Tri- and Tetrasubstituted *N*-Phthalimidoaziridines in 1,3-Dipolar Cycloaddition Reactions

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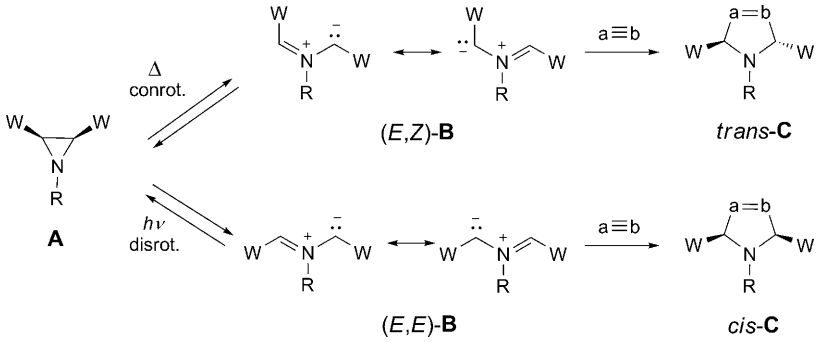
Dedicated to Professor *Manfred Hesse* on the occasion of his 75th birthday

The thermal reactions of the 2,2,3-trisubstituted *N*-phthalimidoaziridine **1a** with dimethyl acetylenedicarboxylate (DMAD), thioketones **4a**–**4d**, and dimethyl azodicarboxylate (**5**) proceed even at room temperature leading to the five-membered cycloadducts **2a**, **6**–**8**, and **12**, respectively, with retention of the spatial arrangement of the aziridine substituents, in contrast to the expectation based on the conservation of orbital symmetry in concerted reactions. The analogous reactions of the tetrasubstituted phthalimidoaziridine **1b** with thioketones at 40° lead to the 1,3-thiazolidine derivatives **10** and **11** as mixtures of diastereoisomers. These unexpected results may be explained by either the isomerization of the intermediate azomethine ylides or a non-concerted stepwise cycloaddition reaction of these ylides with the dipolarophiles. The structures of some adducts have been determined by X-ray crystallography.

Introduction. – As far back as in the sixties of the past century, the reaction of aziridines, *e.g.*, **A**, with active dipolarophiles, *e.g.*, a ≡ b, leading to five-membered N-containing heterocycles **C** was discovered [1–3] (*Scheme 1*). The process is considered to start with a thermally (conrotatory) or photochemically (disrotatory) induced cleavage of the aziridine C–C bond to give azomethine ylides **B**, which are named

Scheme 1



[1]) Part of the Ph.D. thesis of *A. V. U.*, University of Saint-Petersburg, 2009; stay at the University of Zürich, July–September, 2005.

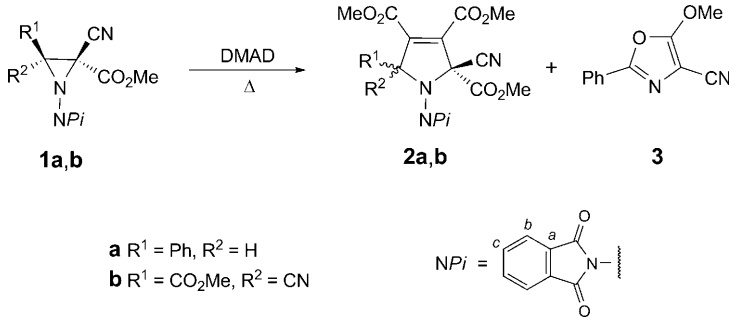
'octet-stabilized 1,3-dipoles' [4]. These reactive intermediates, which can be represented by various mesomeric structures, formally bear a positive charge on the N-atom and negative partial charges on both C-atoms, suggesting that the opening of aziridines **A** to azomethine ylides **B** should be accelerated by electron-withdrawing substituents, which are able to stabilize negative charges on the terminal C-atoms of the formed dipoles. This proposal is supported by experimental data [1–3][5][6]. The reactive 1,3-dipoles **B** subsequently undergo cycloaddition to dipolarophiles or stabilize *via* various other inter- or intramolecular transformations [3–8].

If both reactions of this process are concerted – the conrotatory C–C bond cleavage is thermally allowed according to the *Woodward–Hoffmann* rules [9], and the disrotatory one under photolysis conditions – and no stereoisomerization of the intermediate azomethine ylides **B** takes place, the adduct formation proceeds stereospecifically, and the spatial arrangement of the substituents of the product is determined by that of the starting compounds (see, *e.g.*, [10]). However, sometimes these conditions are not fulfilled, and mixtures of stereo(and regio-)isomers resulted [3][5–7].

The number of publications on the cycloaddition of azomethine ylides generated from aziridines thermally or photochemically grows rapidly. More and more often, this transformation is used in the synthesis of complex natural and biologically active compounds [7][8]. The use of *N*-aminoaziridine derivatives could open a direct way to various *N*-aminoheterocycles; however, only a few examples were described by *Foucaud et al.* in the seventies and eighties of the past century [11]. It was shown that, upon heating (or even at room temperature!), some *N*-phthalimidoaziridines with three or four electron-withdrawing substituents in the presence of dipolarophiles give products, which can be considered as the result of inter- (pyrrolines, azetidines) or intramolecular (oxazolines, oxazoles) transformations of the corresponding azomethine ylides. Similar intramolecular transformations were also described for some *N*-succinimidoaziridines [12].

Nevertheless, all of the few known examples of [2+3] cycloadditions with *N*-phthalimidoazomethine ylides were carried out with a single dipolarophile, the very reactive dimethyl acetylenedicarboxylate (DMAD), and the reports are very scarce and partly contradictory. It was reported in the first communication [11a] that briefly boiling *trans*-aziridine **1a** and DMAD in benzene gives a mixture of 2,5-dihydro-1*H*-pyrrole **2a** (25%) as a *single* stereoisomer and oxazole **3** (65%), which can be considered as the product of a 1,5-dipolar electrocyclization of the intermediate acylazomethine ylide and its subsequent aromatization by loss of phthalimide (*Scheme 2*). If the same reaction was carried out at room temperature in CH_2Cl_2 for two weeks, the yield of 2,5-dihydro-1*H*-pyrrole **2a**, isolated again as a *single* stereoisomer (according to the ^{1}H-NMR data), increased to 85%, and the yield of oxazole **3** decreased to 15% [11b]. But, in the latest article of the same group [11c], it was reported that boiling of the tetrasubstituted *N*-phthalimidoaziridine **1b** in the presence of DMAD in CH_2Cl_2 led to the corresponding 2,5-dihydro-1*H*-pyrrole **2b** (84%) as a 1:1 mixture of diastereoisomers, and the authors affirmed that they had obtained a *mixture of diastereoisomers* of dihydropyrrole **2a** in the earlier described experiment [11b] too! Furthermore, no determination of the relative configuration of any of these 2,5-dihydro-1*H*-pyrroles was carried out.

Scheme 2

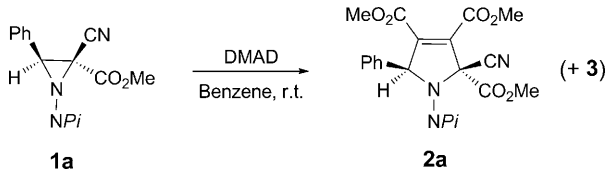


Meanwhile, we reported on the inter- [13–15] and intramolecular [16] cycloaddition of several 2,3-disubstituted *N*-phthalimidoaziridines to a number of dipolarophiles with C,C multiple bonds under forced thermolysis conditions (80–220°), which proceeded in a stereospecific and diastereoselective manner. Therefore, the aim of the present work was to investigate [2+3] cycloaddition reactions of *N*-phthalimidoaziridines **1a** and **1b**, which are activated with three and four electron-withdrawing substituents, respectively, to shed light on the spatial regularities of this process.

The aziridines **1a** and **1b** were obtained by oxidative 'phthalimidoaziridination' of the corresponding unsaturated compounds [17][18]. As far as this reaction occurs completely stereospecifically, the *trans* configuration of compound **1a** follows from the (*E*) configuration of the starting acrylate, which was established by its NOESY spectrum (see *Exper. Part*). The *trans* configuration of **1b** is in agreement with the non-equivalence of the two MeO groups in the ^{1}H-NMR spectrum as a result of the well-known slow inversion of the ring N-atom in *N*-aminoaziridine derivatives [19].

2. Results and Discussion. – 2.1. *Reaction of Aziridine* **1a** *with DMAD.* First, we have repeated the reaction of **1a** with DMAD [11]. Preliminary microscale (*ca.* 35 μmol) experiments in benzene and in CH_2Cl_2 were performed at room temperature. The ^{1}H- and ^{13}C-NMR spectra of the reaction mixture, recorded immediately after the reaction had ceased, revealed the presence of 2,5-dihydro-1*H*-pyrrole **2a**, as a single stereoisomer, and of oxazole **3** in a ratio of *ca.* 1:1 in both cases (*Scheme 3*). The separation of the mixture by chromatography on silica gave *ca.* 60% of **2a**, but only traces (*ca.* 5%) of oxazole **3a**, indicating the low stability of the latter under the separation conditions.

Scheme 3



The preparative-scale reaction of **1a** with DMAD in benzene at room temperature gave, after column chromatography, only **2a** in 60% yield. Its melting point and ^{1}H-NMR spectrum were in a good agreement with the data published earlier [11b], and its structure was unambiguously established as the *trans*-isomer (*rel*-(2*R*,5*R*)-isomer) by X-ray crystallography (*Fig. 1*). Concerning its ^{13}C-NMR spectrum, it should be noted that all signals of the phthalimide C-atoms are broad or even cannot be detected (N–C=O) in the spectrum. This indicates slow rotation of this substituent about the sterically crowded N–N bond.

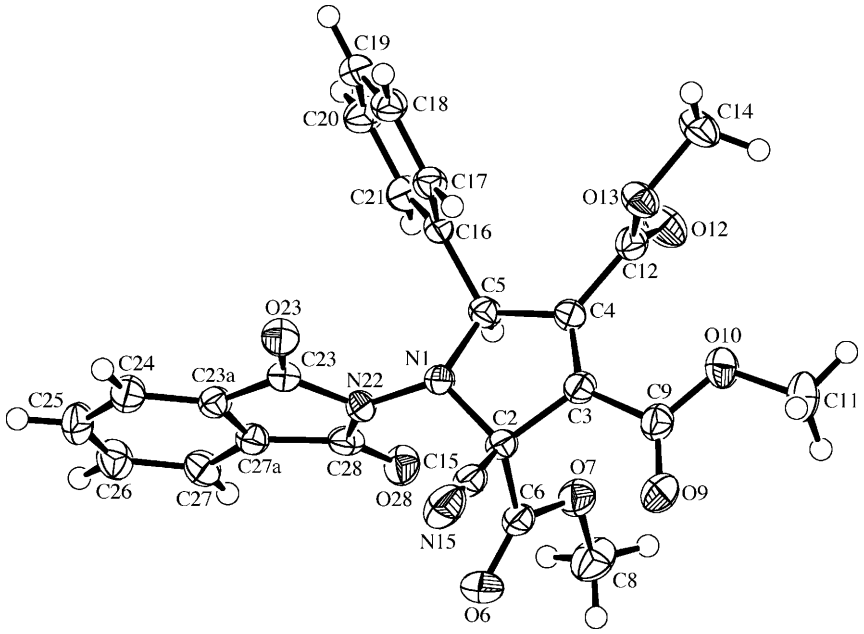


Fig. 1. *ORTEP Plot* [20] *of the molecular structure of* **2a** (arbitrary numbering of atoms; 50% probability ellipsoids)

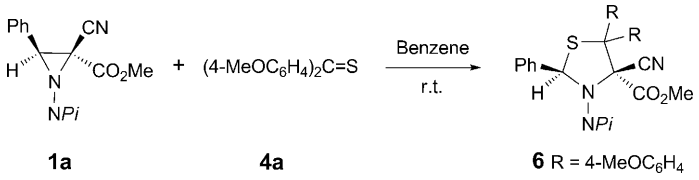
The crystal structure of **2a** clearly shows that the Ph and C≡N groups have the same relative configuration (*cis* orientation) as in the starting aziridine **1a**. This result was unexpected taking into account our experience with 2,3-disubstituted *N*-phthalimidoaziridines [13–16]: we have shown that the thermal ring opening of these aziridines to give *N*-phthalimidoazomethine ylides always proceeded stereospecifically, in full agreement with the *Woodward–Hoffmann* rules, as a conrotatory process, and it led to the *reverse* spatial arrangement of the aziridine substituents in the final cycloadducts. In contrast, the reaction of **1a** with DMAD unequivocally led to **2a** with *retention* of the relative configuration!

With the aim of investigating the general character of this change of the stereochemical outcome of this process by going from disubstituted *N*-phthalimidoaziridines to the thermally less stable three- and tetrasubstituted **1a** and **1b**, we have carried out reactions with very active dipolarophiles, *i.e.*, thioketones **4a**–**4d**, and, in the case of **1a**, also with dimethyl azodicarboxylate (**5**).

2.2. *Reactions of Aziridines* **1a** and **1b** *with Thioketones* **4a**–**4d**. All reactions of **1a** with the deeply colored thioketones **4** were carried out in the same manner as described above with DMAD, *i.e.*, by stirring a solution of the reagents in dry benzene under Ar at room temperature for several days. The progress of the reactions was followed by TLC. In addition, the intense color of the initial reaction mixtures faded or disappeared completely indicating the completion of the reaction.

The reaction of **1a** with bis(4-methoxyphenyl)methanethione (**4a**) after 6 d gave the 1,3-thiazolidine **6** (85%) as a single regio- and diastereoisomer (*Scheme 4*). The product appeared to be a heat-sensitive compound, and decomposed completely by recrystallization from MeOH or by the determination of the melting point. Suitable crystals of **6** were obtained from CH_2Cl_2/hexane, and the structure was determined by single-crystal X-ray diffraction (*Fig. 2*). It shows the conservation of the spatial arrangement of the aziridine substituents in the cycloadduct, *i.e.*, the *trans*-isomer **1a** yielded the *trans*-isomer **6**.

Scheme 4



1a **4a** **6** R = 4-$MeOC_6H_4$

The ^{1}H-NMR spectrum of **6** in (D_6)benzene displays a low-field signal at 7.21 ppm for the single H-atom of the thiazolidine ring, which serves as an indication that this H-atom is at C(2). It could be also noted that the change of the solvent from $CDCl_3$ to (D_6)benzene causes a strong high-field shift of all signals of the phthalimide H-atoms: instead of the usual 7.7–8.0 ppm, the *multiplet* of H–C(*b*) appears at 7.1–7.2 ppm, and the signal of H–C(*c*) even at 6.6–6.7 ppm. The remarkable feature of the ^{13}C-NMR spectrum of this sterically overcrowded compound (as well as of other polysubstituted 3-phthalimido-1,3-thiazolidines obtained in this work; see *Exper. Part*) is a doubling of all signals of the phthalimide C-atoms, which demonstrates the hindered rotation of this fragment about the N–N bond.

The analogous reaction of **1a** and adamantane-2-thione (**4b**) in benzene was sluggish, and, after 16 d at room temperature, 60% of **4b** were recovered (*Scheme 5*). The cycloadduct **7**, which was expected on the basis of the experiment with **4a**, was isolated in only 8% yield (calculated on consumed **4b**). The main product of this reaction was thiazolidine **8** (23%), which could be considered as the result of secondary transformations of **7** with loss of the phthalimide unit. It is remarkable that both **7** and **8** were formed as single diastereoisomers. The relative configurations of both molecules were assumed to be *trans* taking into account the structures of **2a** and **6**, which were established by X-ray crystallography. It is essential to note that the reactions of the unsymmetrical **1a** with also unsymmetrical dipolarophiles **4a** and **4b**, respectively, proceeded regioselectively affording 2-phenyl-1,3-thiazolidines exclusively.

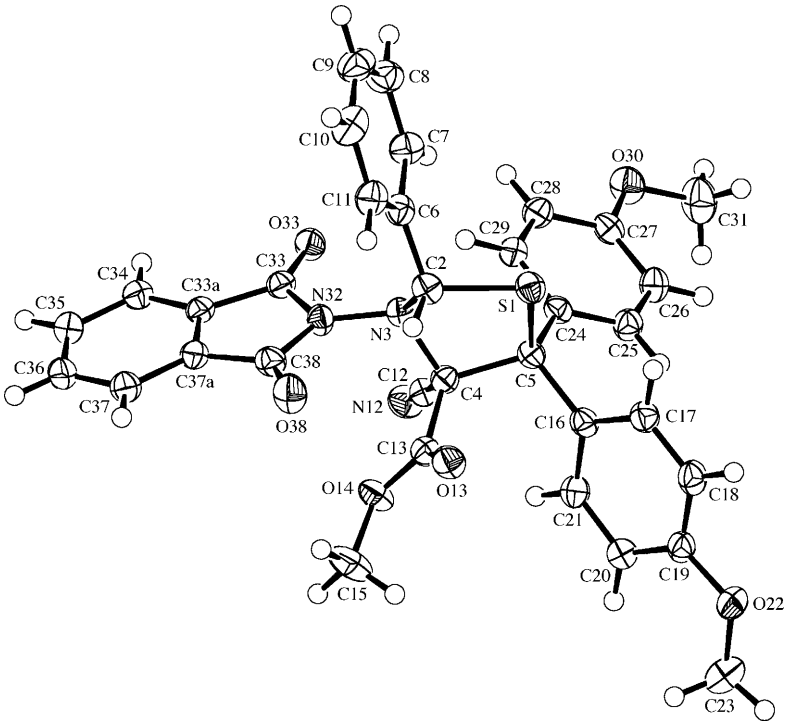
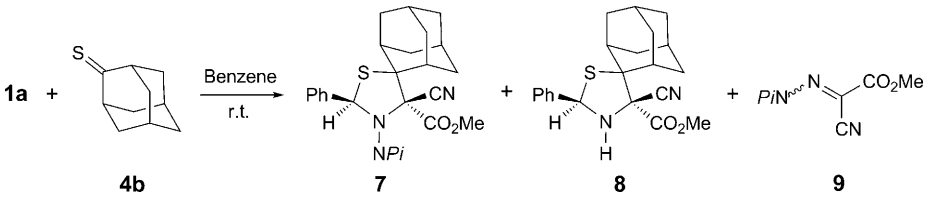


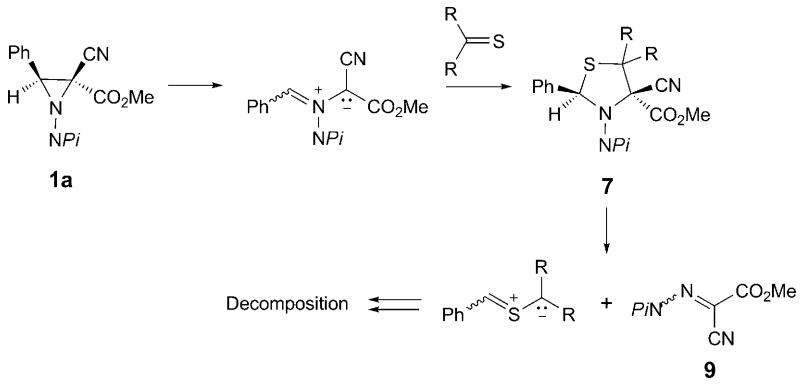
Fig. 2. *ORTEP Plot* [20] *of the molecular structure of* **6** (arbitrary numbering of atoms; 50% probability ellipsoids)

Scheme 5



Beside **7** and **8**, a mixture of phthalimide (18%) and a third product **9** (23%) was isolated. The ^{1}H-NMR spectrum of the latter displayed a *singlet* at 4.07 ppm (MeO) and a characteristic *multiplet* of the phthaloyl H-atoms at 7.85–8.10 ppm. The same product was isolated in pure form from the reaction of **1a** with dimethyl azodicarboxylate (**5**; see *Sect. 2.3*). Its ESI-MS showed a quasimolecular-ion peak at *m*/*z* 312 (100, $[M + \mathrm{Na} + \mathrm{MeOH}]^+$) that corresponds to the molecular weight of 257. Therefore, the product might be considered as being formed by loss of the benzylidene fragment from the starting aziridine **1a**. Taking into account this information as well as the IR-, and ^{1}H- and ^{13}C-NMR spectra, we assume that this product has the structure of hydrazonoacetate **9** with unknown configuration of the C=N bond. Its formation could be explained as depicted in *Scheme 6*.

Scheme 6



The formed 1,3-thiazolidine could undergo a [2 + 3] cycloreversion under the reaction conditions or during the separation of the reaction mixture, which led to **9** and a thiocarbonyl ylide. This ylide apparently decomposed further, *e.g.*, by hydrolysis, to give, in particular, benzaldehyde, whose presence in the mixture was indicated by its characteristic odor. It is worth mentioning that, after some time, the ^{1}H- and ^{13}C-NMR spectra of a solution of **9** showed a second set of signals, which perhaps belong to the second stereoisomer of this hydrazone (the ESI-MS of this mixture was identical with the previous one).

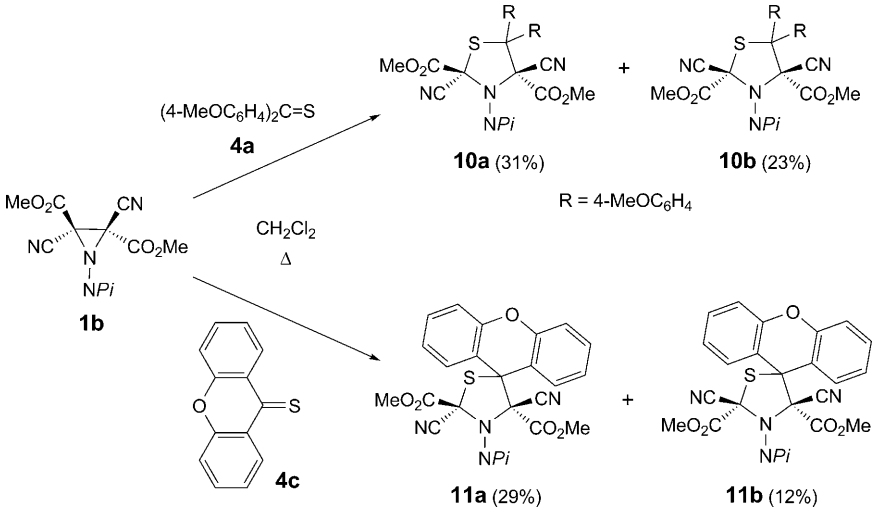
In the course of the analogous reaction of **1a** with xanthenethione (**4c**), TLC control showed the weakening of the spots of the reagents and an increase of the intensity of the spot of a new product. But, all attempts to separate the mixture after the complete conversion of the starting compounds by CC on SiO_2 failed, and only small amounts of **4c** and its hydrolysis product, *i.e.*, xanthone, were isolated. This may be the result of the instability of the corresponding 1,3-thiazolidine(s).

Under the same reaction conditions, the sterically crowded C=S bond of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**4d**; formula not shown) was inert. The generated azomethine ylide underwent the known intramolecular 1,5-electrocyclization [11b][21], instead of the 1,3-dipolar cycloaddition, and after long stirring of a mixture of **1a** and **4d** in benzene and chromatographic workup, 1,3-oxazole **3** was obtained in low yield because of its low stability on silica. In addition, phthalimide was isolated.

Furthermore, the reactions of thioketones **4a**–**4d** with aziridine **1b** were carried out for 6–7 h in boiling CH_2Cl_2 under Ar. Formation of cycloadducts was observed only in the cases of **4a** and **4c**. Both reactions gave a pair of diastereoisomeric 1,3-thiazolidines **10a**/**10b** and **11a**/**11b**, respectively (*Scheme 7*). We could separate the mixture **10a**/**10b** and obtained both isomers in pure form (31 and 23%), but from the mixture of **11a** and **11b**, which, according to the ^{1}H-NMR spectrum of the reaction mixture, were present in a *ca.* 3 : 1 ratio, only **11a** could be isolated in pure form.

The structures of **10a** and **11a** were established unequivocally by X-ray crystal-structure determinations (*Figs. 3* and *4*). In both cases, the molecule is *trans*-configured. In the case of **10a**, the ester group at C(2) is disordered, and the two conformers differ by a *ca.* 180° rotation about the C(2)–C(6) bond.

Scheme 7



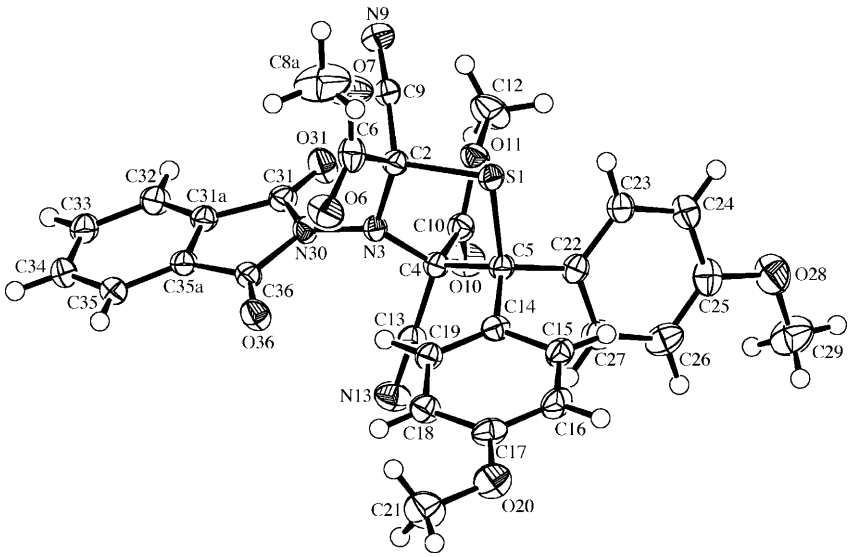


Fig. 3. *ORTEP Plot* [20] *of the molecular structure of one of the conformers of* **10a** (arbitrary numbering of atoms; 50% probability ellipsoids)

It is remarkable that, in both cases, the main product is the 'anomalous' one with the same configuration of the substituents as in the starting aziridine **1b**. It should be mentioned that the reaction of **1b** with DMAD was reported to lead to the mixture of two diastereoisomers too, but in a ratio of *ca.* 1:1 [11d].

2.3. *Reaction of Aziridine* **1a** *with Dimethyl Azodicarboxylate* (**5**). The reaction was carried out in benzene at room temperature for two weeks, and the products were

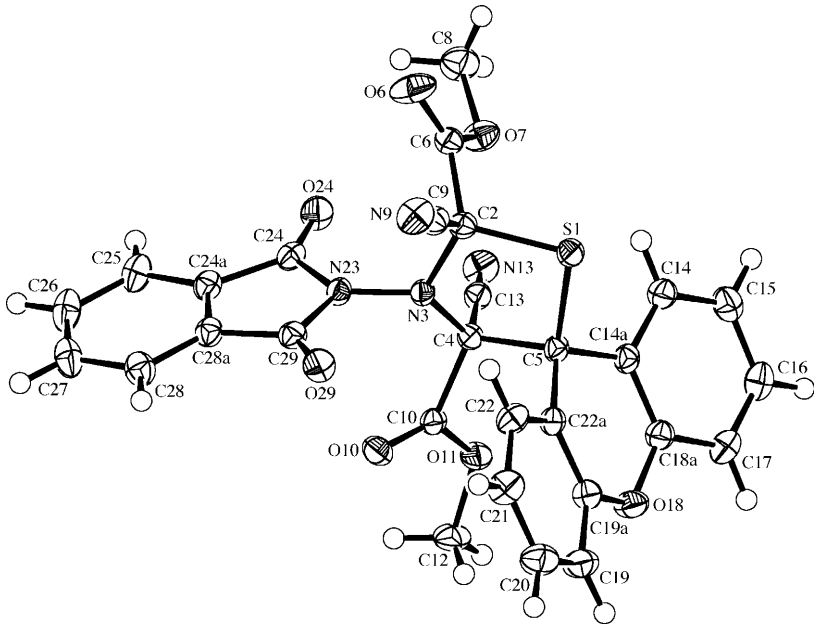
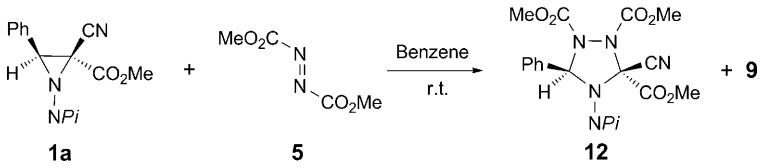


Fig. 4. *ORTEP Plot* [20] *of the molecular structure of* **11a** (arbitrary numbering of atoms; 50% probability ellipsoids)

separated by column chromatography on SiO_2. In addition to phthalimide (41%), the expected trimethyl 3-cyano-5-phenyl-4-phthalimido-1,2,4-triazolidine-1,2,3-tricarboxylate (**12**; 12%) and **9** (4%) were isolated (*Scheme 8*). The identity of **9** with the product obtained from the reaction of **1a** and **4b** was established by the comparison of the ^{1}H- and ^{13}C-NMR spectra. The configuration of **12** was not determined, but, in analogy to products **2a** and **6** of the other reactions with **1a**, we propose the *trans* configuration for **12** too.

Scheme 8



2.4. *Mechanism of the Reactions.* Because of the low thermal stability of the starting aziridines **1a** and **1b**, generally low yields of cycloadducts, and an appreciable sensitivity of the processes under consideration to steric factors, the mechanisms can be discussed only with great care.

First, it was established that the reactions of the trisubstituted aziridine **1a** with DMAD, thioketones **4a** and **4b**, and dimethyl azodicarboxylate (**5**) occur in a

stereoselective way, affording only one of two possible diastereoisomers. Moreover, in two cases it has been shown by X-ray crystallography that the reaction proceeds with the conservation of the spatial arrangement of the aziridine substituents in the final cycloadducts **2a** and **4**. The same stereoselectivity, but to a far less extent, is observed for the reactions with the tetrasubstituted aziridine **1b**. In addition, it can be noted that the cycloaddition of the 'asymmetric' aziridine **1a** onto the C=S bond of thioketones occurs regioselectively, *i.e.*, the S-atom is connected with the less substituted aziridine C-atom.

These observations can be explained in different ways. Provided that the opening of aziridines **1** to the corresponding azomethine ylides and the subsequent cycloaddition are concerted, the rate of the generation of the ylides must be significantly higher than the rate of their cycloaddition. In this case, the initially generated *W*-type (*trans*,*trans*) dipoles (or the less probable *U*-type (*cis*,*cis*) dipoles) have enough time to isomerize completely (or partially, if the cycloaddition rates for the stereoisomers are different) into the more stable *S*-type (*trans*,*cis*) dipoles, which are usually more active in the subsequent cycloadditions [3]. This mechanism is supported by the observation that the pure *trans*-aziridine **1b** in solution, in the absence of a dipolarophile, is slowly transformed to a mixture of *cis*- and *trans*-stereoisomers already at room temperature, which can be explained as the result of the stereoisomerization of the intermediate ylide [11d].

On the other hand, one can assume that the cycloaddition of the tri- and tetrasubstituted azomethine ylides onto dipolarophiles is not concerted, but proceeds as a stepwise nucleophilic addition. In this case, the stereoselectivity of the whole transformation could be determined by the relative stability of the products, which is in agreement with our results too.

In principle, it is necessary to take into account a third possibility, namely that the S-atom of the C=S bond plays the role of an active nucleophilic centre. *A priori*, one cannot exclude that the reaction of thioketones with **1a** and **1b** could start with the attack of the S-atom onto one of the C-atoms of the electron-poor aziridine ring, leading to the opening of the three-membered ring and subsequent ring closure of the five-membered chain. Again, the stereoselectivity of the product formation should mainly be determined by steric factors. But, in this case, the opening of the aziridine should proceed by the cleavage of a C–N bond, and the following ring closure would give 1,3-thiazolidines with the thioketone-derived substituents at C(2), in contrast to the outcome of our experiments.

We thank the analytical sections of our institutes for spectra and analyses, and *F. Hoffmann-La Roche AG*, Basel, for financial support. *A. V. U.* is very grateful for the warm hospitality he experienced at the University of Zürich.

Experimental Part

1. *General.* All reagents and solvents were of reagent-grade and were used without further purification unless otherwise specified. Column chromatography (CC): flash chromatography, *Merck* silica gel *60* (particle size 0.040–0.063 mm) packed in glass columns; for each chromatography, the eluting solvent was optimized by TLC. Anal. TLC: *Macherey-Nagel POLYGRAM SIL G/UV 254* or *ALUGRAM SIL G/UV 254*. M.p.: *Büchi B-540* apparatus; uncorrected. IR Spectra: *Perkin-Elmer-1600* (FT-IR) spectrophotometer; in KBr; absorptions in cm^{-1}. ^1H- (300 or 600 MHz) and ^1H-decoupled

^{13}C-NMR (75.4 or 150.8 MHz) spectra: *Bruker DPX-300*, *ARX-300* or *AMX-600* instruments; in $CDCl_3$ or (D_6)benzene; δ in ppm (TMS = 0 ppm), coupling constants J in Hz. ESI-MS: *Finnigan TSQ-700* instrument. Elemental analyses were performed at the Institute of Organic Chemistry, University of Zürich.

Bis(4-methoxyphenyl)methanethione (**4a**) [22], *adamantane-2-thione* (**4b**) [23], *9*H-*xanthene-9-thione* (**4c**) [24], and *2,2,4,4-tetramethyl-3-thioxocyclobutanone* (**4d**) [25] were prepared by thionation of the corresponding ketones according to literature procedures. *Dimethyl acetylenedicarboxylate* (DMAD) and *dimethyl azodicarboxylate* (**5**) were commercially available (*Fluka*).

2. *Preparation of 1-Phthalimidoaziridines* **1a** *and* **1b**. 2.1. *Methyl (*E*)-2-Cyano-3-phenylprop-2-enoate* was prepared from PhCHO and $NCCH_2COOMe$ on basic Al_2O_3 according to [26]. Yield: 80%. M.p. 91–92° ([26]: 89–90°). ^{1}H-NMR ($CDCl_3$): 3.92 (*s*, MeO); 7.45–7.60 (*m*, 2 H_m, 1 H_p); 7.90–8.05 (*m*, 2 H_o); 8.25 (*s*, CH). Two cross-peaks in the 2D-NOESY spectrum corresponded to the NOE between the vinyl CH and H_o of Ph and the MeO group, resp., establishing the (*E*) configuration of this compound.

2.2. *Methyl* trans-*2-Cyano-3-phenyl-1-phthalimidoaziridine-2-carboxylate* (**1a**). *N*-Aminophthalimide (486 mg, 3 mmol) and $Pb(OAc)_4$ (1.33 g, 3 mmol) were added portionwise (10–15 mg) within 40 min to a stirred suspension of dry K_2CO_3 (1.3 g, 9.4 mmol) in a soln. of methyl (*E*)-2-cyano-3-phenylprop-2-enoate (561 mg, 3 mmol) in dry CH_2Cl_2 (40 ml) at 0°. After the completion of the addition, the stirring was continued for 30 min. The mixture was filtered through a short plug of SiO_2, which was then washed with CH_2Cl_2, and the combined filtrates were concentrated *in vacuo*. The oily residue was mixed with Et_2O (5 ml) and left overnight at −4°. White crystals of **1a** were separated by filtration. Yield: 720 mg (69%). M.p. 165–166° ([17]: 165°). ^{1}H-NMR ($CDCl_3$): 3.87 (*s*, MeO); 4.95 (*s*, CH); 7.40–7.60 (*m*, 5 H, Ph); 7.70–7.90 (*m*, 4 H, *Pi*N).

2.3. *Dimethyl* trans-*2,3-Dicyano-1-phthalimidoaziridine-2,3-dicarboxylate* (**1b**). As described in *2.2*, *N*-aminophthalimide (486 mg, 3 mmol), $Pb(OAc)_4$ (1.33 g, 3 mmol), K_2CO_3 (1.3 g, 9.4 mmol), and dimethyl (2*E*)-2,3-dicyanobut-2-enedioate [27] (582 mg, 3 mmol) gave 365 mg (34%) of **1b**. M.p. 114–116° ([18]: 130°). ^{1}H-NMR (C_6D_6): 3.18 (*s*, 2 MeO); 6.55–6.65 (*m*, 2 H, *Pi*N); 7.00–7.10 (*m*, 2 H, *Pi*N). ^{1}H-NMR ($CDCl_3$): 4.02, 4.10 (2*s*, 2 MeO); 7.80–8.00 (*m*, 4 H, *Pi*N).

3. *Reactions of* **1a** *with Dipolarophiles*. 3.1. *Reaction with DMAD. Trimethyl* trans-*2-Cyano-2,5-dihydro-5-phenyl-1-phthalimido-1*H-*pyrrole-2,3,4-tricarboxylate* (**2a**) was obtained from **1a** and DMAD according to [11b] (1/3 scale) in dry benzene under Ar within 7 d at r.t. The solvent was evaporated *in vacuo*, and the residue was separated by CC (hexane/AcOEt, gradient). Yield: 60%. M.p. 202–203° ([11b]: 208°). ^{1}H-NMR ($CDCl_3$): 3.64, 3.84, 3.86 (3*s*, 3 MeO); 6.24 (*s*, H−C(5)); 7.27–7.35 (*m*, 2 H_m, 1 H_p); 7.40–7.50 (*m*, 2 H_o); 7.70–7.85 (*m*, 4 H, *Pi*N). ^{13}C-NMR ($CDCl_3$): 52.83, 53.14, 54.66 (3 MeO); 70.18, 71.74 (C(2), C(5)); 114.23 (CN); 123–124 (br., 2 C(*b*), *Pi*N); 126.37 (C(3)); 128.51, 128.79 (2 C_o, 2 C_m); 129.82 (C_p); 129–130 (br., 2 C(*a*), *Pi*N); 132.74 (C_{ipso}); 134.90 (br., 2 C(*c*), *Pi*N); 148.40 (C(4)); 159.70, 162.31, 163.13 (3 CO). The signals of the phthalimide CO could not be detected because of the strong broadening.

Suitable crystals for the X-ray crystal-structure determination were obtained from CH_2Cl_2/hexane by slow evaporation of the solvent.

3.2. *Reactions with Thioketones. General Procedure.* A soln. of **1a** (347 mg, 1 mmol) and the thioketone (1 mmol) in dry benzene (10 ml) was stirred at r.t. under Ar, until **1a** disappeared in the mixture (TLC control). The solvent was evaporated *in vacuo*, the residue was treated with hexane/AcOEt 1:1 (10 ml), and the precipitated phthalimide was filtered off. The filtrate was evaporated *in vacuo*, and the residue was separated by CC on SiO_2 (45 g) with hexane/AcOEt (gradient elution).

3.2.1. *Reaction of* **1a** *with* **4a**. *Methyl* trans-*4-Cyano-5,5-bis(4-methoxyphenyl)-2-phenyl-3-phthalimido-1,3-thiazolidine-4-carboxylate* (**6**). After 6 d at r.t., the mixture of **1a** and **4a** was diluted with AcOEt (40 ml) and filtered through a short plug of SiO_2, which was washed with AcOEt (50 ml). The solvent was evaporated *in vacuo*, and the residue was diluted with Et_2O (3 ml). The precipitate formed was filtered and dried. Yield: 513 mg (85%) of **6**. M.p. 149–150° (dec.). IR (KBr): 3067, 3036, 3002 ($C_{arom.}$−H), 2953, 2935, 2836 (OC−H), 1793, 1758 (NC=O), 1737 (OC=O), 1607, 1580, 1509, 1457, 1350, 1297, 1254, 1206, 1186. ^{1}H-NMR (C_6D_6): 3.28 (*s*, 2 MeO); 3.38 (*s*, MeO); 6.59–6.69 (*m*, 2 H−C(*c*), *Pi*N); 6.70, 7.06 (*AA′* of *AA′BB′*, J = 8.7, 9.3, 4 arom. H_m); 6.79 (*t*, J = 7.5, 1 H_p, Ph); 6.91 (*t*, J = 7.5, 2 H_m, Ph); 7.10–7.20 (*m*, 2 H−C(*b*), *Pi*N); 7.21 (*s*, H−C(5)); 7.77 (*d*, J = 7.2, 2 H_o, Ph); 7.93, 8.48 (*BB′* of

AA′BB′, $J = 8.7$, 9.0, 4 arom. H_o). ^{13}C-NMR (C_6D_6): 53.21, 54.75, 54.84 (3 MeO); 66.13, 69.03, 79.97 (C(2), C(3), C(5)); 113.83, 114.05 (4 arom. C_m); 115.49 (CN); 123.17, 123.99 (2 C(*b*), *Pi*N); 128.90 (2 C_m, Ph); 129.20, 129.25 (2 C(*a*), *Pi*N); 130.05 (C_p, Ph); 130.44 (2 C_o, Ph); 131.12 (4 arom. C_o); 132.18, 134.82 (2 arom. C_{ipso}); 134.26, 134.59 (2 C(*c*), *Pi*N); 140.72 (C_{ipso}, Ph); 159.53, 159.85 (2 arom. C_p); 163.57, 165.31, 167.56 (5 CO). ESI-MS: 628 (100, $[M + Na]^+$), 370 (36), 223 (8), 170 (5). Anal. calc. for $C_{34}H_{27}N_3O_6S$ (605.66): C 67.42, H 4.49, N 6.94, S 5.29; found: C 67.16, H 4.44, N 6.86, S 5.26.

Suitable crystals for the X-ray crystal-structure determination were obtained from CH_2Cl_2/hexane by slow evaporation of the solvent.

3.2.2. *Reaction of* **1a** *with Adamantane-2-thione* (**4b**). Reaction time 16 d. The separation of the mixture provided 100 mg (60%) of **4b**, 110 mg of a mixture (molar ratio 2.5 : 1) of phthalimide (calculated: 65 mg, 44%) and *methyl 2-cyano-2-(phthaloylhydrazono)acetate* (**9**; calc.: 45 mg, 18%), 85 mg (23%) of *methyl* trans-*4-cyano-2-phenylspiro[1,3-thiazolidine-5,2′-tricyclo[3.3.1.1^{3,7}]decane]-4-carboxylate* (**8**), and 40 mg (8%) of *methyl* trans-*4-cyano-2-phenyl-3-phthalimidospiro[1,3-thiazolidine-5,2′-tricyclo[3.3.1.1^{3,7}]decane]-4-carboxylate* (**7**).

Data of **7**. M.p. 201–202°. IR (KBr): 3063, 3030, 3010 (ν($C_{arom.}$–H)), 2914, 2861 (C–H), 1795 (NC=O), 1738 (OC=O), 1608, 1456, 1353, 1211. ^{1}H-NMR ($CDCl_3$): 1.65–2.35 (*m*, 11 H, Ad); 2.69 (*d*, $J = 12.3$, 1 H, Ad); 3.06 (*s*, 1 H, Ad); 3.39 (*d*, $J = 12.3$, 2 H, Ad); 4.00 (*s*, MeO); 6.38 (*s*, H–C(2)); 7.10–7.40 (*m*, 2 H_m, 1 H_p); 7.40–7.60 (*m*, 2 H_o); 7.60–7.90 (*m*, 4 H, *Pi*N). ^{13}C-NMR ($CDCl_3$): 26.04, 26.61, 34.31, 34.63, 36.19, 36.76, 37.07, 38.37 (Ad); 53.87 (MeO); 65.60, 67.39, 75.32 (C(2), C(4), C(5)); 116.55 (CN); 123.51, 124.24 (2 C(*b*), *Pi*N); 128.48, 129.47 (5 arom. C); 129.20, 129.29 (2 C(*a*), *Pi*N); 134.62, 134.84 (2 C(*c*), *Pi*N); 135.98 (C_{ipso}); 164.56, 164.76, 167.52 (3 CO). ESI-MS: 536 (100, $[M + Na]^+$). Anal. calc. for $C_{29}H_{27}N_3O_4S$ (513.62): C 67.82, H 5.30, N 8.18, S 6.24; found: C 67.12, H 5.17, N 7.91, S 6.13.

Data of **8**. M.p. 142–143°. IR (KBr): 3319 (ν(NH)), 3064, 3030, 2998 ($C_{arom.}$–H)), 2925, 2906, 2869, 2855 (C–H), 2230 (C≡N), 1743 (C=O), 1624, 1494, 1475, 1457, 1441, 1262. ^{1}H-NMR ($CDCl_3$): 1.45–2.40 (*m*, 13 H, Ad); 2.68 (*s*, 1 H, Ad); 3.70 (br. *s*, NH); 3.91 (*s*, MeO); 5.67 (*s*, H–C(2)); 7.30–7.45 (*m*, 2 H_m, 1 H_p); 7.45–7.55 (*m*, 2 H_o). ^{13}C-NMR ($CDCl_3$): 25.90, 26.58, 33.58, 34.39, 36.41, 37.42, 38.10, 39.43, 41.08 (Ad); 54.40 (MeO); 66.85, 75.05, 79.55 (C(2), C(4), C(5)); 115.52 (CN); 127.71, 128.94 (C_o, C_m); 129.14 (C_p); 137.37 (C_{ipso}); 167.13 (CO). ESI-MS: 391 (100, $[M + Na]^+$), 364 (5), 225 (42).

Data of **9** (mixture with phthalimide). ^{1}H-NMR ($CDCl_3$): 4.07 (*s*, MeO); 7.85–8.10 (*m*, 4 H, *Pi*N).

3.2.3. *Reaction of* **1a** *with 9*H*-Xanthene-9-thione* (**4c**). The reaction was followed by TLC. After 7 d, starting material **1a** (R_f 0.3, hexane/AcOEt 2 : 1 (*v*/*v*)) had almost disappeared, and a new product with R_f 0.35 has formed. After CC on SiO_2, only **4c** (135 mg, 64%) and traces of xanthone were obtained.

3.2.4. *Reaction of* **1a** *with 2,2,4,4-Tetramethyl-3-thioxocyclobutanone* (**4d**). After 7 d, CC on SiO_2 gave starting material **4d** (64 mg, 41%), phthalimide (75 mg, 51%), and *5-methoxy-2-phenyl-1,3-oxazole-4-carbonitrile* (**3**). Yield: 45 mg (23%). M.p. 106–107° ([11d]: 106°). ^{1}H-NMR ($CDCl_3$): 4.30 (*s*, MeO); 7.40–7.55 (*m*, 3 arom. H); 7.80–7.95 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 60.03 (MeO); 88.86 (C(4)); 112.89 (CN); 125.66 (C_{ipso}); 125.66, 128.95 (C_o, C_m); 131.05 (C_p); 152.26 (C(2)); 164.49 (C(5)).

3.3. *Reaction of* **1a** *with* **5**. Reaction time 2 weeks. After CC, phthalimide (60 mg, 41%), *trimethyl 3-cyano-5-phenyl-4-phthalimido-1,2,4-triazolidine-1,2,3-tricarboxylate* (**12**; 60 mg, 12%), and **9** (10 mg, 4%) were isolated.

Methyl 2-Cyano-2-(phthaloylhydrazono)acetate (**9**). M.p. 201–202°. IR (KBr): 3087 ($C_{arom.}$–H), 2963 (OC–H), 1795, 1765 (NC=O), 1714 (OC=O), 1600, 1570, 1466, 1441, 1363, 1344, 1251. ^{1}H-NMR ($CDCl_3$): 4.07 (*s*, MeO); 7.85–8.10 (*m*, 4 H, *Pi*N). ^{13}C-NMR ($CDCl_3$, 150.8 MHz): 54.82 (MeO); 109.78 (CN); 125.46 (2 C(*b*), *Pi*N); 130.33 (2 C(*a*), *Pi*N); 133.56 (2 C(*c*), *Pi*N); 136.11 (C=N); 158.70 (COO); 161.25 (CON). ESI-MS: 312 (100, $[M + Na + MeOH]^+$), 285 (19).

Data of **12**. M.p. 209–210°. IR (KBr): 3066, 3009 ($C_{arom.}$–H), 2985, 2958 (C–H), 1799 (NC=O), 1750 (OC=O), 1610, 1443, 1371, 1332, 1284, 1213. ^{1}H-NMR ($CDCl_3$, 600 MHz): 3.79, 3.90, 3.94 (3*s*, 3 MeO); 6.55 (*s*, H–C(5)); 7.30–7.40 (*m*, 2 H_m, 1 H_p); 7.69–7.75 (*m*, 2 H_o); 7.75–7.88 (*m*, 4 H, *Pi*N). ^{13}C-NMR ($CDCl_3$, 150.8 MHz): 54.54, 54.58, 55.09 (3 MeO); 65.97 (C(3)); 80.13 (br. *s*, C(5)); 111.33 (br. *s*, CN); 124.32 (2 C(*b*), *Pi*N); 127.72, 128.81 (2 C_o, 2 C_m); 129.04 (C_p); 129.86 (2 C(*a*), *Pi*N); 133.78 (br. *s*, C_{ipso}); 135.17 (2 C(*c*), *Pi*N); 161.20 (COO); 165.07 (br. *s*, CON). ESI-MS: 548 (7, $[M + Na + MeOH]^+$), 532 (17, $[M + K]^+$), 516 (100, $[M + Na]^+$), 432 (10), 259 (14).

4. *Reactions of* **1b** *with Thioketones. General Procedure.* A soln. of **1b** (354 mg, 1 mmol) and the thioketone (1 mmol) in dry CH_2Cl_2 (5 ml) was heated under reflux with stirring under Ar, until **1b** disappeared (TLC control). The solvent was evaporated *in vacuo*, and the residue was separated by CC on SiO_2 (45 g) with hexane/AcOEt (gradient elution).

4.1. *Reaction of* **1b** *with* **4a**. After 6 h under reflux, the mixture was left overnight at r.t. After CC on SiO_2, **4a** (80 mg, 31%) and **1b** (30 mg, 9%) were isolated as well as *dimethyl* trans-*2,4-dicyano-5,5-bis(4-methoxyphenyl)-3-phthalimido-1,3-thiazolidine-2,4-dicarboxylate* (**10a**; 187 mg, 31%) and *dimethyl* cis-*2,4-dicyano-5,5-bis(4-methoxyphenyl)-3-phthalimido-1,3-thiazolidine-2,4-dicarboxylate* (**10b**; 143 mg, 23%). Taking into account the recovered **4a**, the total yield of the two adducts is 78%.

Data of **10a**. M.p. 222–223° (dec). IR (KBr): 3079, 3008 ($C_{arom.}$–H), 2956, 2910, 2840 (C–H), 1802, 1775 (NC=O), 1750 (OC=O), 1607, 1511, 1466, 1434, 1351, 1299, 1258, 1218, 1188. ^{1}H-NMR (C_6D_6): 3.20, 3.22, 3.23, 3.63 (4*s*, 4 MeO); 6.60, 6.90 (*AA′* of *AA′BB′*, J = 9.0, 9.3, 4 H_m); 6.71, 6.77 (2*t*, J = 7.2, 2 H–C(*c*), *Pi*N); 7.15 (1 H–C(*b*), *Pi*N, overlapped by solvent signal); 7.36 (*d*, J = 6.6, 1 H–C(*b*), *Pi*N); 7.55, 8.13 (*BB′* of *AA′BB′*, J = 9.0, 9.3, 4 H_o). ^{13}C-NMR (C_6D_6): 53.08, 54.37, 54.76, 54.88 (4 MeO); 67.35, 67.53, 81.25 (C(2), C(4), C(5)); 113.82, 114.01 (CN, 4 C_m); 115.38 (CN); 124.03, 124.34 (2 C(*b*), *Pi*N); 128.84, 128.90, 129.12, 137.44 (2 C(*a*), *Pi*N, 2 C_{ipso}); 130.95, 131.08 (4 C_o); 134.87, 134.93 (2 C(*c*), *Pi*N); 159.99, 160.37 (2 C_p); 163.50, 163.85, 165.01, 165.40 (2 COO, 2 CON). ESI-MS: 667 (17, $[M+Na+MeOH]^+$), 635 (100, $[M+Na]^+$), 377 (26), 258 (7). Anal. calc. for $C_{31}H_{24}N_4O_8S$ (612.61): C 60.78, H 3.95, N 9.15, S 5.23; found: C 60.71, H 4.06, N 8.94, S 5.17.

Suitable crystals for the X-ray crystal-structure determination were obtained from CH_2Cl_2/hexane/benzene by slow evaporation of the solvent.

Data of **10b**. M.p. 208–209° (dec). IR (KBr): 3070, 3038, 3000 ($C_{arom.}$–H), 2956, 2908, 2840 (C–H), 1800 (NC=O), 1749 (OC=O), 1607, 1580, 1511, 1467, 1434, 1359, 1300, 1259, 1217, 1187. ^{1}H-NMR (C_6D_6): 3.20, 3.21, 3.23, 3.25 (4*s*, 4 MeO); 6.54, 7.01 (*AA′* of *AA′BB′*, J = 9.0, 4 H_m); 6.70–6.85 (*m*, 2 H–C(*c*), *Pi*N); 7.25–7.40 (*m*, 2 H–C(*b*), *Pi*N); 7.53, 8.30 (*BB′* of *AA′BB′*, J = 9.0, 4 H_o). ^{13}C-NMR (C_6D_6): 53.22, 54.24, 54.78, 54.85 (4 MeO); 66.68, 68.19, 78.97 (C(2), C(4), C(5)); 113.71, 115.24 (2 CN); 113.90, 114.28 (4 C_m); 123.66, 124.52 (2 C(*b*), *Pi*N); 128.86, 136.10 (2 C_{ipso}); 129.16, 129.37 (2 C(*a*), *Pi*N); 130.81 (4 C_o); 134.72, 134.95 (2 C(*c*), *Pi*N); 160.27, 163.22, 164.57, 166.65 (2 COO, 2 CON). ESI-MS: 635 (100, $[M+Na]^+$), 377 (29), 258 (7). Anal. calc. for $C_{31}H_{24}N_4O_8S$ (612.61): C 60.78, H 3.95, N 9.15, S 5.23; found: C 60.89, H 4.11, N 8.91, S 5.32.

4.2. *Reaction of* **1b** *with* **4c**. After 7 h under reflux, the mixture was left at r.t. overnight. After CC on SiO_2, **4c** (95 mg, 45%), *dimethyl* trans-*2,4-dicyano-3-phthalimidospiro[1,3-thiazolidine-5,9′-xanthene]-2,4-dicarboxylate* (**11a**; 50 mg, 9%), and a mixture (*ca.* 2:1) of **11a** and *dimethyl* cis-*2,4-dicyano-3-phthalimidospiro[1,3-thiazolidine-5,9′-xanthene]-2,4-dicarboxylate* (**11b**; 180 mg, 32%) were isolated. Taking into account the recovered **4c**, the total yield of the two adducts is *ca.* 75%.

Data of **11a**. M.p. 195–196° (dec). IR (KBr): 3038, 3072 ($C_{arom.}$–H), 2954, 2927, 2847 (C–H), 1803, 1772 (NC=O), 1749 (OC=O), 1598, 1475, 1445, 1361, 1315, 1286, 1246, 1220. ^{1}H-NMR ($CDCl_3$): 3.41, 4.10 (2*s*, 2 MeO); 7.10–7.26 (*m*, H–C(4′,5′)); 7.36–7.53 (*m*, H–C(2′,3′,6′,7′)); 7.70–8.00 (*m*, H–(1′,8′), 2 H–C(*c*), *Pi*N); 8.55–8.35 (*m*, 1 H–C(*b*), *Pi*N); 8.60 (*d*, J = 7.8, 1 H–C(*b*), *Pi*N). ^{13}C-NMR ($CDCl_3$): 54.12, 55.40 (2 MeO); 112.99, 113.96 (2 CN); 115.96, 116.53 (C(4′), C(5′)); 116.93, 117.91 (C(8a′), C(9a′)); 123.52, 124.25 (C(2′), C(7′)); 124.73 (br., 2 C(*b*), *Pi*N); 131.81, 132.51, 132.85 (C(1′), C(3′), C(6′), C(8′)); 135.20 (br., 2 C(*c*), *Pi*N); 150.80, 152.87 (C(4a′), C(10a′)); 161.04, 163.61 (2 COO). The signals of the phthalimido CO(N) and C(*a*) atoms could not be detected because of a strong broadening. ESI-MS: 589 (100, $[M+Na]^+$), 540(8), 393(16), 377(48), 355(8), 327(8), 213(16).

Suitable crystals for the X-ray crystal-structure determination were obtained from CH_2Cl_2/hexane by slow evaporation of the solvent.

Data of **11b** (in a mixture with **11a**). ^{1}H-NMR ($CDCl_3$): 3.40, 3.97 (2*s*, 2 MeO); 7.15–7.32, 7.40–7.56 (2*m*, H–C(2′–7′)); 7.70–7.95 (*m*, H–C(1′,8′), 2 H–C(*c*), *Pi*N); 8.25, 8.53 (2*d*, J = 9.6, 9.3, 2 H–C(*b*), *Pi*N). ^{13}C-NMR ($CDCl_3$): 54.14, 55.32 (2 MeO); 111.75, 114.37 (2 CN); 116.35, 116.79, 118.51 (C(4′), C(5′), C(8a′), C(9a′)); 123.67, 124.10 (C(2′), C(7′)); 124.25, 124.67 (2 C(*b*), *Pi*N); 131.30, 131.58, 131.73, 132.50 (C(2′), C(3′), C(6′), C(7′)); 135.21 (2 C(*c*), *Pi*N); 152.10, 152.48 (C(4a′), C(10a′)); 162.46, 162.75 (2 COO). The signals of the phthalimido CO(N) and C(*a*) atoms could not be detected because of a strong broadening. Probably, some signals overlapped with the signals of the main stereoisomer.

Table. *Crystallographic Data for Compounds* **2a**, **6**, **10a**, *and* **11a**

	2a	**6**	**10a**	**11a**
Crystallized from	CH_2Cl_2/hexane	CH_2Cl_2/hexane	CH_2Cl_2/hexane/benzene	CH_2Cl_2/hexane
Empirical formula	$C_{25}H_{19}N_3O_8$	$C_{34}H_{27}N_3O_6S$	$C_{31}H_{24}N_4O_8S \cdot CH_2Cl_2$	$C_{29}H_{18}N_4O_7S$
Formula weight	489.44	605.66	697.54	566.54
Crystal color, habit	colorless, prism	colorless, prism	colorless, prism	colorless, tablet
Crystal dimensions [mm]	$0.12 \times 0.20 \times 0.25$	$0.12 \times 0.20 \times 0.22$	$0.20 \times 0.25 \times 0.30$	$0.08 \times 0.20 \times 0.32$
Temp. [K]	160(1)	160(1)	160(1)	160(1)
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	2	4	2	2
Reflections for cell determination	6595	43412	57549	26942
2θ Range for cell determination [°]	4–60	4–55	4–55	4–55
Unit cell parameters:				
a [Å]	9.0440(5)	12.0555(2)	9.4698(2)	10.3444(2)
b [Å]	10.7822(6)	15.4406(4)	10.4545(2)	11.2660(3)
c [Å]	12.9930(5)	15.7613(4)	17.2477(3)	12.8331(3)
α [°]	90.033(3)	90	106.768(1)	97.802(1)
β [°]	95.431(3)	92.980(2)	90.070(1)	113.232(1)
γ [°]	111.387(2)	90	104.585(1)	107.099(2)
V [Å^3]	1173.6(1)	2929.9(1)	1577.23(5)	1258.45(6)
D_x [g cm^{-3}]	1.385	1.373	1.469	1.495
μ(MoK_α) [mm^{-1}]	0.105	0.163	0.331	0.188
Scan type	ϕ and ω	ϕ and ω	ϕ and ω	ϕ and ω
$2\theta_{(max)}$ [°]	60	55	55	55
Transmission factors (min; max)	–	0.910; 0.980	0.784; 0.977	0.909; 0.986
Total reflections measured	29572	62124	37891	29228
Symmetry-independent reflections	6817	6722	7211	5756
Reflections with $I > 2\sigma(I)$	3941	4501	5441	4910
Reflections used in refinement	6812	6720	7208	5753
Parameters refined; restraints	328; 0	401; 0	468; 34	372; 0
Final $R(F)$ ($I > 2\sigma(I)$ reflections)	0.0592	0.0487	0.0470	0.0398
$wR(F^2)$ (all data)	0.1656	0.1225	0.1278	0.1031
Weighting parameters (a; b)[a]	0.0796; 0.021	0.0568; 0.7841	0.0610; 0.7728	0.0469; 0.6911
Goodness-of-fit	1.035	1.039	1.038	1.028
Secondary extinction coefficient	–	0.0026(6)	0.006(2)	–
Final Δ_{max}/σ	0.010	0.001	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.34; −0.35	0.26; −0.36	0.52; −0.48	0.30; −0.33

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

Elemental analysis for the mixture of **11a** and **11b** (*ca.* 2:1). Anal. calc. for $C_{29}H_{18}N_4O_7S$ (566.54): C 61.48, H 3.20, N 9.89, S 5.66; found: C 61.30, H 3.47, N 9.62, S 5.55.

5. *X-Ray Crystal-Structure Determination of* **2a**, **6**, **10a**, *and* **11a** (*Table* and *Figs. 1–4*[2]). All measurements were performed on a *Nonius KappaCCD* diffractometer [28] 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. 1–4*. Data reduction was performed with *HKL Denzo* and *Scalepack* [29]. The intensities were corrected for *Lorentz* and polarization effects, and, in the cases of **6**, **10a**, and **11a**, an absorption correction based on the multi-scan method [30] was applied. Equivalent reflections were merged. The structures were solved by direct methods using SIR92 [31], which revealed the positions of all non-H-atoms. In the case of **10a**, the asymmetric unit contains one molecule of **10a** plus one molecule of CH_2Cl_2. The CH_2Cl_2 molecule is disordered. Two sets of overlapping positions were defined for the atoms of CH_2Cl_2, and the site occupation factor of the major position refined to 0.509(8). One of the ester groups in **10a** is disordered through a *ca.* 180° rotation of the parent C–C bond. This manifests itself in two positions being detected for the terminal Me group. These two positions were included in the model, and the site occupation factor of the major position refined to 0.510(6). Similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered atoms. Neighboring atoms within and between each conformation of the disordered CH_2Cl_2 molecule were restrained to have similar atomic displacement parameters. The non-H-atoms were refined anisotropically. All of the H-atoms in all of the structures 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 Me groups). 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 in the cases of **6**, **10a**, and **11a**. In the cases of **2a**, **6**, **10a**, and **11a**, five, two, three, and three reflections, resp., whose intensities were considered to be extreme outliers, were omitted from the final refinement. Neutral atom scattering factors for non-H-atoms were taken from [32a], and the scattering factors for H-atoms were taken from [33]. Anomalous dispersion effects were included in F_c [34]; the values for f' and f'' were those of [32b]. The values of the mass attenuation coefficients were those of [32c]. All calculations were performed using the SHELXL97 [35] program.

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