

Reactions of Acid Chlorides/Ketenes with 2-Substituted 4,5-Dihydro-4,4-dimethyl-1,3-thiazoles: Formation of Penam Derivatives

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Addition reactions of acid chlorides with various 2-substituted 4,5-dihydro-4,4-dimethyl-5-(methylsulfanyl)-1,3-thiazoles under basic conditions were studied. Two kinds of products were obtained from these additions, β -lactams and non- β -lactam adducts. When the reaction was carried out with 4,5-dihydro-1,3-thiazoles with a Ph substituent at C(2), the reaction proceeded *via* formal [2 + 2] cycloaddition and led to the corresponding β -lactam. On the other hand, acid chlorides and 4,5-dihydro-1,3-thiazoles bearing an α -H-atom at the C(2)-substituent underwent C(α)- and/or N-addition reactions and furnished non- β -lactam adducts, *i.e.*, C(α)- and/or N-acylated 1,3-thiazolidines. The attempted transformations of sulfonyl esters of *exo*-6-hydroxy penams to *endo*-6-azido penams failed, although they were successful with mono- β -lactams under the same conditions.

1. Introduction. – A convenient synthesis of 4,4-disubstituted 1,3-thiazole-5(4*H*)-thiones **1**, the less well-known disulfur analogs of 1,3-oxazol-5(4*H*)-ones (azlactones), was developed in the 1980s [2]. The method also allowed the preparation of enantiomerically pure examples [3]. In a series of experiments, it has been shown that the C=S group of **1** is the most reactive part of the molecule [4]. Therefore, derivatives **1** have been used as models for 1,3-dipolar cycloadditions [5], hetero-*Diels–Alder* reactions [6], and [2 + 2] cycloadditions [7] with C=S compounds, as well as for the study of BF₃-catalyzed reactions with oxiranes [8] and thiophilic vs. carbophilic additions of organometallic compounds [9].

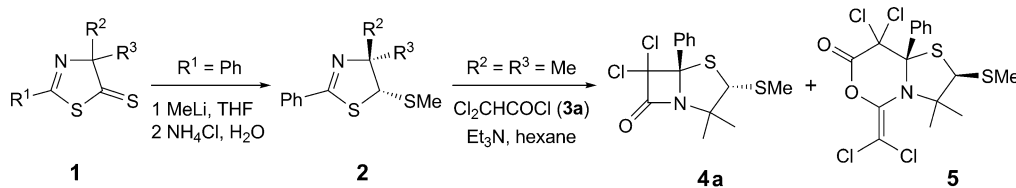
After transformation of the C=S group of **1a** (R¹ = Ph, R² = R³ = Me) to the MeS derivative **2a** (R² = R³ = Me), treatment of the latter with 1 mol-equiv. of dichloroacetyl chloride (Cl₂CHCOCl; **3a**) followed by addition of Et₃N led to a 2 : 1 mixture of the β -lactam derivative **4a** (a ‘penam’) and the 2-methyliden-1,3-oxazin-6-one **5**³⁾ in a total yield of 44% [10] (*Scheme 1*). Under analogous reaction conditions, *cis*-**2b** (R² = Me, R³ = ⁱPr) gave a single product **4b** with all-*cis*-configuration (all substituents MeS, ⁱPr, and Ph in *exo* positions) in 94% yield. The reaction of **2a** with N₃CH₂COCl yielded the penam of type **4** with *exo*-orientation of the N₃ group at C(6) [10].

¹⁾ Part of the Ph.D. thesis of J. S., Universität Zürich, 1993; presented in part at the 55th Annual Meeting of the Polish Chemical Society, Białystok, 2012, Abstracts, S06_K06, p. 227 [1].

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³⁾ The structure of **5** was established by X-ray crystallography (H. Heimgartner, J. H. Bieri, R. Prewo, A. Linden, C. Jenny, Private Communication CCDC, Cambridge, England, 1993; CSD refcode: HACPUW).

Scheme 1



β -Lactam antibiotics belong to the most efficient agents in fighting bacterial infections⁴). Mostly, the β -lactam antibiotics are the products of fermentation and semi-synthesis, and, despite many efforts, only a couple of monocyclic β -lactams are produced by total synthesis. Nevertheless, there is a continuing interest in new synthetic methods towards this highly desired class of compounds (see, *e.g.*, [12]). Among the various methods for the preparation of β -lactams, the acid chloride/imine (ketene/imine) addition is one of the most frequently used. Since its discovery by *Staudinger* in 1907 [13], the scope and limitations of this method have been studied extensively, and much progress has been made on the synthesis of monocyclic β -lactams [14]. However, for the synthesis of bicyclic β -lactams, *e.g.*, penams, this method suffers in two ways: the poor yield of the reaction, and the low or inappropriate stereoselectivity. Although the problem of the undesired configuration at C(6) has been solved by the transformation of 6-epipenicillin to penicillin [15], the epimerization is a multistep process and affords the product only in low yield. Therefore, a number of studies concerning the formation of the penam skeleton *via* the reaction of 4,5-dihydro-1,3-thiazoles with various acetyl chlorides/base, *i.e.*, the imine/ketene addition, have been published [16]. Furthermore, the continuing interest in penam derivatives is reflected by the elaboration of new methods for their preparation (*e.g.*, [17]), the synthesis of analogs such as selenapenams [18], and the modification of known compounds, *e.g.*, 6-aminopenicillic acid (6-APA) [19].

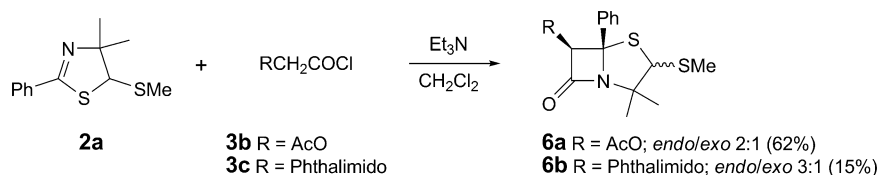
The aim of the present study was the extension of the reaction $2 \rightarrow 4$ to 4,5-dihydro-1,3-thiazoles of type **2** with a PhCH_2 or a Me group at C(2), as well as on acetyl chlorides bearing an AcO or phthalimido group. Furthermore, a method for transformation of 6-*exo*-substituted penams to the corresponding 6-*endo*-azido derivatives should be elaborated.

2. Results and Discussion. – 2.1. *Reactions of 4,5-Dihydro-1,3-thiazoles 2 with Acetyl Chlorides and Et₃N.* The substituted 4,5-dihydro-4,4-dimethyl-5-(methylsulfonyl)-1,3-thiazoles **2** were synthesized by treatment of the corresponding 4,4-dimethyl-1,3-thiazole-5(4*H*)-thione **1** with MeLi in THF at -78° [9a]. When **2a** was treated with (acetoxy)acetyl chloride ($\text{AcOCH}_2\text{COCl}$; **3b**) in CH_2Cl_2 at room temperature in the presence of Et_3N , two products, *endo*-**6a** and *exo*-**6a**, were formed in a ratio of *ca.* 2:1, isolated in 62% yield after chromatographic workup. The two stereoisomers were separated by preparative TLC. On the basis of the spectroscopic data, the structures of

⁴) For recent reviews, see [11].

isomeric penams **6** were assigned (*Scheme 2*). As it has been shown that, in [2 + 2] cycloadducts of 4,5-dihydro-1,3-thiazoles with ketenes, the ring S-atom is unmistakably oriented *trans* to the group with a heteroatom at C(6) [20], *endo-6a* and *exo-6a* were assigned both as 5,6-*trans* products. Then, the remaining possibility for the presence of isomers must be the result of different configurations of the MeS substituent at C(2), as the reaction started from racemic **2a**. Hence, *endo-6a* and *exo-6a* were assigned as the diastereoisomers with 2-*endo*- and 2-*exo*-5,6-*trans*-bicyclic penams, respectively. Finally, the structure of *endo-6a* was confirmed by X-ray crystallography (*Fig. 1*). Similarly, the reaction of **2a** and phthalimidoacetyl chloride **3c** also gave a mixture of two diastereoisomers, *endo-6b*/*exo-6b* 3:1 in a low yield of 15% (*Scheme 2*).

Scheme 2



Since the space group of *endo-6a* is centrosymmetric, the compound in the crystal is racemic. Whereas the AcO group at the β -lactam ring is *exo*-oriented, *i.e.*, *cis* to the Ph group, the MeS group at the thiazolidine ring occupies the *endo*-position.

On the other hand, acid chlorides **3a**–**3c** reacted with the 2-PhCH₂-substituted 4,5-dihydro-1,3-thiazole **2b** under the same conditions (CH_2Cl_2 , room temperature) to give different products. The reaction of **2b** with excess **3a** furnished two products in almost equal amounts. According to the NMR spectra, the second product consists of a 1:1 mixture of diastereoisomers. The mass and NMR spectra revealed that they were derived from 1:1 and 1:2 adducts of **2b** and **3a** by elimination of 1 and 2 equivalents, respectively, of HCl. The IR spectra excluded the presence of β -lactam structures, as both products lack the absorption at *ca.* 1750 cm⁻¹, *i.e.*, the characteristic β -lactam C=O stretching band. In both compounds, an amide/lactam group was indicated by IR absorptions at 1700 and 1720/1710 cm⁻¹, and ¹³C-NMR signals at 163.9 and 159.5 ppm, respectively. On the basis of the spectroscopic data, structures **7a** and **8** were proposed for these products (*Scheme 3*). Treatment of **7a** with excess **3a** and Et₃N in boiling hexane led to **8** in 31% yield.

The same starting materials **2a** and **3a** reacted in refluxing hexane in the presence of Et₃N, and the same product **7a** was formed together with a new compound **9**. Again, lack of absorptions for a corresponding C=O group indicated that no β -lactam was formed; the C=O signals appeared at 1600 cm⁻¹ and 179.5 ppm. Furthermore, a NH signal was detected at 10.92 ppm in the ¹H-NMR spectrum. The structure of **9** was established by X-ray crystallography (*Fig. 2*).

Similar reactions of **2b** with **3b** and **3c**, respectively, in refluxing hexane gave a single 1:1 adduct **7b** or **7c** in each case (*Scheme 4*). Furthermore, 4,5-dihydro-2-methyl-1,3-thiazole **2c** reacted with **3a** under similar conditions to give the '1:2 adduct' **10** in low yield. The structures of all these products were determined on the basis of their

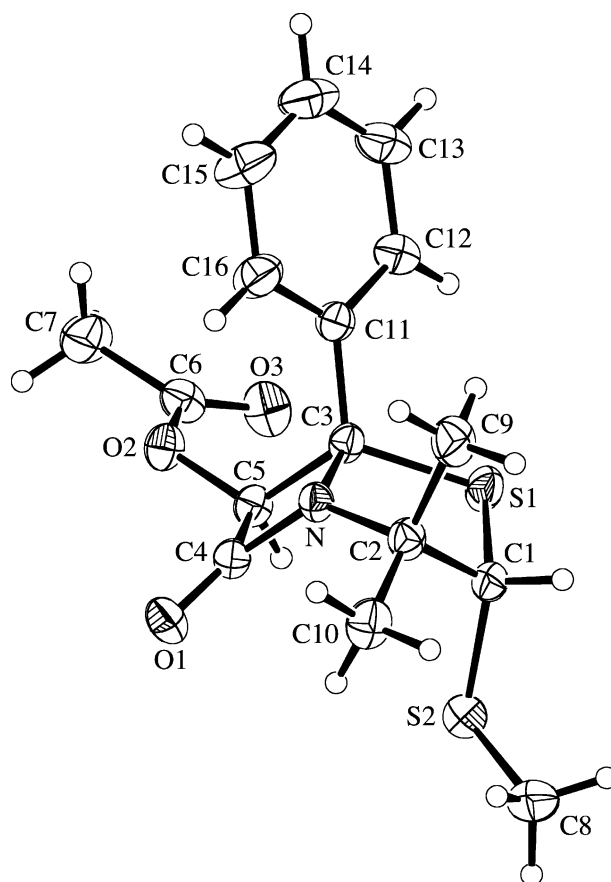
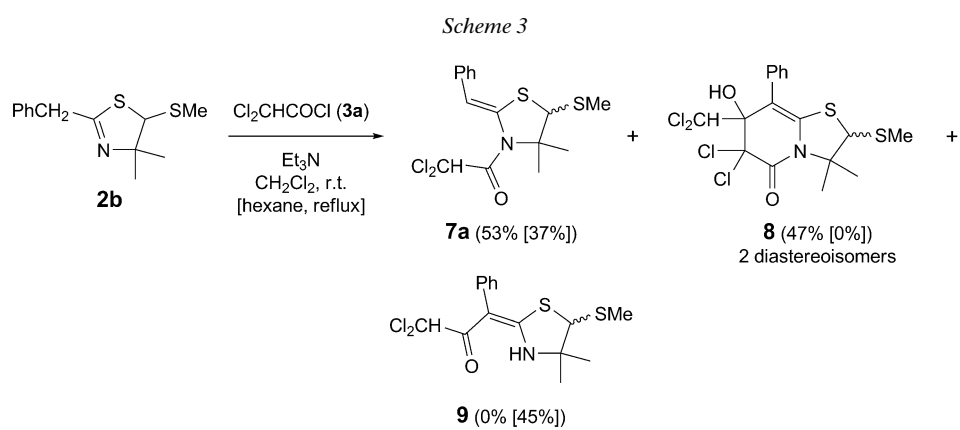


Fig. 1. ORTEP Plot [21] of the molecular structure of *endo*-**6a** (with 30% probability ellipsoids; arbitrary numbering of atoms)



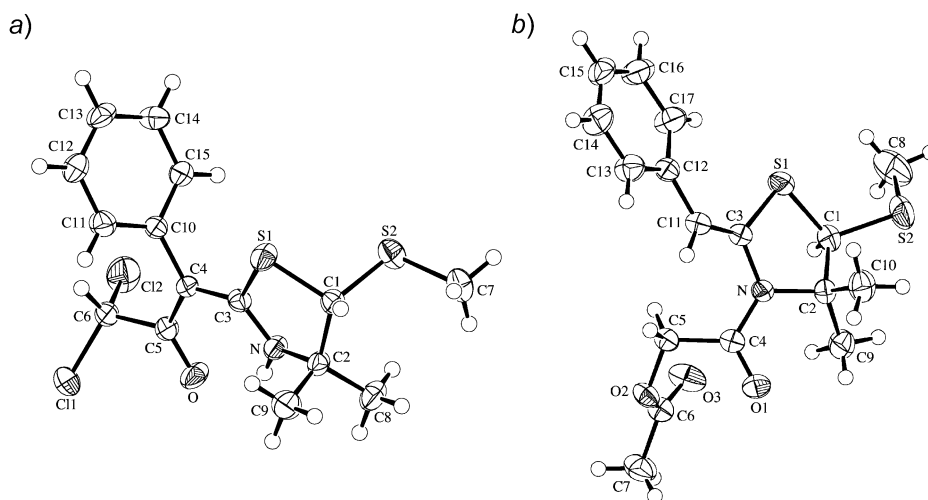
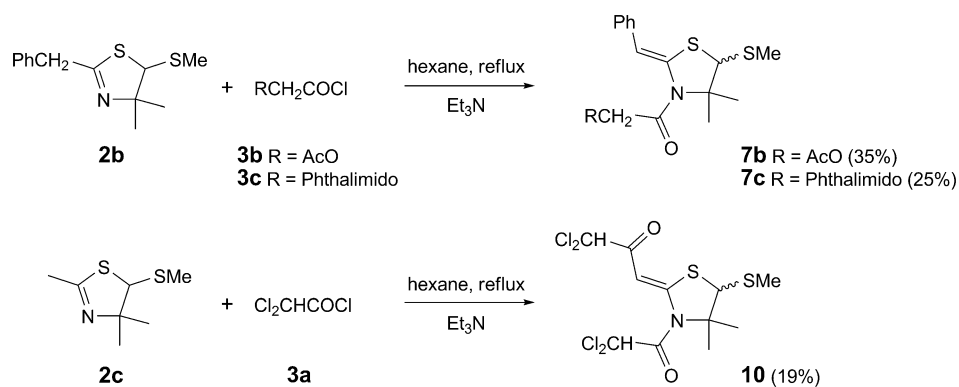


Fig. 2. ORTEP Plots [21] of the molecular structures of a) **9** and b) **7b** (with 50% probability ellipsoids; arbitrary numbering of atoms)

Scheme 4



spectroscopic and analytical data and, in the case of **7b**, the structure was established by X-ray crystallography (Fig. 2).

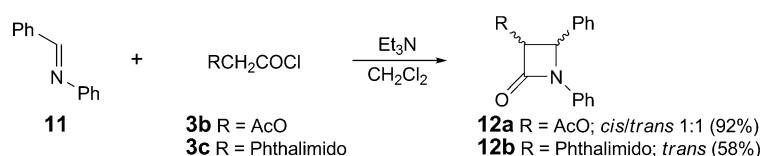
The space groups of **9** and **7b** are centrosymmetric, therefore, the compounds in the crystals are racemic. The thiazolidine NH group of **9** forms an intramolecular H-bond with the O-atom of the side-chain C=O group; graph set motif [22] S(6). In the case of **7b**, the exocyclic C=C bond is (Z)-configured.

It should be mentioned that all attempts to synthesize spiropenam by the acid chloride/imine cycloaddition failed. Under various conditions, C(4)-spirocyclic 4,5-dihydro-1,3-thiazoles [9c] reacted neither with **3a** nor with **3b** in the presence of Et₃N. In most cases, the starting materials were recovered in high yields. Similarly, the bulky

2-(*tert*-butyl)-4,5-dihydro-4,4-dimethyl-5-(methylsulfanyl)-1,3-thiazole [9c] also failed to react with **2a** and **2b** under similar conditions.

2.2. Synthesis of Monocyclic α -Hydroxy β -Lactams and Attempted Transformations to α -Azido β -Lactams. With the aim of elaborating reaction conditions for the transformation of penams of type **6** to the corresponding 6-*endo*-azido derivatives, monocyclic β -lactams were prepared as model compounds. Thus, benzalaniline (*N*-benzylideneaniline; **11**), in CH_2Cl_2 and in the presence of Et_3N , was reacted with acid chlorides **3b** and **3c**, respectively, at room temperature to give the corresponding monocyclic β -lactams **12a** and **12b** in good-to-excellent yield (Scheme 5)⁵. In the case of **3c**, only the *trans*-isomer **12b** was obtained, whereas, in the case of **3b**, a 1 : 1 mixture of *cis*- and *trans*-**12a** was isolated. The *cis/trans*-configurations were assigned on the basis of the $J(\text{H}-\text{C}(3), \text{H}-\text{C}(4))$ values in the ^1H -NMR spectra [24] (see also [23]).

Scheme 5



In several publications, the transformation of *cis*- and *trans*-substituted 3-hydroxyazetidinones to the corresponding 3-azido derivatives with inverted configuration has been described (*e.g.*, [25]). Our intention was to use the mixture of *cis/trans*-**12a** as a model for this purpose. First, **12a** was hydrolyzed by treatment with NaHCO_3 in $\text{MeOH}/\text{H}_2\text{O}$ at 0° to give *cis/trans*-3-hydroxy- β -lactams **13** [23a][23c][25b][26] (Scheme 6). The diastereoisomers *trans*-**13** and *cis*-**13** were separated successfully by flash chromatography. Their subsequent sulfonylation with 4-chlorophenylsulfonyl chloride (*cf.* [23a][25]) gave the sulfonates *trans*-**14** and *cis*-**14**, respectively, in excellent yields. Treatment of the sulfonates with NaN_3 in DMF at $50-60^\circ$ afforded *via* stereoselective $\text{S}_{\text{N}}2$ reaction the 3-azido- β -lactams *cis*-**15** and *trans*-**15**, respectively, with complete conversion of the configurations (Scheme 6).

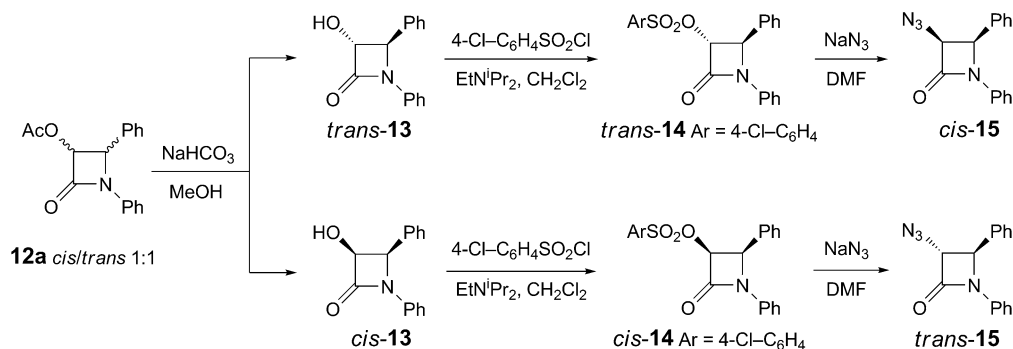
The successful replacement of the OH group in monocyclic β -lactams by the N_3 group (see above and [25]) encouraged us to apply this method to the bicyclic β -lactams **6a**. In analogy to the monocyclic β -lactams **12**, the diastereoisomer mixture **6a**, as well as the separated 2-*endo*- and 2-*exo*-diastereoisomers *endo*-**6a** and *exo*-**6a**, were hydrolyzed under mild conditions to give the corresponding 6-hydroxypenams **16** (Scheme 7). The diastereoisomers *endo*-**16** and *exo*-**16** formed from the mixture *endo*-**6a**/*exo*-**6a** could be separated easily by preparative TLC⁶.

The structure of *exo*-**16** was established by X-ray crystallography (Fig. 3). Since the space group is centrosymmetric, the compound in the crystal is racemic. The

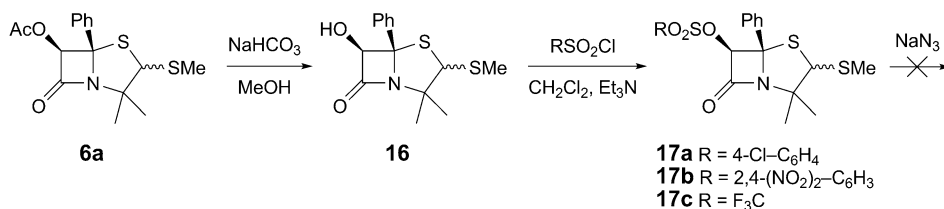
⁵) For analogous recent studies, see [12b][23]. Selective syntheses of *cis*-**12a** under similar conditions [23a] or at -78° [23b] were reported, those of *cis*- and *trans*-**12b** were described in [23d][23e].

⁶) The hydrolyses of the pure diastereoisomers *endo*-**6a** and *exo*-**6a** led to pure *endo*-**16** and *exo*-**16**, respectively, in a stereospecific manner.

Scheme 6



Scheme 7



substituents MeS, Ph, and OH are all *exo*-oriented. The OH group forms an intermolecular H-bond with the C=O O-atom of a neighboring 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 [22] of C(5).

Sulfonylation of **16** in $\text{CH}_2\text{Cl}_2/\text{Et}_3\text{N}$ at 0° with (4-chlorophenyl)- and (2,4-dinitrophenyl)sulfonyl chlorides gave the corresponding sulfonates **17a** and **17b**, respectively, in high yields. Under the same conditions, the reaction of **16** with (trifluoromethyl)sulfonyl chloride was carried out, but the corresponding (sulfonyloxy)penam **17c** was obtained in only 27% yield as a crude and unstable product. Surprisingly, 4,5-dihydro-4,4-dimethyl-5-(methylsulfanyl)-2-phenyl-1,3-thiazole (**2a**) was formed *via* a decomposition reaction.

Substitution of the sulfonate **17a** with NaN_3 under same conditions, as in the case of monocyclic β -lactams **14**, failed; no substitution product, *i.e.*, a 6-azidopenam, was formed, and mainly starting material was recovered. Even reactions with the more active substrates **17b** and **17c** did not result in any desired azido product. Instead, some decomposition product **2a** was formed. As the unstable triflated bicyclic penam **17c** decomposed already under the conditions of its preparation, triflation, and substitution with NaN_3 were conducted in a one-pot reaction under mild conditions (0°). However, this also failed to afford the desired azido compound, and again some cleavage product **2a** was isolated. All further attempts to use the more nucleophilic and better soluble azido reagents LiN_3 and Bu_4NN_3 were also unsuccessful to give an azido penam.

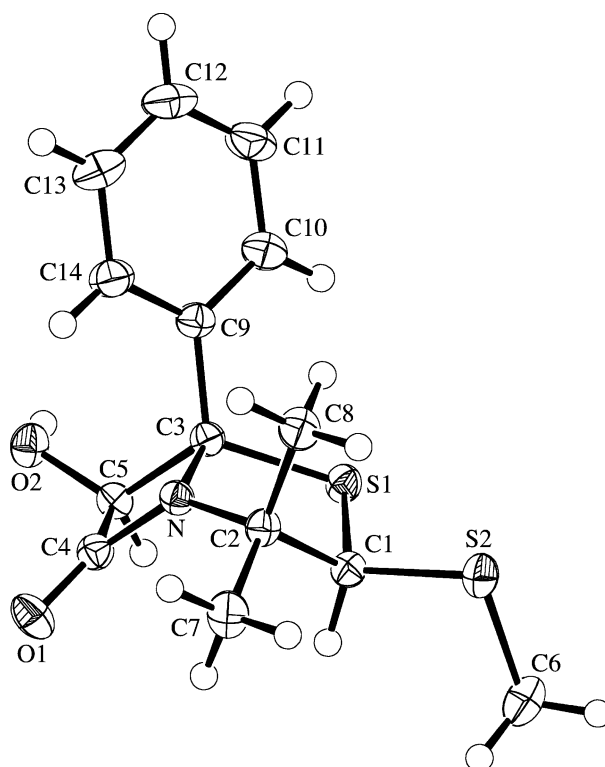


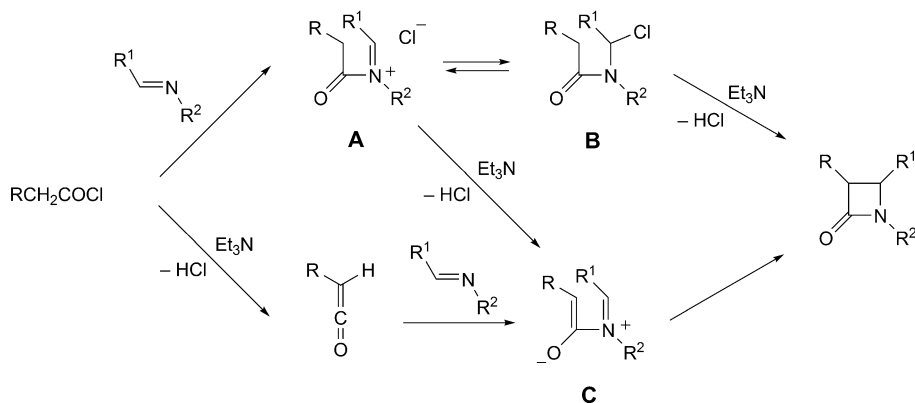
Fig. 3. ORTEP Plot [21] of the molecular structure of *exo*-**16** (with 50% probability ellipsoids; arbitrary numbering of atoms)

3. Conclusions. – The acid chloride/imine cycloaddition has been studied extensively, and three mechanistic pathways have been proposed [27]: 1) direct acylation of the imine with the acid chloride leads to the intermediate *N*-acyliminium chloride **A** or the chloroalkyl amide **B**, which reacts with base to give the β -lactam; 2) the initial formation of a ketene and subsequent [2 + 2] cycloaddition with an imine, perhaps *via* the zwitterionic intermediate **C**, yields the β -lactam; 3) deprotonation of the initially formed **A** leads to **C**, which reacts to give the β -lactam (*Scheme 8*). However, it is not possible to predict the stereochemical course of all of the reported reactions with a single mechanisms, and it is likely that more than one mechanism is involved⁷⁾.

In the acid chloride/imine cycloaddition, especially with cyclic imines, the heteroatom at the imine C-atom plays an important role in the determination of the relative configuration of the resulting β -lactam. It has been reported that a 4,5-dihydro-1,3-thiazole gives exclusively the 5,6-*trans*-configured penam from the reaction with *N*-protected glycyl chloride [20]. This observation was confirmed in the present study, in which only the 5,6-*trans*- β -lactams **6a** and **6b** were formed in the reaction of 4,5-

⁷⁾ For some recent relevant articles and reviews, see [28][29].

Scheme 8



dihydro-1,3-thiazole **2a** with (acetoxy)acetyl chloride (**3b**) and phthalimidoacetyl chloride (**3c**), respectively (Scheme 2).

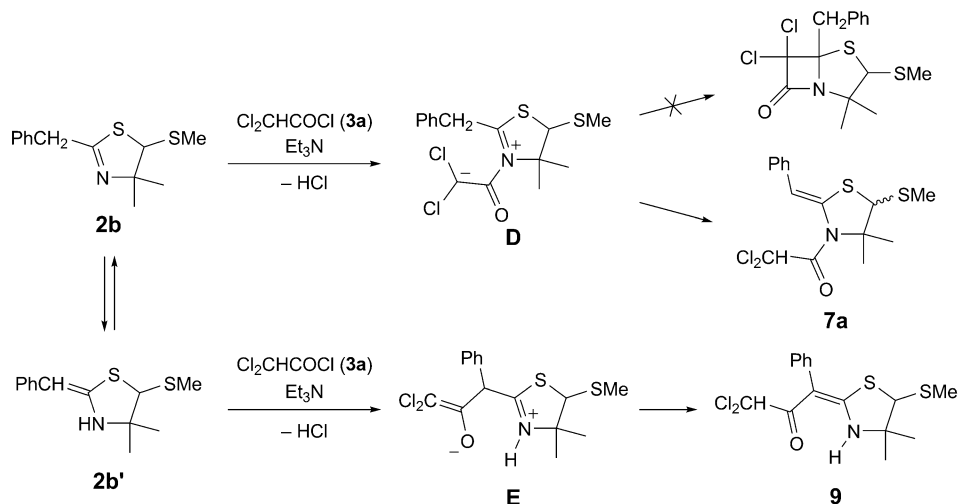
The substituent at C(α) of the acid chloride also has an influence on the configuration of the formed β -lactam. It was found that a relatively bulky acid chloride leads to the 3,4-*trans*-configured β -lactam, while a less sterically hindered acid chloride had a minor influence on the configuration of the product. For instance, **3c** and benzalaniline (**11**) gave exclusively the β -lactam *trans*-**12b**, while **3b**, under analogous conditions, afforded a 1:1 mixture *cis*-**12a**/*trans*-**12a** (Scheme 5).

The efficiency of the cycloaddition reaction with cyclic imines depends to a great extent on the substituent at the imine C-atom. For instance, the reaction of a 2-unsubstituted 4,5-dihydro-1,3-thiazole with $\text{N}_3\text{CH}_2\text{COCl}$ gave the corresponding penam in a very poor yield [30], while the 2-Ph-substituted **2a** afforded the bicyclic β -lactams **6a** in a much higher yield (see also [10]). However, a sterically bulky substituent at C(2) may obstruct the reaction, as the 2-*t*Bu analog of **2a** failed to react with **3a** and with **3b**, respectively. For similar reasons, 4,4-spiro-4,5-dihydro-1,3-thiazoles of type **2a** failed to give any β -lactam under analogous reaction conditions.

When the substituent at C(2) of the 4,5-dihydro-1,3-thiazole **2** bears a H-atom in α -position, the reaction with acid chlorides/ Et_3N proceeded *via* another pathway leading to *N*- and/or *C*-acylated products. The formation of *N*-acylated products in reactions with acid chlorides/ Et_3N has previously been reported [31]. They might be formed by the nucleophilic attack of the imine *N*-atom onto the ketene or acid chloride (**2b** $\rightarrow$ **D**, Scheme 9), followed by a proton shift in the zwitterion **D** to give **7a**. Apparently, this process is favored over ring closure to form a β -lactam.

To the best of our knowledge, the *C*-acylation of a 4,5-dihydro-1,3-thiazole by an acid chloride or a ketene has not been reported so far. A reasonable mechanism for the reaction **2b** $\rightarrow$ **9** is depicted in Scheme 9: the enamine moiety in the tautomeric structure **2b'** may attack the ketene or acyl chloride to give **E**, followed by a prototropic isomerization. Control experiments indicated that the *C*-acylation is even more favored in the absence of Et_3N (16% of **7a** and 64% of **9**). Therefore, an initial deprotonation

Scheme 9



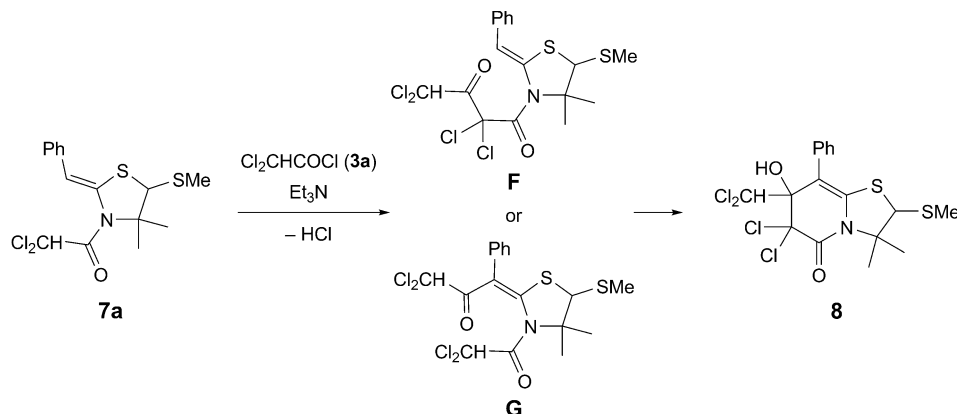
of **2b** by the base, to give a benzyl anion, which then could attack the ketene to give **E**, is not necessary.

The formation of 2 : 1 adducts in reactions of ketenes and 4,5-dihydro-1,3-thiazoles, *i.e.*, 2-methyliden-1,3-oxazin-6-ones or piperidine-2,4-diones, has already been reported [10][32]. However, the structure of compound **8** is different from those of the above reported bicycles, in which the substituents at C(2) were not involved in the formation of the fused ring system. A control experiment showed that **8** was also formed *via* a second acylation of the *N*-acylation product **7a**: in refluxing hexane, in the presence of **3a** and Et_3N , **8** was obtained. A likely reaction mechanism is outlined in Scheme 10. Deprotonation of **7a** and subsequent addition to a second ketene molecule could form intermediate **F**, which may undergo a cyclization *via* nucleophilic attack of the enamine moiety onto the C=O group. An alternative reaction sequence *via* C-acylation of **7a** to give **G**, deprotonation of the *N*-acyl moiety, and cyclization is also conceivable.

The exchange of the OH for the N_3 group was successful in monocyclic β -lactams **13** (Scheme 6), but it failed in our bicyclic β -lactams **16** (Scheme 7). The reason could be the stereochemical hindrance around the 6-sulfonate moiety in **17**; both the fused thiazolidine ring and the 5-Ph substituent contribute to this hindrance. The first contribution was confirmed by the successful substitution in **13**, and the latter was supported by a report, in which a 5-unsubstituted 6-*exo*-hydroxy penam was converted to the 6-*endo*-azido penam under similar conditions as ours [33].

The acid chloride/imine cycloaddition provides a versatile and convenient way to produce monocyclic β -lactams in high yields. By choosing appropriate substituents on both the acid chloride and the imine, a stereoselective formation of products could be achieved. However, for bicyclic β -lactams, the yields are generally poor, especially for the most desired 5-unsubstituted penams. To solve the problem, Nagao *et al.* [16e] introduced a MeSe substituent at C(2) of 4,5-dihydro-1,3-thiazoles. With this

Scheme 10



promoting group, the yield of the cycloadditions improved dramatically. The MeSe group could be removed afterwards by selective reduction with Bu_3SnH . Concerning the configuration of the products, the method afforded exclusively the undesired stereoisomers, namely the *trans*- β -lactams with the *exo*-oriented substituent at C(6). Thus, to access biologically interesting products, an epimerization at C(6) is needed. As the *exo* $\rightarrow$ *endo* transformation was reported to be successful in bicyclic β -lactams [33], the combination of Nagao's cycloaddition, deselenation, and the above transformation would open the way to the synthesis of biologically attractive penams.

We thank the analytical sections 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*. Solvents: CH_2Cl_2 , Et_2O , MeCN, hexane, and toluene were distilled over CaH_2 and stored over molecular sieves (4 Å); THF was distilled over Na; DMF, MeOH, and EtOH (*Merck*) were dried over molecular sieves (4 Å). TLC: *Merck* TLC aluminum sheets, silica gel (SiO_2) 60 F_{254} . Column chromatography (CC): SiO_2 *Merck* 60 (0.04–0.063 mm). M.p.: *Mettler-FP5* apparatus; uncorrected. IR Spectra: *Perkin-Elmer* 297 or *Perkin-Elmer* 781 spectrophotometer; in CHCl_3 unless otherwise stated; $\tilde{\nu}$ in cm^{-1} . ^1H -NMR Spectra: *Bruker AC-300* (300 MHz), *Bruker AM-400* (400 MHz), and *Varian EM-390* (90 MHz) spectrometer, in CDCl_3 at 300 K unless otherwise stated; δ in ppm; TMS (0 ppm) or residual CHCl_3 (7.27 ppm) as internal standards; coupling constants J in Hz. ^{13}C -NMR Spectra: *Varian XL-200* (50.4 MHz) spectrometer; δ in ppm; CDCl_3 as internal standard (77.0 ppm); signal multiplicity from DEPT spectra. MS: *Varian MAT-711*, *Varian MAT-112*, *Finnigan MAT-90*, *Finnigan SSQ-700*, or *Finnigan TSQ-700* mass spectrometers; EI mode: direct injection, 70 eV; CI mode: with 2-methylpropane or NH_3 ; m/z (rel. %).

2. *Acid Chloride/Imine Cycloaddition. General Procedure 1 (GP 1)*. Into a soln. of imine (4,5-dihydro-1,3-thiazole **2** or benzalaniline (**11**); 5 mmol) and Et_3N (1.01 g, 10 mmol) in CH_2Cl_2 (50 ml) at r.t., a soln. of acid chloride **3** (10 mmol) in CH_2Cl_2 (2 ml) was added within 1 h. After stirring for 1 d, 505 mg (5 mmol) of Et_3N was added in one portion, and additional **3** (5 mmol) was added dropwise within 1 h. The mixture was maintained at r.t. for another 2–3 d, and then filtered through a SiO_2 column.

The filtrate was washed subsequently with 2N HCl, 5% NaHCO₃, and brine. After removal of the solvent *in vacuo*, the residue was either chromatographed or recrystallized.

General Procedure 2 (GP 2). A soln. of imine (**2** or **11**; 1 mmol) and acid chloride **3** (1.2 mmol) in hexane (15 ml) was heated at reflux for 3 h. Then, a soln. of Et₃N (3 mmol) in hexane (1 ml) was added within 1 h, and the mixture was maintained at reflux for another 3 h. After addition of Et₂O (30 ml), the mixture was filtered through a short SiO₂ column, the filtrate was concentrated *in vacuo*, and the residue was chromatographed or recrystallized.

2.1. Formation of Bicyclic β -Lactams. 2.1.1. 6-exo-Acetoxy-2,2-dimethyl-3-endo-(methylsulfanyl)- and 6-exo-acetoxy-2,2-dimethyl-3-exo-(methylsulfanyl)-5-phenyl-4-thia-1-azabicyclo[3.2.0]heptan-7-one (endo-**6a** and exo-**6a**, resp.). According to GP 1, with 4,5-dihydro-4,4-dimethyl-5-(methylsulfanyl)-2-phenyl-1,3-thiazole [9a] (**2a**; 762 mg, 3.215 mmol), Et₃N (1.30 g, 12.86 mmol), and (acetoxy)acetyl chloride (**3b**, 1.754 mg, 12.86 mmol). CC (hexane/Et₂O 10:1) yielded 672 mg (62%) of **6a/6a'**. 2:1 After prep. TLC (hexane/Et₂O 4:1; 4 $\times$ developing), endo-**6a** and exo-**6a** were isolated in pure form.

Data of endo-6a. White crystals. M.p. 126–128°. IR: 2985w, 2920w, 1785s, 1755s, 1450w, 1390w, 1370m, 1275m, 1255w, 1235m, 1180m, 1160w, 1125m, 1060w, 1025w, 915w, 700m. ¹H-NMR: 7.35–7.3 (m, 5 arom. H); 6.02 (s, H–C(6)); 4.55 (s, H–C(3)); 2.26 (s, MeS); 1.94 (s, endo-Me–C(3)); 1.64 (s, MeCO); 1.29 (s, exo-Me–C(3)). ¹³C-NMR: 167.9 (s, C(7)); 167.8 (s, MeCO); 136.9 (s, 1 arom. C); 128.1, 127.8, 126.2 (3d, 5 arom. CH); 84.4 (d, C(6)); 80.5 (s, C(5)); 72.7 (d, C(3)); 70.5 (s, C(2)); 27.5, 21.3 (2q, Me₂C); 19.5 (q, MeCO); 16.6 (q, MeS). CI-MS: 340 (12), 339 (20), 338 (100, [M + 1]⁺), 290 (17), 238 (17). Anal. calc. for C₁₆H₁₉NO₃S₂ (337.46): C 56.95, H 5.68, N 4.15, S 19.00; found: C 56.91, H 5.49, N 4.37, S 19.28.

Suitable crystals for the X-ray crystal-structure determination were grown from hexane/Et₂O by slow evaporation of the solvent at r.t.

Data of exo-6a. White crystals. M.p. 100.5–101.5°. IR: 2990w, 2920w, 1770s, 1760s, 1450w, 1390w, 1370m, 1275m, 1250m, 1240m, 1185m, 1120m, 1050w, 1030m, 920w, 700m. ¹H-NMR: 7.35–7.3 (m, 5 arom. H); 5.90 (s, H–C(6)); 4.62 (s, H–C(3)); 2.28 (s, MeS); 1.87 (s, endo-Me–C(3)); 1.63 (s, MeCO); 1.10 (s, exo-Me–C(3)). ¹³C-NMR: 168.5 (s, MeCO); 167.7 (s, C(7)); 137.0 (s, 1 arom. C); 128.2, 127.7, 126.3 (3d, 5 arom. CH); 85.3 (d, C(6)); 79.0 (s, C(5)); 70.7 (d, C(3)); 68.9 (s, C(2)); 22.2, 22.0 (2q, Me₂C); 19.5 (q, MeCO); 17.3 (q, MeS). CI-MS: 340 (11), 339 (19), 338 (100, [M + 1]⁺), 304 (19), 290 (16), 280 (16), 278 (10), 238 (35), 234 (26), 188 (7), 178 (7). Anal. calc. for C₁₆H₁₉NO₃S₂ (337.46): C 56.95, H 5.68, N 4.15, S 19.00; found: C 57.11, H 5.48, N 4.19, S 18.88.

2.1.2. 2,2-Dimethyl-3-endo/exo-(methylsulfanyl)-5-phenyl-6-exo-phthalimido-4-thia-1-azabicyclo[3.2.0]heptan-7-one (= 2-[2,2-Dimethyl-3-(methylsulfanyl)-7-oxo-5-phenyl-4-thia-1-azabicyclo[3.2.0]hept-6-yl]-1H-isoindole-1,3(2H)-dione; 6b). According to GP 2, with **2a** (119 mg, 0.5 mmol), phthalimidoacetyl chloride (**3c**, 134 mg, 0.6 mmol), and Et₃N (152 mg, 1.5 mmol). Prep. TLC (hexane/Et₂O 10:1): 31 mg (15%) of **6b** as a mixture of two diastereoisomers. White crystals. M.p. 88°. IR: 3030w, 3000w, 2980w, 2930w, 1790s, 1775s, 1725s, 1385s, 1270m, 1250m, 1110m, 965w, 710w, 700w. ¹H-NMR (2 diastereoisomers, 1:3): 7.65–7.05 (m, 9 arom. H); 5.84, 5.67 (2s, H–C(6)); 4.67, 4.60 (2s, H–C(3)); 2.30 (s, MeS); 2.06, 1.99, 1.45, 1.26 (4s, Me₂C). ¹³C-NMR (2 diastereoisomers, 1:3): 168.0 (s, C(7)); 167.3 (s, 2 C=O); 137.3, 130.9 (2s, 3 arom. C); 134.1, 128.00, 127.97, 127.8, 125.5, 123.3 (6d, 9 arom. C); 79.4 (s, C(5)); 73.1, 70.4 (2d, C(6)); 71.1, 69.6 (2s, C(2)); 69.2, 68.3 (2d, C(3)); 28.3, 22.5, 21.6, 22.3 (4q, Me₂C); 17.4, 16.8 (2q, MeS). CI-MS: 425 (11, [M + 1]⁺), 260 (16), 259 (100), 238 (21), 145 (5), 72 (5). Anal. calc. for C₂₂H₂₀N₂O₃S₂ (424.54): C 62.24, H 4.75, N 6.60, S 15.11; found: C 62.12, H 4.66, N 6.39, S 15.35.

2.2. Formation of Monocyclic β -Lactams. 2.2.1. 3-Acetoxy-1,4-diphenylazetidin-2-one (**12a**) [23a,b]. According to GP 1, with **3b** (2.048 g, 15 mmol) and benzalaniline (= N-benzylideneaniline; **11**, 0.905 g, 5 mmol). CC (hexane/Et₂O 12:1): 1.299 g (92%) of **12a** (2 diastereoisomers). White crystals. M.p. 138–139°. IR: 1765s, 1760s, 1600w, 1500m, 1390m, 1380m, 1240m, 1145m, 1100w, 700m. ¹H-NMR (2 diastereoisomers, 1:1): 7.45–7.25 (m, 9 arom. H); 7.15–7.05 (m, 1 arom. H); 5.97, 5.41 (2d, J = 4.9, 1.7, H–C(3)); 5.40, 4.96 (2d, J = 4.9, 1.7, H–C(4)); 2.21, 1.69 (2s, Me). ¹³C-NMR (2 diastereoisomers, 1:1): 169.6, 161.7 (2s, 2 C=O); 136.8–117.4 (12 arom. C); 82.4, 76.2 (2d, C(3)); 63.6, 61.3 (2d, C(4)); 20.4, 19.7 (2q, Me). CI-MS: 283 (19), 282 (100, [M + 1]⁺), 234 (9), 224 (8), 222 (10), 195 (11), 183 (10), 182 (60), 163 (12), 147 (19), 133 (7), 101 (15), 94 (47), 93 (9). Anal. calc. for C₁₇H₁₅NO₃ (281.32): C 72.58, H 5.37, N 4.98; found: C 72.55, H 5.15, N 5.17.

2.2.2. *3,4-trans-1,4-Diphenyl-3-phthalimidoazetidin-2-one* (= *3,4-trans-2-(2-Oxo-1,4-diphenylazetidin-3-yl)-1H-isoindole-1,3(2H)-dione*; **12b**) [23d,e]. According to *GP 1*, with **3c** (3.353 g, 15 mmol) and **11** (0.905 g, 5 mmol). Recrystallization from Et₂O/CH₂Cl₂/hexane: 1.068 g (58%) of **12b**. White crystals. M.p. 224–225° ([23d]: 224–230°). IR: 1765m, 1725s, 1600w, 1500m, 1390m, 1150w, 1105w, 1090w, 970w, 715w, 700w. ¹H-NMR (400 MHz): 7.9–7.85 (m, 2 arom. H); 7.8–7.75 (m, 2 arom. H); 7.4–7.25 (m, 9 arom. H); 7.1–7.05 (m, 1 arom. H); 5.40 (d, *J* = 2.7, H–C(3)); 5.30 (d, *J* = 2.7, H–C(4)). ¹³C-NMR: 166.7 (s, 2 C=O); 162.0 (s, C(2)); 137.1–117.6 (18 arom. C); 62.7 (d, C(3)); 61.2 (d, C(4)). CI-MS: 387 (16), 386 (100, [*M* + NH₄]⁺), 369 (25, [*M* + 1]⁺), 366 (14). Anal. calc. for C₂₃H₁₆N₂O₃ (368.40): C 74.99, H 4.38, N 7.60; found: C 74.78, H 4.66, N 7.63.

3. *Reactions of Acid Chlorides with 4,5-Dihydro-1,3-thiazoles 2b and 2c* 3.1. (2*Z*)-3-(2,2-Dichloroacetyl)-4,4-dimethyl-5-(methylsulfanyl)-2-(phenylmethylidene)-1,3-thiazolidine (= 2,2-Dichloro-1-[(2*Z*)-4,4-dimethyl-5-(methylsulfanyl)-2-(phenylmethylidene)-1,3-thiazolidin-3-yl]ethanone; **7a**) and 6,6-Dichloro-7-(dichloromethyl)-2,3,6,7-tetrahydro-7-hydroxy-3,3-dimethyl-2-(methylsulfanyl)-8-phenyl-5H-[1,3]thiazolo[3,2-*a*]pyridin-5-one (**8**). a) According to *GP 1*, with **2b** (147 mg, 0.586 mmol), Et₃N (237 mg, 2.35 mmol), and **3a** (348 mg, 2.35 mmol). CC (hexane/Et₂O 10:1): 114 mg (53%) of **7a** and 130 mg (47%) of **8** (mixture of 2 diastereoisomers).

Data of 7a. Brown crystals. M.p. 97–99°. IR: 2960s, 2920s, 2860s, 1700s, 1600w, 1460w, 1375m, 1355m, 1340m, 1255w, 1170w. ¹H-NMR: 7.35–7.3 (m, 5 arom. H); 6.64 (s, PhCH=C); 6.11 (s, Cl₂CH); 4.35 (s, H–C(5)); 2.21 (s, MeS); 1.59, 1.47 (2s, Me₂C). ¹³C-NMR: 163.9 (s, C=O); 136.4 (s, C(2)); 134.7 (s, 1 arom. C); 128.6, 127.9, 127.2 (3d, 5 arom. CH); 113.4 (d, PhCH=C); 67.6 (s, C(4)); 65.2 (d, Cl₂CH); 64.3 (d, C(5)); 24.3, 20.5 (2q, Me₂C); 16.0 (q, MeS). CI-MS: 366 (2), 364 (8), 362 (11, [*M* + 1]⁺), 252 (57), 236 (6), 206 (5), 205 (15), 204 (100), 191 (10), 135 (14). Anal. calc. for C₁₅H₁₇Cl₂NOS₂ (362.34): C 49.72, H 4.73, Cl 19.57, N 3.87, S 17.70; found: C 50.00, H 5.00, Cl 19.65, N 3.72, S 17.51.

Data of 8. Yellow oil. IR: 3540m, 3020w, 3000m, 2980m, 2920w, 1720s, 1710s, 1630s, 1510m, 1385s, 1370s, 1360s, 1310m, 1280m, 1250m, 1170m, 1125s, 1040m, 1020m, 910m, 850m, 810m, 700m, 650m. ¹H-NMR (2 diastereoisomers, 1:1): 7.5–7.4 (m, 5 arom. H); 6.20, 6.18 (2s, Cl₂CH); 4.24, 4.21 (2s, H–C(2)); 3.22, 3.17 (2s, OH); 2.20, 2.14 (2s, MeS); 1.81, 1.74, 1.73, 1.55 (4s, Me₂C). ¹³C-NMR (2 diastereoisomers, 1:1): 159.5 (s, C=O); 139.9 (s, C(8a)); 135.5, 135.1 (2s, 1 arom. C); 131.4, 131.3, 128.7, 128.6, 128.56, 128.5 (6d, 5 arom. CH); 128.8, 128.7 (2s, C(8)); 106.3, 105.0 (2s, C(7)); 81.8, 81.6 (2s, C(6)); 76.3, 76.2 (2d, Cl₂CH); 72.1, 71.8 (2s, C(3)); 62.0, 61.8 (2d, C(2)); 25.2, 24.3, 21.8, 19.0 (4q, Me₂C); 16.5, 14.9 (2q, MeS). CI-MS: 478 (13), 476 (53), 474 (100), 472 (76, [*M* + 1]⁺), 456 (6), 447 (8), 442 (7), 440 (16), 439 (6), 438 (34), 436 (35), 428 (12), 426 (24), 424 (21), 422 (14), 420 (13), 402 (13), 400 (27), 398 (20), 396 (15), 364 (8), 362 (6), 354 (6).

b) Into a soln. of **7a** (66 mg, 0.18 mmol) and Et₃N (55 mg, 0.54 mmol) in hexane (5 ml), 32 mg (0.22 mmol) of **3a** were added dropwise. The mixture was heated at reflux for 4 h. After removal of the solvent *in vacuo*, the residue was chromatographed with hexane/Et₂O 10:1 to furnish 26 mg (31%) of **8**.

3.2. (2*E*)-2-(3,3-Dichloro-2-oxo-1-phenylpropylidene)-4,4-dimethyl-5-(methylsulfanyl)-1,3-thiazolidine (= (3*E*)-1,1-Dichloro-3-[4,4-dimethyl-5-(methylsulfanyl)-1,3-thiazolidin-2-ylidene]-3-phenylpropan-2-one; **9**). a) According to *GP 2*, with 2-benzyl-4,5-dihydro-4,4-dimethyl-5-(methylsulfanyl)-1,3-thiazole (**2b**; 301 mg, 1.2 mmol), **3a** (195 mg, 1.32 mmol), and Et₃N (303 mg, 3 mmol). CC (hexane/Et₂O 10:1): 159 mg (37%) of **7a** and 195 mg (45%) of **9**. White crystals. M.p. 138.5–140°. IR (KBr): 2950m, 1600s, 1510s, 1505s, 1380s, 1370s, 1330m, 1260m, 1165m, 1135m, 980w, 820m, 800m, 770m, 705m, 695m, 650m. ¹H-NMR: 10.92 (s, NH); 7.6–7.25 (m, 5 arom. H); 5.91 (s, Cl₂CH); 4.39 (s, H–C(5)); 2.17 (s, MeS); 1.57 (s, Me₂C). ¹³C-NMR: 179.5 (s, C=O); 170.8 (s, C(2)); 136.2 (s, 1 arom. C); 131.8, 129.0, 128.4 (3d, 5 arom. CH); 100.4 (s, PhC=C); 69.1 (s, C(4)); 68.0 (d, Cl₂CH); 63.2 (d, C(5)); 27.5, 23.3 (2q, Me₂C); 15.5 (q, MeS). CI-MS: 366 (17), 365 (13), 364 (74), 363 (20), 362 (100, [*M* + 1]⁺), 330 (7), 328 (7). Anal. calc. for C₁₅H₁₇Cl₂NOS₂ (362.34): C 49.72, H 4.73, Cl 19.57, N 3.87, S 17.70; found: C 49.50, H 4.48, Cl 19.77, N 3.99, S 17.40.

Suitable crystals for the X-ray crystal-structure determination were grown from hexane/Et₂O by slow evaporation of the solvent.

b) Into a soln. of **2b** (189 mg, 0.75 mmol) in hexane (10 ml), **3a** (167 mg, 1.13 mmol) was added. The mixture was heated under reflux for 3 h. After addition of Et₂O (30 ml), the mixture was filtered through

a short SiO₂ column, and the filtrate was concentrated *in vacuo*. CC (hexane/Et₂O 10:1) afforded 43 mg (16%) of **7a** and 174 mg (64%) of **9**.

3.3. (2Z)-3-[2-(Acetoxy)acetyl]-4,4-dimethyl-5-(methylsulfanyl)-2-(phenylmethylidene)-1,3-thiazolidine (=2-(Acetyloxy)-1-[2Z]-4,4-dimethyl-5-(methylsulfanyl)-2-(phenylmethylidene)-1,3-thiazolidin-3-yl]ethanone; **7b**). According to GP 2, with **2b** (228 mg, 0.908 mmol), **3b** (248 mg, 1.817 mmol), and Et₃N (367 mg, 3.63 mmol). CC (hexane/Et₂O 10:1): 112 mg (35%) of **7b**. White crystals. M.p. 87–88.5°. IR: 3005w, 2920w, 1745s, 1680s, 1610w, 1490w, 1445w, 1420w, 1385s, 1370m, 1315m, 1240m, 1170m, 1070m, 910m, 695m. ¹H-NMR: 7.4–7.35 (*m*, 5 arom. H); 6.32 (*s*, PhCH=C); 4.93 (*s*, CH₂); 4.37 (*s*, H–C(5)); 2.26 (*s*, MeCO); 2.17 (*s*, MeS); 1.68, 1.53 (2*s*, Me₂C). ¹³C-NMR: 170.3 (*s*, MeCO); 166.5 (*s*, C=O); 135.7 (*s*, C(2)); 135.2 (*s*, 1 arom. C); 128.4, 127.8, 126.8 (3*d*, 5 arom. CH); 114.5 (*d*, PhCH=C); 67.4 (*s*, C(4)); 64.5 (*d*, C(5)); 63.3 (*t*, CH₂); 24.9 (*q*, MeCO); 21.0, 20.4 (2*q*, Me₂C); 16.0 (*q*, MeS). CI-MS: 354 (12), 353 (21), 352 (100, [*M* + 1]⁺), 351 (11), 304 (7). Anal. calc. for C₁₇H₂₁NO₃S₂ (351.49): C 58.09, H 6.02, N 3.99, S 18.24; found: C 58.22, H 5.91, N 4.02, S 18.03.

Suitable crystals for the X-ray crystal-structure determination were grown from hexane/Et₂O by slow evaporation of the solvent.

3.4. (2Z)-4,4-Dimethyl-5-(methylsulfanyl)-2-(phenylmethylidene)-3-(phthalimidoacetyl)-1,3-thiazolidine (=2-[2-(2Z)-4,4-Dimethyl-5-(methylsulfanyl)-2-(phenylmethylidene)-1,3-thiazolidin-3-yl]-2-oxoethyl)-1H-isindole-1,3(2H)-dione; **7c**). According to GP 2, with **2b** (69 mg, 0.275 mmol), **3c** (74 mg, 0.33 mmol), and Et₃N (83 mg, 0.82 mmol). CC (hexane/Et₂O 8:1): 30 mg (25%) of **7c**. Pale-yellow powder. M.p. 55–56°. IR (KBr): 2920w, 1770w, 1720s, 1680m, 1610w, 1420m, 1390m, 1370m, 1290w, 1270w, 1230w, 1110w, 955w, 750w, 715w, 695w. ¹H-NMR: 7.9–7.85 (*m*, 2 arom. H); 7.75–7.7 (*m*, 2 arom. H); 7.4–7.25 (*m*, 5 arom. H); 6.57 (*s*, CH=C); 4.84, 4.76 (*AB*, *J* = 16.4, CH₂); 4.41 (*s*, H–C(5)); 2.29 (*s*, MeS); 1.68, 1.52 (2*s*, Me₂C). ¹³C-NMR: 167.6, 165.7 (2*s*, 3 C=O); 135.7 (*s*, C(2)); 135.2, 131.9 (2*s*, 3 arom. C); 133.9, 128.4, 127.9, 126.8, 123.3 (5*d*, 9 arom. CH); 115.5 (*d*, CH=C); 67.7 (*s*, C(4)); 64.4 (*d*, C(5)); 41.7 (*t*, CH₂); 24.9, 21.0 (2*q*, Me₂C); 15.9 (*q*, MeS). CI-MS: 441 (12), 440 (28), 439 (100, [*M* + 1]⁺), 391 (5). Anal. calc. for C₂₃H₂₂N₂O₃S₂ (438.57): C 62.99, H 5.06, N 6.39, S 14.62; found: C 63.18, H 5.32, N 6.34, S 14.41.

3.5. (2Z)-3-(Dichloroacetyl)-2-(3,3-dichloro-2-oxopropylidene)-4,4-dimethyl-5-(methylsulfanyl)-1,3-thiazolidine (= (3Z)-1,1-Dichloro-3-[3-(2,2-dichloroacetyl)-4,4-dimethyl-5-(methylsulfanyl)-1,3-thiazolidin-2-ylidene]propan-2-one; **10**). According to GP 2, with 4,5-dihydro-2,4,4-trimethyl-5-(methylsulfanyl)-1,3-thiazole (**2c**; 175 mg, 1 mmol), **3a** (178 mg, 1.2 mmol), and Et₃N (251 mg, 2.5 mmol). CC (hexane/Et₂O 10:1): 53 mg (19%) of **10**. Yellow oil. IR: 3200w, 3000m, 2980m, 2920m, 1725s, 1660m, 1595m, 1530s, 1515s, 1505s, 1390m, 1370m, 1320s, 1270m, 1160s, 1120m, 810m. ¹H-NMR: 6.52 (*s*, CH=C); 6.27, 5.90 (2*s*, 2 Cl₂CH); 4.29 (*s*, H–C(5)); 2.29 (*s*, MeS); 1.65, 1.59 (2*s*, Me₂C). ¹³C-NMR: 184.7, 165.7 (2*s*, 2 C=O); 163.2 (*s*, C(2)); 96.1 (*d*, CH=C); 71.6 (*s*, C(4)); 69.5, 64.5 (2*d*, 2 Cl₂CH); 62.1 (*d*, C(5)); 24.0, 20.4 (2*q*, Me₂C); 15.8 (*q*, MeS). CI-MS: 402 (8), 400 (28), 399 (9), 398 (49), 397 (9), 396 (35, [*M* + 1]⁺), 312 (5), 290 (13), 289 (9), 288 (69), 287 (14), 286 (100), 202 (6).

4. Hydrolysis of 3-Acetoxyazetidin-2-one **12a** and 6-Acetoxy Penam **6a**. 4.1. *trans*- and *cis*-3-hydroxy-1,4-diphenylazetidin-2-one (*trans*-**13** and *cis*-**13**, resp.). Into a soln. of **12a** (410 mg, 1.46 mmol) in MeOH (50 ml) at 0°, a soln. of sat. aq. NaHCO₃ (2 ml) was added. The mixture was maintained at 0° for 30 min. Then, AcOEt (200 ml) and H₂O (80 ml) were added. The org. phase was separated, and the aq. phase was extracted with AcOEt (3 × 120 ml). The combined org. phase was washed with brine, dried (Na₂SO₄), filtered, and concentrated *in vacuo*. CC (hexane/Et₂O 8:1) of the residue afforded 153 mg (44%) of *trans*-**13** and 151 mg (43%) of *cis*-**13**.

Data of trans-13 [25b]. White crystals. M.p. 181–183° ([25b]: 180–181°). IR: 3350w, 1750s, 1600w, 1505m, 1385m, 1140w. ¹H-NMR: 7.4–7.2 (*m*, 9 arom. H); 7.1–7.05 (*m*, 1 arom. H); 4.92 (*d*, *J* = 1.8, H–C(4)); 4.76 (*dd*, *J* = 1.8, 6.2, H–C(2)); 3.49 (*d*, *J* = 6.2, OH). ¹³C-NMR ((D₅)pyridine): 168.0 (*s*, C=O); 138.3, 137.9 (2*s*, 2 arom. C); 129.6, 128.8, 126.6, 124.3, 117.9 (5*d*, 10 arom. CH); 85.5 (*d*, C(3)); 66.6 (*d*, C(4)). CI-MS: 258 (16), 257 (100, [*M* + NH₄]⁺), 241 (16), 240 (100, [*M* + 1]⁺). Anal. calc. for C₁₅H₁₃NO₂ (239.28): C 75.30, H 5.48, N 5.85; found: C 75.42, H 5.27, N 6.00.

Data of cis-13 [25b]. White crystals. M.p. 199–201° ([25b]: 206–207°). IR: 3600w, 3000w, 1750s, 1600w, 1500m, 1455w, 1385m, 1265m, 1150w, 1115m, 700m. ¹H-NMR: 7.45–7.25 (*m*, 9 arom. H); 7.15–7.05 (*m*, 1 arom. H); 5.33 (*d*, *J* = 5.4, H–C(4)); 5.21 (*dd*, *J* = 5.4, 9.2, H–C(3)); 2.21 (*d*, *J* = 9.2, OH).

^{13}C -NMR ((D_5)pyridine): 168.3 (s, C=O); 138.6, 135.7 (2s, 2 arom. C); 129.6, 128.9, 128.6, 128.4, 124.3, 117.8 (6d, 10 arom. CH); 78.6 (d, C(3)); 63.3 (d, C(4)). CI-MS: 258 (17), 257 (100, $[M + \text{NH}_4]^+$), 241 (5), 240 (30, $[M + 1]^+$), 58 (5). Anal. calc. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$ (239.28): C 75.30, H 5.48, N 5.85; found: C 75.51, H 5.27, N 5.97.

4.2. 6-exo-Hydroxy-2,2-dimethyl-3-endo- and 3-exo-(methylsulfanyl)-5-phenyl-4-thia-1-azabicyclo[3.2.0]heptan-7-one (*endo*-**16** and *exo*-**16**, resp.). In analogy to *Exper. 4.1*, the reaction of **6a** (460 mg, 1.36 mmol) with sat. NaHCO_3 (3 ml) at 0° for 1 h afforded, after CC (hexane/ Et_2O 5:1), 307 mg (76%) of **16** as a mixture of two diastereoisomers. Prep. TLC (hexane/ Et_2O 4:1) furnished *endo*- and *exo*-**16** in pure form.

Data of endo-16. White crystals. M.p. 103.5–104.5°. IR: 3560m, 3380m, 3000m, 2980m, 2920m, 1760s, 1600w, 1480w, 1460w, 1445m, 1390m, 1370m, 1280s, 1210s, 1180s, 1150s, 1060m, 1030m, 1005m, 980m, 870m, 850m, 700s, 640m. ^1H -NMR: 7.45–7.35 (m, 5 arom. H); 5.22 (d, $J = 9.6$, H–C(6)); 4.54 (s, H–C(3)); 2.32 (d, $J = 9.6$, OH); 2.24 (s, MeS); 1.91, 1.32 (2s, Me_2C). ^{13}C -NMR: 173.3 (s, C=O); 138.1 (s, 1 arom. C); 128.3, 128.1, 126.2 (3d, 5 arom. CH); 86.9 (d, C(6)); 81.7 (s, C(5)); 72.8 (d, C(3)); 69.9 (s, C(2)); 27.8, 21.3 (2q, Me_2C); 16.7 (q, MeS). CI-MS: 296 (25, $[M + 1]^+$), 240 (9), 239 (14), 238 (100). Anal. calc. for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{S}_2$ (295.43): C 56.92, H 5.80, N 4.74, S 21.71; found: C 56.64, H 5.79, N 4.54, S 21.50.

Data of exo-16. White crystals. M.p. 141.5–142.7°. IR: 3560w, 3330w, 2980m, 2920w, 1760s, 1450m, 1390m, 1370m, 1290m, 1260m, 1170m, 1145m, 700m. ^1H -NMR: 7.45–7.35 (m, 5 arom. H); 5.07 (d, $J = 9.6$, H–C(6)); 4.54 (s, H–C(3)); 2.27 (s, MeS); 2.14 (d, $J = 9.6$, OH); 1.85, 1.13 (2s, Me_2C). ^{13}C -NMR ((D_6)acetone): 172.2 (s, C=O); 139.8 (s, 1 arom. C); 128.3, 128.1, 126.9 (3d, 5 arom. CH); 89.6 (d, C(6)); 80.9 (s, C(5)); 70.4 (d, C(3)); 68.8 (s, C(2)); 22.4, 22.3 (2q, Me_2C); 17.0 (q, MeS). CI-MS: 313 (100, $[M + \text{NH}_4]^+$), 296 (25, $[M + 1]^+$), 284 (18), 283 (14), 269 (17), 267 (25), 238 (43).

Suitable crystals of *exo-16* for the X-ray crystal-structure determination were grown from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ /hexane by slow evaporation of the solvent.

5. Sulfonylation of 3-Hydroxyazetidin-2-ones **13** and 6-Hydroxy Penams **16**. 5.1. *trans-3-[(4-Chlorophenyl)sulfonyl]oxy-1,4-diphenylazetidin-2-one* (= *trans-2-Oxo-1,4-diphenylazetidin-3-yl 4-Chlorobenzenesulfonate*; *trans-14*). Into a soln. of *trans-13* (190 mg, 0.795 mmol) in CH_2Cl_2 at 0° , Hünig's base (103 mg, 0.80 mmol) was added. After stirring for 10 min, a soln. of (4-chlorophenyl)sulfonyl chloride (252 mg, 1.19 mmol) in CH_2Cl_2 (2 ml) was added dropwise. The mixture was stirred overnight allowing the temp. to rise to r.t. Then, CH_2Cl_2 (50 ml) was added. The org. phase was washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Crystallization of the residue ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ /hexane) furnished 296 mg (90%) of *trans-14*. White crystals. M.p. 187.0–187.5°. IR: 1770s, 1600w, 1590w, 1500m, 1385s, 1190m, 1185m, 1145m, 1090m, 1070m, 870m, 845m, 830m, 700w. ^1H -NMR: 7.85–7.8 (m, 2 arom. H); 7.55–7.5 (m, 2 arom. H); 7.45–7.35 (m, 3 arom. H); 7.3–7.2 (m, 6 arom. H); 7.15–7.05 (m, 1 arom. H); 5.15 (d, $J = 1.6$, H–C(3)); 5.11 (d, $J = 1.6$, H–C(4)). ^{13}C -NMR ((D_6)DMSO): 159.1 (s, C=O); 140.2, 135.8, 133.9, 133.2 (4s, 4 arom. C); 130.0, 129.8, 129.1, 128.9, 128.7, 126.9, 124.8, 117.6 (8d, 14 arom. CH); 84.7 (d, C(3)); 62.2 (d, C(4)). CI-MS: 433 (30), 432 (27), 431 (100, $[M + \text{NH}_4]^+$), 414 (12, $[M + 1]^+$). Anal. calc. for $\text{C}_{21}\text{H}_{16}\text{ClNO}_4\text{S}$ (413.88): C 60.94, H 3.90, Cl 8.57, N 3.38, S 7.75; found: C 61.10, H 4.05, Cl 8.85, N 3.37, S 7.49.

5.2. *cis-3-[(4-Chlorophenyl)sulfonyl]oxy-1,4-diphenylazetidin-2-one* (= *cis-2-Oxo-1,4-diphenylazetidin-3-yl 4-Chlorobenzenesulfonate*; *cis-14*). In analogy to *Exper. 5.1*, from *cis-13* (160 mg, 0.67 mmol), Hünig's base (203 mg, 2.35 mmol), and (4-chlorophenyl)sulfonyl chloride (495 mg, 2.35 mmol). Crystallization ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ /hexane): 259 mg (94%) of *cis-14*. White crystals. M.p. 209–211°. IR: 1765s, 1600w, 1500m, 1385m, 1190m, 1175m, 1085m, 870m, 830m, 700w. ^1H -NMR: 7.5–7.25 (m, 13 arom. H); 7.15–7.05 (m, 1 arom. H); 5.85 (d, $J = 5.0$, H–C(3)); 5.34 (d, $J = 5.0$, H–C(4)). ^{13}C -NMR ((D_6)DMSO): 160.0 (s, C=O); 139.8, 136.2, 133.6, 131.9 (4s, 4 arom. C); 129.8, 129.2, 129.0, 128.7, 128.4, 127.8, 124.7, 117.1 (8d, 14 arom. C); 79.8 (d, C(3)); 60.2 (d, C(4)). EI-MS: 413 (9, M^+), 296 (25), 295 (12), 294 (67), 239 (14), 238 (86), 221 (9), 183 (15), 182 (100), 181 (31), 180 (59), 175 (22), 159 (27), 152 (11), 131 (34). Anal. calc. for $\text{C}_{21}\text{H}_{16}\text{ClNO}_4\text{S}$ (413.88): C 60.94, H 3.90, Cl 8.57, N 3.38, S 7.75; found: C 60.81, H 3.79, Cl 8.29, N 3.38, S 7.97.

5.3. 6-exo-[(4-Chlorophenyl)sulfonyl]oxy-2,2-dimethyl-3-endo-(methylsulfanyl)-5-phenyl-4-thia-1-azabicyclo[3.2.0]heptan-7-one (= 2,2-Dimethyl-3-endo-(methylsulfanyl)-7-oxo-5-phenyl-4-thia-1-azabicyclo[3.2.0]hept-6-yl 4-Chlorobenzenesulfonate; *endo-17a*) and 6-exo-[(4-Chlorophenyl)sulfonyl]

l[oxy]-2,2-dimethyl-3-exo-(methylsulfanyl)-5-phenyl-4-thia-1-azabicyclo[3.2.0]heptan-7-one (**exo-17a**). Into a soln. of the diastereoisomer mixture of **16** (139 mg, 0.47 mmol) in CH₂Cl₂ (5 ml) at 0°, Et₃N (95 mg, 0.94 mmol) was added. After 10 min, a soln. of (4-chlorophenyl)sulfonyl chloride (149 mg, 0.705 mmol) in CH₂Cl₂ (1 ml) was added dropwise. The mixture was maintained at r.t. overnight; then, CH₂Cl₂ (30 ml) was added. The soln. was washed with brine, dried (Na₂SO₄), filtered, and concentrated *i.v.* The residue, after purification by CC (hexane/Et₂O 15:1), afforded 197 mg (90%) of **17** as a 2:1 mixture of diastereoisomers. Prep. TLC provided **endo-17a** and **exo-17a** in pure form.

Data of endo-17a. White crystals. M.p. 122–123°. IR: 1785s, 1590w, 1480w, 1385m, 1270m, 1190m, 1180m, 1090m, 990w, 890m, 825m, 700m, 650m. ¹H-NMR: 7.5–7.3 (*m*, 9 arom. H); 5.84 (*s*, H–C(6)); 4.53 (*s*, H–C(3)); 2.26 (*s*, MeS); 1.89 (*s*, *endo*-Me–C(2)); 1.20 (*s*, *exo*-Me–C(2)). ¹³C-NMR: 166.4 (*s*, C=O); 140.7, 136.6, 134.1 (3*s*, 3 arom. C); 129.4, 129.0, 128.5, 128.1, 126.4 (5*d*, 9 arom. CH); 87.4 (*d*, C(6)); 80.6 (*s*, C(5)); 72.9 (*d*, C(3)); 70.8 (*s*, C(2)); 27.3, 21.3 (2*q*, Me₂C); 16.7 (*q*, MeS). CI-MS: 487 (7), 472 (9), 470 (19, [*M* + 1]⁺), 240 (9), 239 (14), 238 (100), 145 (6). Anal. calc. for C₂₀H₂₀ClNO₄S₃ (470.03): C 51.11, H 4.29, N 2.98, S 20.46; found: C 51.40, H 4.10, N 3.07, S 20.93.

Data of exo-17a. White crystals. M.p. 131.5–132.7°. IR: 2980m, 2930w, 1785s, 1590m, 1480m, 1450m, 1400m, 1390m, 1375m, 1275m, 1260m, 1190s, 1180m, 1090s, 1050m, 1000m, 895m, 825m, 700m, 650m, 625m. ¹H-NMR: 7.5–7.25 (*m*, 9 arom. H); 5.71 (*s*, H–C(6)); 4.57 (*s*, H–C(3)); 2.27 (*s*, MeS); 1.81 (*s*, *endo*-Me–C(2)); 1.01 (*s*, *exo*-Me–C(2)). ¹³C-NMR: 165.1 (*s*, C=O); 140.7, 136.1, 134.0 (3*s*, 3 arom. C); 129.4, 129.0, 128.5, 127.9, 126.5 (5*d*, 9 arom. CH); 88.2 (*d*, C(6)); 79.1 (*s*, C(5)); 70.9 (*d*, C(3)); 69.1 (*s*, C(2)); 25.3, 22.1 (2*q*, Me₂C); 17.3 (*q*, MeS). CI-MS: 491 (6), 490 (10), 489 (48), 488 (23), 487 (100, [*M* + NH₄]⁺), 472 (5), 470 (11, [*M* + 1]⁺).

5.4. 2,2-Dimethyl-3-endo/exo-(methylsulfanyl)-6-exo-[(2,4-dinitrophenyl)sulfonyl]oxy-5-phenyl-4-thia-1-azabicyclo[3.2.0]heptan-7-one (= 2,2-Dimethyl-3-(methylsulfanyl)-7-oxo-5-phenyl-4-thia-1-azabicyclo[3.2.0]hept-6-yl 2,4-Dinitrobenzenesulfonate; **17b**). In analogy to *Exper. 5.3*, from **16** (2:1 mixture of 3-*endo*- and 3-*exo*-isomers; 267 mg, 0.9 mmol) and (2,4-dinitrophenyl)sulfonyl chloride (360 mg, 1.35 mmol), 410 mg (87%) of **17b** were obtained as a 2:1 mixture of diastereoisomers. Pale yellow foam. M.p. 55–57°. IR: 3090w, 3030w, 3010w, 2920w, 1785s, 1610w, 1560s, 1545s, 1450w, 1410m, 1390m, 1375m, 1350s, 1270w, 1190s, 1090m, 1050w, 1000w, 980m, 890m, 830m, 700m, 645m, 620m. ¹H-NMR (3-*endo*/3-*exo*-isomers, 2:1): 8.6–8.55 (*m*, 1 arom. H); 8.5–8.4 (*m*, 1 arom. H); 8.15–8.0 (*m*, 1 arom. H); 7.45–7.15 (*m*, 5 arom. H); 5.98, 5.90 (2*s*, H–C(6)); 4.62, 4.55 (2*s*, H–C(3)); 2.28, 2.27 (2*s*, MeS); 1.89, 1.82, 1.23, 1.03 (4*s*, Me₂C). ¹³C-NMR: 165.5, 164.2 (2*s*, C=O); 150.3, 147.8, 147.7, 136.2, 135.8, 134.6, 134.4 (7*s*, 4 arom. C); 132.7, 132.6, 128.7, 128.5, 128.2, 127.9, 127.8, 126.8, 126.4, 126.2, 120.1 (11*d*, 8 arom. CH); 89.8, 88.9 (2*d*, C(6)); 80.4, 78.9 (2*s*, C(5)); 72.8, 70.9 (2*s*, C(2)); 71.0, 69.2, (2*d*, C(3)); 27.2, 22.0, 21.6, 21.2 (4*q*, Me₂C); 17.3, 16.6 (2*q*, MeS). CI-MS: 545 (17), 544 (23), 543 (100, [*M* + NH₄]⁺), 527 (5), 526 (10, [*M* + 1]⁺), 511 (3). Anal. calc. for C₂₀H₁₉N₃O₈S₃ (525.58): C 45.71, H 3.64, N 7.99, S 18.30; found: C 45.86, H 3.74, N 8.18, S 18.09.

6. Substitution Reaction of **14** with Azides. 6.1. *cis*-3-Azido-1,4-diphenylazetidin-2-one (**cis-15**) [24b]. A mixture of *trans*-**14** (100 mg, 0.24 mmol) and NaN₃ (156 mg, 2.4 mmol) in DMF (5 ml) was heated to 55° for 1 d. Then, AcOEt (30 ml) and brine (10 ml) were added. The aq. phase was extracted with AcOEt (3 × 10 ml). The combined org. phase was dried (Na₂SO₄), filtered, and concentrated *in vacuo*. The residue, after purification by CC (hexane/Et₂O 20:1), furnished 53 mg (82%) of **cis-15**. White crystals. M.p. 130–131° ([24b]: 132–134°). IR: 2120s, 1760s, 1600w, 1500m, 1385m, 1135m, 700w. ¹H-NMR: 7.35–7.3 (*m*, 3 arom. H); 7.3–7.2 (*m*, 6 arom. H); 7.05–7.0 (*m*, 1 arom. H); 5.26 (*d*, *J* = 5.4, H–C(3)); 4.97 (*d*, *J* = 5.4, H–C(4)). ¹³C-NMR: 161.4 (*s*, C=O); 136.0, 132.4 (2*s*, 2 arom. C); 129.1, 129.0, 128.8, 127.4, 124.7, 117.4 (6*d*, 10 arom. CH); 67.3 (*d*, C(3)); 60.6 (*d*, C(4)). CI-MS: 283 (14), 282 (100, [*M* + NH₄]⁺), 265 (3, [*M* + 1]⁺), 254 (31), 237 (12). Anal. calc. for C₁₅H₁₂N₄O (264.29): C 68.17, H 4.58, N 21.20; found: C 68.26, H 4.38, N 20.93.

6.2. *trans*-3-Azido-1,4-diphenylazetidin-2-one (**trans-15**). *a*) In analogy to *Exper. 6.1*, from **cis-14** (166 mg, 0.4 mmol) and NaN₃ (260 mg, 4 mmol), 92 mg (87%) of **trans-15** were obtained. Colorless oil ([24b]: m.p. 81–83°). IR: 3060w, 3030w, 3005w, 2920w, 2115s, 1760s, 1600s, 1500s, 1490s, 1455m, 1380s, 1355m, 1330m, 1320m, 1300m, 1280m, 1260m, 1145s, 1105w, 1090w, 1080w, 1030w, 990w, 900w, 850m, 700s, 690s, 630w, 605m. ¹H-NMR: 7.45–7.25 (*m*, 9 arom. H); 7.15–7.05 (*m*, 1 arom. H); 4.88 (*d*, *J* = 2.1, H–C(3)); 4.52 (*d*, *J* = 2.1, H–C(4)). ¹³C-NMR: 161.3 (*s*, C=O); 136.6, 135.2 (2*s*, 2 arom. C); 129.3, 129.2,

Table 1. Crystallographic Data for Compounds endo-6a, 7b, 9, and exo-16

	endo-6a	7b	9	exo-16
Crystallized from	hexane/Et ₂ O	hexane/Et ₂ O	hexane/Et ₂ O	CH ₂ Cl ₂ /Et ₂ O/hexane
Empirical formula	C ₁₆ H ₁₉ NO ₃ S ₂	C ₁₇ H ₂₁ NO ₃ S ₂	C ₁₅ H ₁₇ Cl ₂ NO ₃ S ₂	C ₁₄ H ₁₇ NO ₂ S ₂
Formula weight [g/mol]	337.45	351.48	362.33	295.41
Crystal color, habit	colorless, prism	colorless, prism	colorless, prism	colorless, prism
Crystal dimensions [mm]	0.19 × 0.43 × 0.44	0.26 × 0.37 × 0.42	0.16 × 0.40 × 0.46	0.30 × 0.32 × 0.40
Temp. [K]	297(1)	213(1)	213(1)	173(1)
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>Pbcn</i>
<i>Z</i>	4	4	8	8
Reflections for cell determination	25	25	25	24
2 θ Range for cell determination [°]	30–36	30–34	28–32	15–22
Unit cell parameters:				
<i>a</i> [Å]	10.426(4)	5.9871(12)	13.6699(15)	10.047(3)
<i>b</i> [Å]	11.718(2)	18.954(4)	13.0980(15)	11.423(3)
<i>c</i> [Å]	13.928(2)	16.040(2)	18.965(2)	24.770(4)
β [°]	98.50(2)	98.733(15)	90	90
<i>V</i> [Å ³]	1682(1)	1799.2(6)	3395.7(1)	2842(1)
<i>D_x</i> [g cm ^{−3}]	1.332	1.297	1.417	1.380
μ (MoK α) [mm ^{−1}]	0.327	0.309	0.626	0.371
Scan type	ω	ω	ω	ω
2 θ _(max) [°]	55	55	55	60
Total reflections measured	5146	4930	4993	5362
Symmetry-independent reflections	3858	4126	3907	4178
Reflections with <i>I</i> > 2 σ (<i>I</i>)	2600	3098	2472	3323
Reflections used in refinement	3857	4126	3907	4178
Parameters refined	203	212	197	179
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>) reflections]	0.0476	0.0460	0.0541	0.0348
^w <i>R</i> (<i>F</i> ²) (all data)	0.1201	0.1085	0.1263	0.0983
Weighting parameters [<i>a</i> ; <i>b</i>] ^{a)}	0.0499; 0.4814	0.0190; 1.2021	0.0419; 4.0593	0.0477; 0.6891
Goodness of fit	1.020	1.016	1.006	1.038
Final Δ _{max} /σ	0.001	0.001	0.001	0.001
$\Delta\rho$ (max; min) [e Å ^{−3}]	0.31; −0.20	0.62; −0.31	0.57; −0.28	0.43; −0.19

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

129.1, 125.9, 124.6, 117.4 (6d, 10 arom. CH); 72.3 (d, C(3)); 62.8 (d, C(4)). CI-MS: 299 (100, $[M + 1 + 2 \text{NH}_3]^+$), 282 (73, $[M + \text{NH}_4]^+$), 271 (39), 265 (2, $[M + 1]^+$), 254 (27), 237 (8). Anal. calc. for $\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}$ (264.29): C 68.17, H 4.58, N 21.20; found: C 68.18, H 4.67, N 20.95.

b) In analogy to *Exper. 6.1*, from *cis*-**14** (83 mg, 0.2 mmol) and LiN_3 (98 mg, 2 mmol), 52 mg (98%) of *trans*-**15** were obtained.

7. *Attempted Substitution Reactions of 17*. In analogy to *Exper. 6*, the mixture of diastereoisomers **17a** (ca. 0.3 mmol) and NaN_3 (ca. 3 mmol) in DMF (5 ml) was heated to 50–60°. After usual workup, only starting material was recovered. Under similar conditions, reactions with **17b** and **17c** were also not successful, and, in addition to starting material, significant amounts of **2a** were isolated.

8. *X-Ray Crystal-Structure Determinations of endo-6a, 7b, 9, and exo-16* (see *Table* and *Figs. 1–3*)⁸⁾. The measurements for compounds *endo*-**6a**, **7b**, and **9** were conducted on a *Nicolet R3* diffractometer, those for compound *exo*-**16** on a *Rigaku AFC5R* diffractometer and a 12-kW rotating anode generator, using graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. In all cases, equivalent reflections were merged. Data collection and refinement parameters are given in the *Table*. The structures were solved by direct methods using SHELXS86 [34], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. In the cases of **9** and *exo*-**16**, the H-atom of the NH and OH group, resp., were placed in the positions indicated by a difference electron-density map, and their positions were allowed to refine together with an isotropic displacement parameter. All other H-atoms in all structures were placed in geometrically calculated positions and refined by 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 atom (1.5 U_{eq} for the Me groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. One reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement of the structure of *endo*-**6a**.

Neutral-atom scattering factors for non-H-atoms were taken from [35a], and the scattering factors for H-atoms were taken from [36]. Anomalous dispersion effects were included in F_c [37]; the values for f' and f'' were those of [35b]. The values of the mass-attenuation coefficients are those of [35c]. All calculations were performed using the SHELXL97 [38] program.

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⁸⁾ CCDC-933805–933808 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre* via www.ccdc.cam.ac.uk/data_request/cif.

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