> (= 0 ppm). EI-MS: Varian-MAT-90 spectrometer; at 70 eV; m/z (rel.%). Elemental analyses were performed in the microanalytical laboratories of the Polish Academy of Sciences (CBMiM) in Łódź and the Institut of Organic Chemistry of the University of Zürich.

2. Starting Materials. The 1,1'-(carbonothioyl)bis[1H-imidazole] (1) was prepared in 87% yield from 1-(trimethylsilyl)-1H-imidazole and CSCl<sub>2</sub> [50]: yellow crystals, m.p.  $103-105^{\circ}$  ([50b]:  $105-106^{\circ}$ ). The substance decomposed during storage and was purified before use. The 1,1,3,3-tetramethyl-5-thia-7,8-diazaspiro[3,4]oct-7-en-2-one (2a) and 2,5-dihydrospiro[1,3,4-thiadiazole-2,2'-tricyclo[3,3,1.1<sup>3,7</sup>]decane] (2b) were prepared by addition of CH<sub>2</sub>N<sub>2</sub> to a soln. of 2,2,4,4-tetramethyl-3-thioxocyclobutanone [51a] and tricyclo[3,3,1.1<sup>3,7</sup>]decane-2-thione [51b], respectively. Diazo compounds were synthesized according to known procedures: methyl and ethyl diazoacetate (8a,b) by diazotization of the corresponding glycinates [52], diazo(phenyl)methane (= (diazomethyl)benzene; 8c) by thermal decomposition of the sodium salt of benzaldehyde tosylhydrazone in pyridine [53], and diazodiphenylmethane (= 1,1'-(diazomethylene)bis[benzene]; 8f) by oxidation of benzophenone hydrazone with yellow HgO [54]. Diazoethane and CH<sub>2</sub>N<sub>2</sub> were prepared in Et<sub>2</sub>O soln. according to [55].

3. Reactions of 1 with in situ Generated 'Thiocarbonyl Ylides' 3a,b: General Procedure. A stirred soln. of freshly purified 1 (890 mg, 5 mmol) and 2,5-dihydro-1,3,4-thiadiazole 2 (5 mmol) in CHCl<sub>3</sub> (10 ml) was heated to  $45^{\circ}$  (oil bath). The evolution of N<sub>2</sub> was controlled volumetrically using a 'gas burette' attached to the reaction vessel. After 3 h, the N<sub>2</sub> evolution ceased (*ca.* 120 ml N<sub>2</sub>). The solvent was removed, and the crude residues were analyzed by <sup>1</sup>H-NMR. The cycloadducts **4a,b** were purified by fractional crystallization from benzene; yields refer to anal. pure materials.

1,1,3,3-Tetramethyl-6,6-di (1H-imidazol-1-yl)-5,8-dithiaspiro[3.4]octan-2-one (4a): 1.18 g (68%). Colorless crystals. M.p. 160–162°. IR: 3110s, 2980s, 1780vs (C=O), 1510m, 1480s, 1460s, 1510m, 1230vs, 1210vs, 1090vs, 1080vs, 1030vs, 940s, 900s, 850m, 810s. <sup>1</sup>H-NMR: 7.78, 7.13, 7.02 (3 br. s, 6 H (im)); 3.92 (s, CH<sub>2</sub>); 1.18 (s, 4 Me). <sup>13</sup>C-NMR: 216.6 (s, C=O); 136.2, 131.1, 118.0 (3d, 6 CH (im)); 93.3 (s, C(6)); 75.8 (s, C(4)); 67.1 (s, C(1), C(3)); 49.9 (t, CH<sub>2</sub>); 24.8, 21.9 (2q, 4 Me). EI-MS: 278 (8), 213 (9), 211 (100), 210 (86), 195 (27), 192 (9), 188 (41), 143 (16), 124 (11), 93 (17), 86 (38), 85 (27), 71 (32), 69 (89), 68 (33). Anal. calc. for C<sub>16</sub>H<sub>20</sub>N<sub>4</sub>OS<sub>2</sub> (348.49): C 55.15, H 5.78, N 16.08, S 18.40; found: C 55.50, H 5.78, N 16.26, S 18.52.

4,4-Di(1H-imidazol-1-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1<sup>3.7</sup>]decane] (= 1,1'-(Spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1<sup>3.7</sup>]decan]-4-ylidene)bis[1H-imidazole]; **4b**): 950 mg (53%). Colorless crystals. M.p. 160–162°. IR: 3110s, 2920vs, 2850s, 1460s, 1450m, 1300s, 1210vs, 1095vs, 1060vs, 1020m, 840m, 820m, 730s. <sup>1</sup>H-NMR: 7.62, 7.13, 7.03 (3br. s, 6 H (im)); 4.05 (s, CH<sub>2</sub>); 2.25–1.75 (m, 14 H). <sup>13</sup>C-NMR: 136.4, 130.8, 118.0 (3d, 6 CH (im)); 92.3 (s, C(4)); 78.9 (s, C(2)); 48.0 (t, CH<sub>2</sub>(5)); 41.6, 36.7, 35.8 (3t, 5 CH<sub>2</sub> (ad)); 37.1, 26.2, 26.0 (3d, 4 CH (ad)). CI-MS (NH<sub>3</sub>): 293 (8), 292 (15), 290 (100,  $[M - C_3H_4N_2]^+$ ). Anal. calc. for  $C_{18}H_{22}N_4S_2$  (358.52): C 60.30, H 6.19, N 15.63, S 17.88; found: C 60.22, H 5.90, N 15.75, S 17.83.

The reaction of 1 and 2b was repeated in the presence of 1*H*-imidazole (*ca.* 20% in relation to 1). <sup>1</sup>H-NMR of the crude mixture revealed the presence of 4b along with 4-(1H-imidazol-1-yl)spiro[1,3-dithiole-2,2'-tricy-clo[3.3.1.1<sup>3,7</sup>]decan] (= 1-(spiro[1,3-dithiole-2,2'-tricyclo[3.3.1.1<sup>3,7</sup>]decan]-4-yl)-1H-imidazole; 5) and <math>1-[(2-methylthio)tricyclo[3.3.1.1<sup>3,7</sup>]dec-2-yl]-1H-imidazole (6) in a ratio of*ca.*5:2:2. After chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> with increasing amount of acetone), only 5 and 6 were isolated.

**5** (CH<sub>2</sub>Cl<sub>2</sub>/acetone 9:1; recrystallized from benzene): 261 mg (18%). Colorless crystals. M.p. 153–155°. IR: 3030*m*, 2900vs, 1585*m*, 1510s, 1480vs, 1470*m*, 1450*m*, 1285vs, 1230s, 1210*m*, 1100*m*, 1080s, 1030vs, 900s, 800vs, 785s, 730s. <sup>1</sup>H-NMR: 7.72, 7.15, 7.10 (3br. *s*, 3 H (im)); 6.07 (*s*, = CH); 2.2–1.7 (*m*, 14 H). <sup>13</sup>C-NMR: 136.6, 129.8, 119.0 (3*d*, 3 CH (im)); 126.9 (*s*, C(4)); 106.2 (*d*, CH(5)); 81.9 (*s*, C(2)); 39.7, 37.3, 34.3 (3*t*, 5 CH<sub>2</sub> (ad)); 35.2, 26.9 (2*d*, 4 CH (ad)). EI-MS: 290 (100,  $M^{++}$ ), 257 (6), 230 (6), 201 (10), 169 (90), 124 (15), 105 (21), 91 (64), 79 (42), 53 (19). Anal. calc. for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub> (290.44): C 62.03, H 6.25, N 9.65, S 22.08; found: C 62.31, H 6.18, N 9.58, S 21.87.

6 (CH<sub>2</sub>Cl<sub>2</sub>/acetone 4:1; recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub>): 124 mg (10%). M.p. 77-79° ([21]: 79-81°).

4. Reactions of 1 with Diazo Compounds 8a-f: General Procedure. To a stirred soln. of 1 (535 mg, 3 mmol) in  $CH_2Cl_2$  (4 ml) was added diazo compound 8 (3 mmol), dissolved in a small amount of  $CH_2Cl_2$  or  $Et_2O$ , at r.t. (8a-c, f). The mixtures with 8a, b were stirred overnight. In the cases of 8d, e, the  $Et_2O$  soln. was added at  $0-5^\circ$  until the yellow color of 1 disappeared. In the case of 8f, the rapid decoloration of the soln. was accompanied by a vigorous evolution of N<sub>2</sub>. After evaporation, the crude residues were purified by chromatography (SiO<sub>2</sub>) and recrystallization. Yields refer to anal. pure materials.

*Ethyl 5-(1H-Imidazol-1-yl)-1,3,4-thiadiazole-2-carboxylate* (**10a**): 363 mg (54%). M.p. 121–123° ([14]: 124–125°). <sup>1</sup>H-NMR: 8.26, 7.59, 7.27 (3 br. *s*, 3 H (im)); 4.55 (*q*, *J* = 7, MeCH<sub>2</sub>O); 1.48 (*t*, *J* = 7, MeCH<sub>2</sub>O). <sup>13</sup>C-NMR: 162.1, 158.0 (2*s*, C(2), C(5)); 136.6, 132.1, 118.6 (3*d*, 3 CH (im)); 63.8 (*t*, MeCH<sub>2</sub>O); 14.2 (*q*, MeCH<sub>2</sub>O).

*Methyl* 5-(1H-Imidazol-1-yl)-1,3,4-thiadiazole-2-carboxylate (10b): Crystallization from benzene gave 448 mg (71%). M.p. 168–170°. IR: 3120*m*, 1720*s* (C=O), 1630*m*, 1510*s*, 1450*s*, 1360*m*, 1310*s*, 1250*m*, 1110*s*, 1040*s*, 920*m*. <sup>1</sup>H-NMR: 8.26, 7.59, 7.27 (3br. *s*, 3 H (im)); 4.09 (*s*, MeO). <sup>13</sup>C-NMR: 162.2, 158.0 (2*s*, C(2), C(5)); 136.6, 132.2, 118.7 (3*d*, 3 CH (im)); 54.1 (*q*, MeO). EI-MS: 210 (100,  $M^{+1}$ ), 183 (60,  $[M - \text{HCN}]^+$ ), 178 (6), 152 (9), 125 (7), 111 (8), 98 (37), 93 (26), 84 (13), 79 (11), 72 (24), 71 (41), 66 (28). Anal. calc. for C<sub>7</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub>S (210.24): C 39.99, H 2.88, N 26.65; found: C 40.02, H 3.11, N 26.63.

2-(1H-Imidazol-1-yl)-5-phenyl-1,3,4-thiadiazole (**10c**): Trituration with Et<sub>2</sub>O, filtration, and recrystallization from CHCl<sub>3</sub>/Et<sub>2</sub>O gave 363 mg (53%). M.p. 197–199°. IR: 3160*m*, 1550*m*, 1510*vs*, 1460*s*, 1310*s*, 1250*s*, 1095*s*, 1040*s*, 920*s*. <sup>1</sup>H-NMR: 8.21, 7.58, 7.25 (3 br. *s*, 3 H (im)); 7.95–7.9 (*m*, 3 arom. H); 7.55–7.5 (*m*, 2 arom. H). <sup>13</sup>C-NMR: 165.7, 158.2 (2*s*, C(2), C(5)); 136.5, 131.6, 118.6 (3*d*, 3 CH (im)); 131.5, 129.4, 127.7 (3*d*, 5 arom. CH); 115.2 (*s*, 1 arom. C). EI-MS: 228 (100,  $M^+$ ), 201 (19,  $[M - \text{HCN}]^+$ ), 161 (11), 125 (6), 121 (27), 103 (28), 98 (14), 77 (21), 71 (15), 52 (11), 51 (10). Anal. calc. for C<sub>11</sub>H<sub>8</sub>N<sub>4</sub>S (228.27): C 57.88, H 3.53, N 24.54; found: C 57.57, H 3.58, N 24.55.

2-(1H-Imidazol-1-yl)-5-methyl-1,3,4-thiadiazole (10d): Chromatography with  $CH_2Cl_2/acetone 7:3$  and recrystallization from hexane/ $CH_2Cl_2$  gave 319 mg (64 %). M.p. 115–117°. IR: 3080*m*, 1520vs, 1485s, 1375s, 1330s, 1265s, 1210s, 1130s, 1120s, 1065s, 950s, 860s, 750s. <sup>1</sup>H-NMR: 8.15, 7.53, 7.21 (3 br. s, 3 H (im)); 2.80 (s, Me). <sup>13</sup>C-NMR: 162.3, 159.0 (2s, C(2), C(5)); 136.5, 131.3, 118.7 (3d, 3 CH (im)); 16.1 (q, Me). EI-MS: 166 (100,  $M^+$ ), 139 (40,  $[M - HCN]^+$ ), 125 (5), 99 (20), 59 (20). Anal. calc. for  $C_6H_6N_4S$  (166.18): C 43.36, H 3.64, N 33.71; found: C 43.54, H 3.75, N 33.66.

2-(1H-Imidazol-1-yl)-1,3,4-thiadiazole (10e): 292 mg (64%). M.p.  $117-119^{\circ}$  ([14]: 118-119°). <sup>1</sup>H-NMR: 9.06 (s, H-C(5)); 8.23, 7.59, 7.25 (3 br. s, 3 H (im)). <sup>13</sup>C-NMR: 159.4 (s, C(2)); 148.9 (d, CH(5)); 136.7, 131.6, 118.9 (3d, 3 CH (im)).

1,1'-(2,2-Diphenylethenylidene)bis[1H-imidazole] (11): Chromatography with  $CH_2Cl_2/acetone 1:1$  and recrystallization from benzene gave 497 mg (53%). M.p. 181–183°. IR: 3080*m*, 1660s (C=C), 1480s, 1395s, 1300s, 1290s, 1140s, 1100*m*, 1040s, 900s. <sup>1</sup>H-NMR: 7.32, 7.00 (2 br. *s*, 4 and 6 arom. H, resp.); 7.22, 6.78 (2 br. *s*, 4 and 2 H (im), resp.). <sup>13</sup>C-NMR: 138.1 (*s*, 2 arom. C); 138.0, 130.2, 119.1 (3*d*, 6 CH (im)); 131.1, 124.2 (2*s*, C=C); 129.2, 128.8, 128.3 (3*d*, 10 arom. CH). EI-MS: 312 (100,  $M^+$ ), 272 (10), 245 (48), 243 (20), 217 (23), 190 (24), 178 (16), 165 (69), 142 (10), 128 (9), 115 (16), 89 (9), 82 (14), 44 (56). Anal. calc. for  $C_{20}H_{16}N_4$  (312.36): C 76.90, H 5.16, N 17.94; found: C 77.03, H 5.43, N 17.83.

	10a	10d
Crystallized from	benzene	hexane/CH <sub>2</sub> Cl <sub>2</sub>
Empirical formula	C <sub>8</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub> S	C <sub>6</sub> H <sub>6</sub> N <sub>4</sub> S
Formula weight	224.24	166.20
Crystal color, habit	colorless, needle	colorless, tablet
Crystal dimensions [mm]	$0.07 \times 0.15 \times 0.45$	$0.18 \times 0.30 \times 0.40$
Temperature [K]	173 (1)	173 (1)
Crystal system	triclinic	monoclinic
Space group	<i>P</i> 1	$P2_1/c$
Z	4	4
Reflections for cell determination	25	25
$2\theta$ range for cell determination [°]	36-40	39-40
Unit cell parameters a [Å	9.939 (1)	10.513 (1)
<i>b</i> [Å]	11.486 (2)	9.987 (2)
c [Å]	8.811 (1)	7.093 (2)
α [°]	90.86(1)	90
$\beta$ [°]	106.75 (1)	108.73 (1)
γ [°]	82.46 (1)	90
$V[Å^3]$	954.6 (3)	705.3 (2)
$D_{\rm x} [{\rm g}{\rm cm}^{-3}]$	1.560	1.565
$\mu(MoK_a) [mm^{-1}]$	0.324	0.387
$2\theta_{(max)}[^{\circ}]$	55	60
Total reflections measured	4624	2312
Symmetry-independent reflections	4376	2044
Reflections used $[I > 2\sigma(I)]$	3296	1722
Parameters refined	288	125
Final R	0.0433	0.0322
$wR (w = [\sigma^2(F_o) + (0.005 F_o)^2]^{-1})$	0.0452	0.0340
Goodness of fit	1.741	2.132
Secondary extinction coefficient	$2.6(6) \times 10^{-7}$	$1.9(2) \times 10^{-6}$
Final $\Delta_{\rm max}/\sigma$	0.0002	0.0002
$\Delta \rho$ (max; min) [e Å <sup>-3</sup> ]	0.36; -0.29	0.36; -0.27

Table. Crystallographic Data of 10a and 10d

<sup>&</sup>lt;sup>10</sup>) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-10/64. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: + 44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

5. Crystal-Structure Determination of **10a** and **10d** (see Table and Fig.)<sup>10</sup>). All measurements were made on a Rigaku-AFC5R diffractometer in the  $\omega/20$ -scan mode using graphite-monochromated MoK<sub>x</sub> radiation ( $\lambda$  0.71069 Å) and a 12 kW rotating anode generator. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Data collection and refinement parameters are listed in the Table, views of the molecules are shown in the Figure. The structures were solved by direct methods using SHELXS86 [56], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms, were located in difference electron density maps, and, for **10d**, their positions were allowed to refine together with individual isotropic displacement parameters. For **10a**, the H-atoms were subsequently fixed in geometrically idealized positions (d(C-H) = 0.95 Å), and only their isotropic displacement parameters were refined. All refinements were carried out on F using full-matrix least-squares procedures. A correction for secondary extinction was applied for both structures. Neutral-atom scattering factors for non-H-atoms were taken from [57a] and the scattering factors for H-atoms from [58]. Anomalous dispersion effects were included in F<sub>cale</sub> [59]; the values for f' and f''' were those of [57b]. All calculations were performed using the TEXSAN crystallographic software package [60].

There are two symmetry-independent molecules A and B of **10a** in the asymmetric unit. The molecules differ in that both residues at the 1,3,4-thiadiazole ring are rotated by *ca*. 180° in molecule B, when compared with molecule A. Both molecules are essentially planar with the maximum angle between the plane of the 1,3,4-thiadiazole ring and the planes of the two substitutents being 6.4°. The corresponding angle in **10d** between the planes of the two rings is 26.1°.

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