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REACTIVITY OF *N*-ALKYLTHIIRANIMINES TOWARD SIMPLE NUCLEOPHILES AND ISO(THIO)CYANATES

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Abstract – Hydrolysis of *N*-(1-dimethylcarbamoyl-1-methylethyl)-thiiranimines occurs with S-C(sp^2) ring cleavage while attack of hydrochloric acid results in S-C(sp^3) ring opening. The latter mode of ring opening is also observed in [3+2] cycloaddition reactions with iso(thio)cyanates where the heterocumulene reacts *via* the C-chalcogen bond; only a sterically less hindered isopropyl substituted thiiranimine adds to the C=N bond in isocyanates to yield 4-thiohydantoins. The cycloadducts give a variety of hydrolysis products, in particular imidazo[2,1-*b*]oxazoles and –thiazoles, oxazolones, and stable thietes. Insertion of a thiocarbonyl into an isopropyl CH bond is observed yielding an annulated cyclopropane unit.

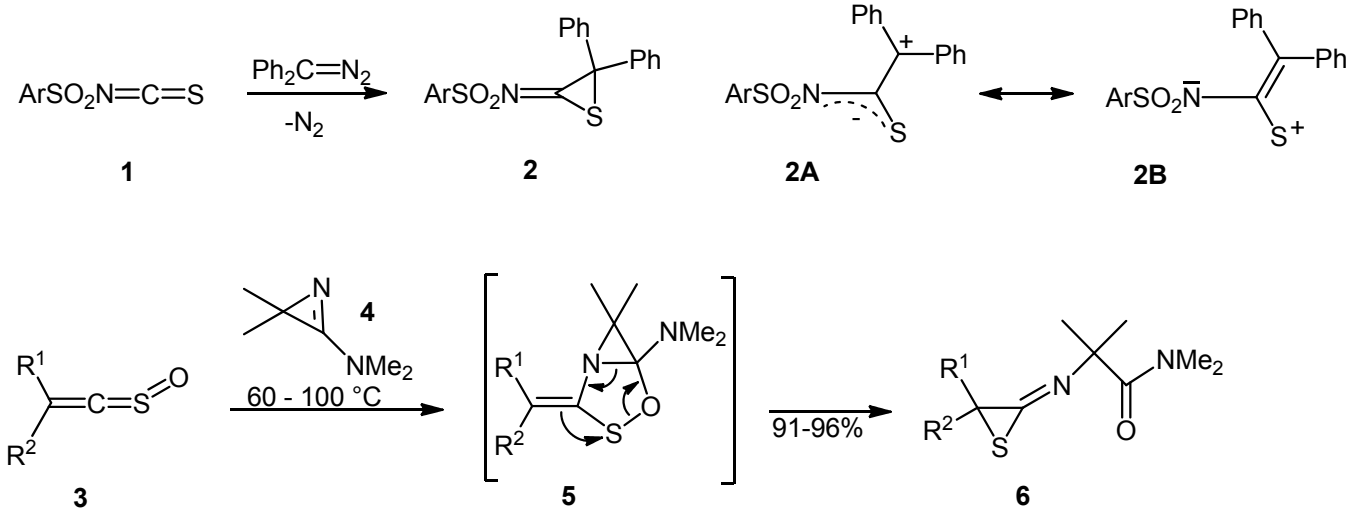
INTRODUCTION

The study of small ring compounds has played an important role in the development of our understanding of reactivity and bonding in organic chemistry.[1] In handling these systems, problems resulting from ring strain are less pronounced for sulfur-containing compounds because bonds to carbon are long and smaller angles are tolerated.[2] So α-thiolactones can be isolated in contrast to their unstable oxygen congeners[3] and, in contrast to the unknown oxiranimines,[4] stable *N*-sulfonyl-thiiranimines (**2**) can be obtained from arenesulfonyl isothiocyanates (**1**) and diphenyldiazomethane (Scheme 1).[4-6] A thiadiazoline as [3+2] cycloadduct can be assumed as intermediate and a thiadiazoline also allows access to a silyl substituted thiiranimine where the exocyclic nitrogen is part of an azine unit.[7] In contrast to these "rational" methods,

Dedicated to Professor Albert Padwa on the occasion of his 75th birthday

an unexpected route to thiiranimines **6** employs the reaction of thioketene *S*-oxides **3** with aminoazirines such as **4**.[8] The reaction is apparently initiated by a [3+2] cycloaddition of the sulfine unit in **3** to the C=N bond to give oxathiazolidines **5** as intermediates. This reactivity of *S*-oxides **3** is remarkable as non-cumulated sulfines only rarely react as 1,3-dipoles.[9,10]

So far, only the reactivity of sulfonyl derivatives **2** was probed. The uniform feature is ring-opening by cleavage of the S-C(sp^3) bond.[4] This is in line with a polarization as in diheterotrimethylenemethanes[11] **2A**,**B** where the negative charge is efficiently stabilized by the electron-withdrawing sulfonyl group (Scheme 1). In contrast, in thiiranimines **6** the electronic effect of the carboxamido group is certainly negligent and so the *N*-substituent is of the alkyl type. This should lead to a different reaction behavior. This consideration marks the starting point of the present study.



3-**6a**: $R^1=R^2=Me_2C(CH_2)_3CMe_2$
b: $R^1=R^2=t$-Bu
c: $R^1=t$-Bu, $R^2=i$-Pr

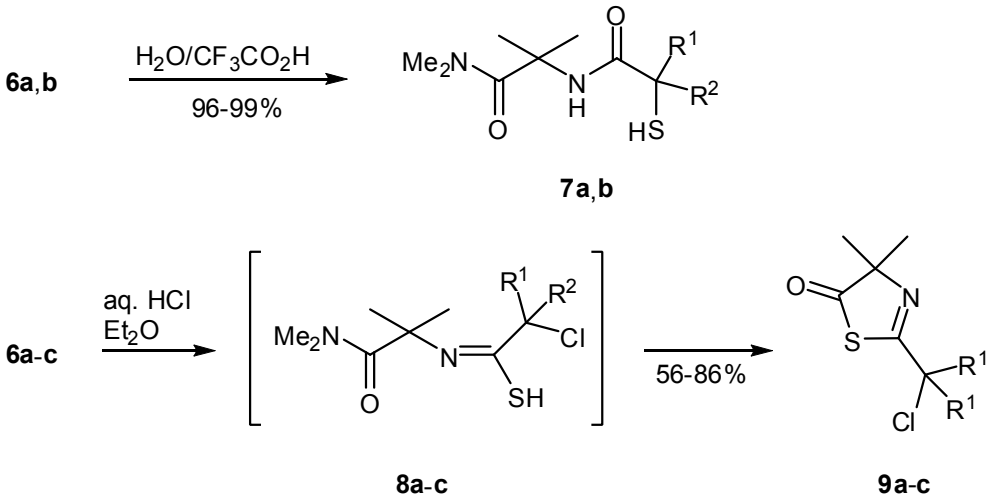
Scheme 1. Syntheses of thiiranimines **2**, **6**

RESULTS AND DISCUSSION

In contrast to thiiranimines **2**, the bulky *C*-alkyl substituents in **6** prevent an uncatalyzed reaction with methanol, but hydrolytic ring-opening of **6** is achieved under catalysis by trifluoroacetic acid (Scheme 2). The spectroscopic data allow to assign structure **7** to the water addition product. Thus, ring opening occurs *via* primary attack of water at the imino carbon and leads to S-C(sp^2) ring opening.

Aqueous hydrochloric acid and **6** give only trace amounts of **7**, but mainly thiazolinones **9**. This means that a nucleophilic attack of chloride on C-3 prevails in spite of the extreme steric screening of this carbon

and then sulfur is the best possible leaving group leading to **8** as a result of S-C(sp^3) bond cleavage formally as in thiiranimines **2**.[4] The nucleophilic thiol sulfur in **8** finally displaces the amino group to give recyclization product **9** (Scheme 2). The structure of **9a** was unambiguously established by a singe-crystal X-ray study (Figure 1).[12]



7-9a: $R^1+R^2=Me_2C(CH_2)_3CMe_2$
b: $R^1=R^2=t$-Bu
c: $R^1=t$-Bu, $R^2=i$-Pr

Scheme 2. Attack of simple nucleophiles on thiiranimines **6**

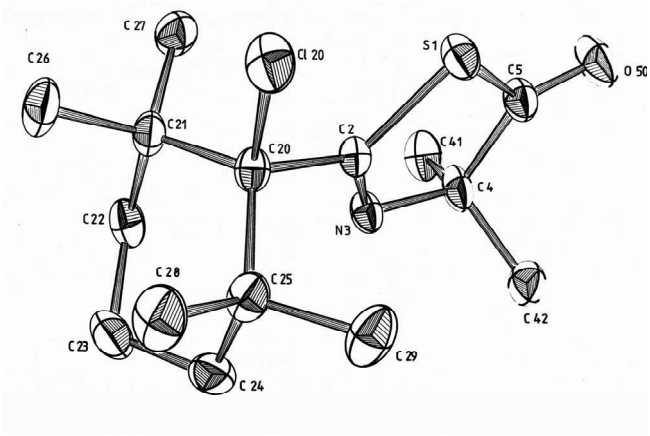


Figure 1. Perspective ORTEP presentation of the molecular structure of thiazolinone **9a** (hydrogen atoms not shown)

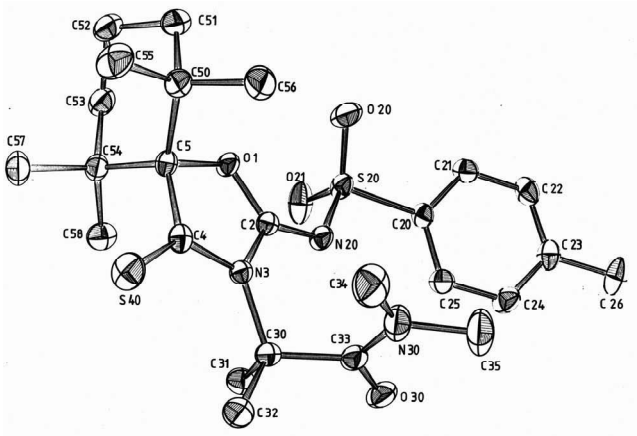


Figure 2. Perspective ORTEP presentation of the molecular structure of 2-imino-oxazolidine-4-thione **11a** (hydrogen atoms not shown)

N-Sulfonyl-thiiranimines **2** give [3+2] cycloadducts with enamines, ynamines, and aldehydes, but do not react with iso(thio)cyanates.[4] In contrast, thiiranimines **6** proved unreactive toward ynamines, acetylene

dicarboxylate, isonitriles, or tetracyanoethylene, but undergo a smooth reaction with isocyanates as well with isothiocyanates. Thus, the symmetrically substituted thiiranimines **6a**,**b** react with sulfonylisocyanates **10a,b** at 0 °C and with aryl isocyanates **10c**,**d** on gentle warming to give 1:1 cycloadducts **11** (Scheme 3). This structure is derived from the spectroscopic data and from an X-ray investigation of **11a** (Figure 2).[13] So the isocyanates **10** show the unusual reaction across their carbonyl group.[14] The same reaction behavior is seen for the very reactive sulfonylisocyanates **10e**,**f**. However, here the exocyclic sulfonyl moiety is easily hydrolyzed on chromatographic work-up and so yields are low (starting from **10e**) or cycloadducts **11h**,**i** (starting from **10f**) are only seen in the crude reaction mixture. Hydrolytic loss of the sulfonyl moiety leads to bicyclic compounds **12**; apparently the initial product of hydrolysis is an imino compound (**11** with R^3 = H) which then attacks the exocyclic amide unit with extrusion of dimethylamine and cyclization (Scheme 3). This reaction pathway is substantiated by independent hydrolysis experiments with **11a**,**b** to give **12a**,**b**. Structure **12** is proven by the X-ray structural investigation of **12a** (Figure 3).[15] Under the more forcing conditions of half-concentrated hydrochloric acid, also the *N*-aryl-substituted oxazolin-4-thiones **11d**,**e** can be hydrolyzed. These reaction conditions result in complete displacement of the exocyclic imino group by the oxo unit of **14** and by a transition from the dimethylcarbamoyl to a monosubstituted amide derived from the original isocyanate (Scheme 3). Here, we assume the intermediacy of **13** with a tetrahedral carbon resulting from attack of water on the imino carbon. The high density of heteroatoms again called for a single-crystal X-ray study which proved the structure of **14a** (Figure 4).[16]

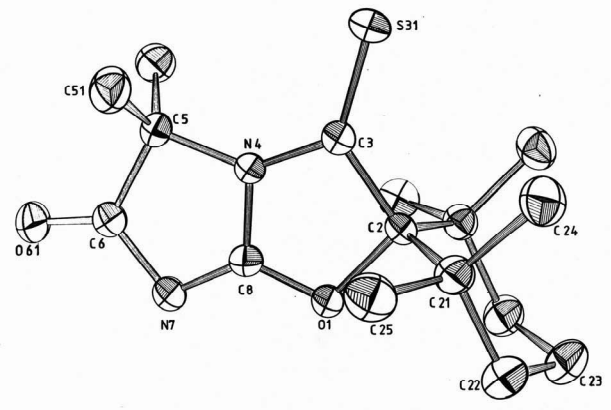


Figure 3. Perspective ORTEP presentation of the molecular structure of imidazo[2,1-b]oxazol-4-one **12a** (hydrogen atoms not shown)

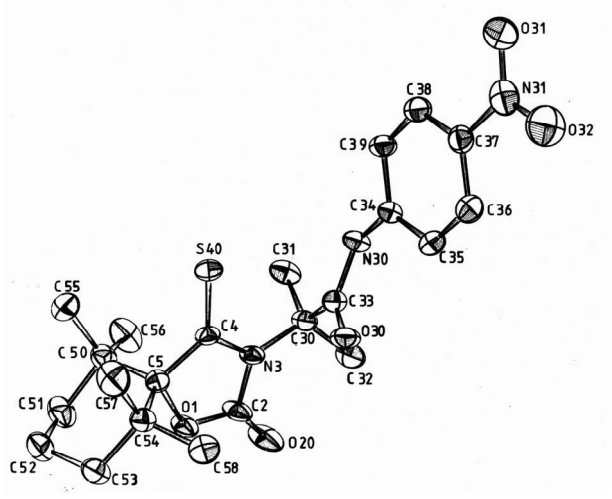
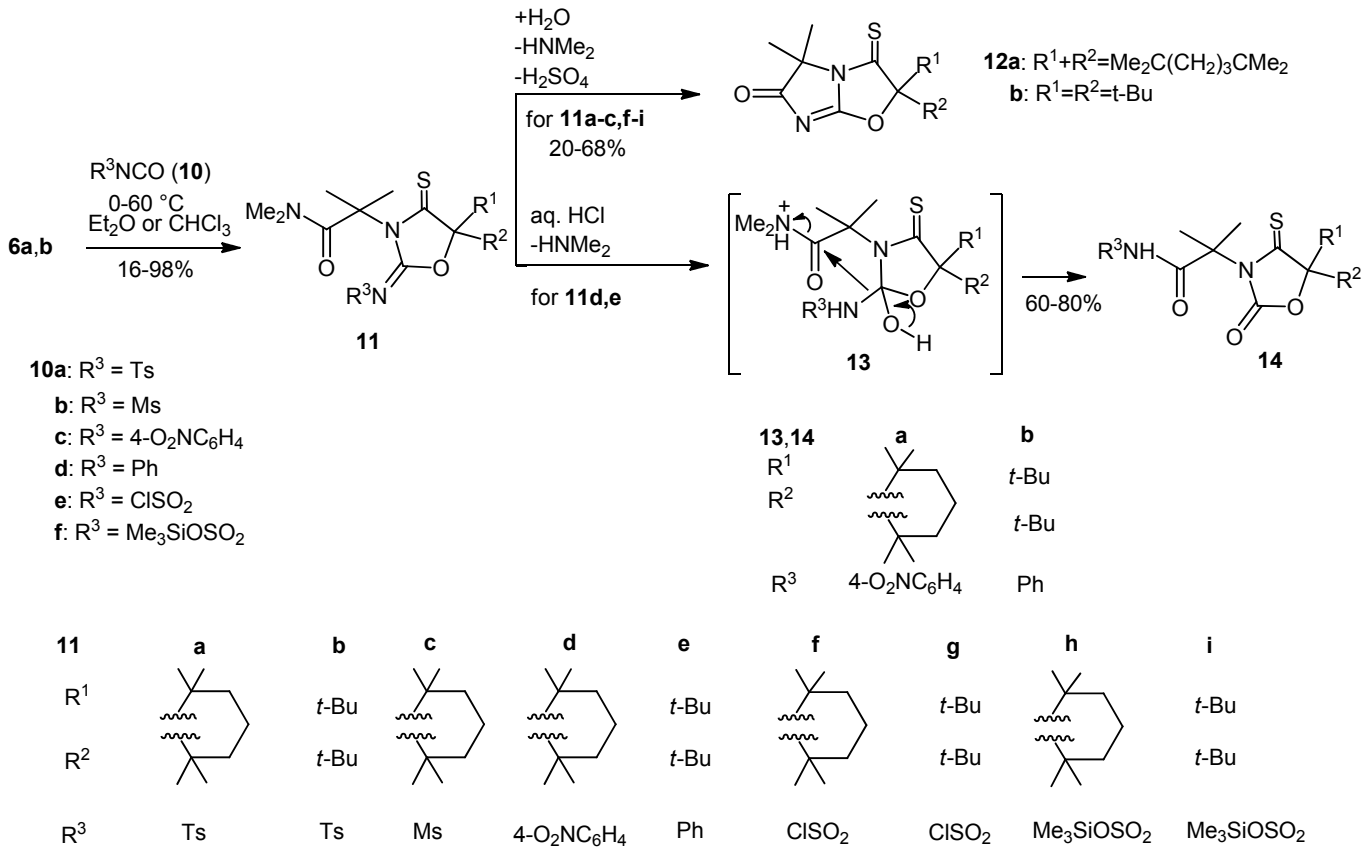


Figure 4. Perspective ORTEP presentation of the molecular structure of 4-thioxo-oxazolidin-2-one **14a** (hydrogen atoms not shown)

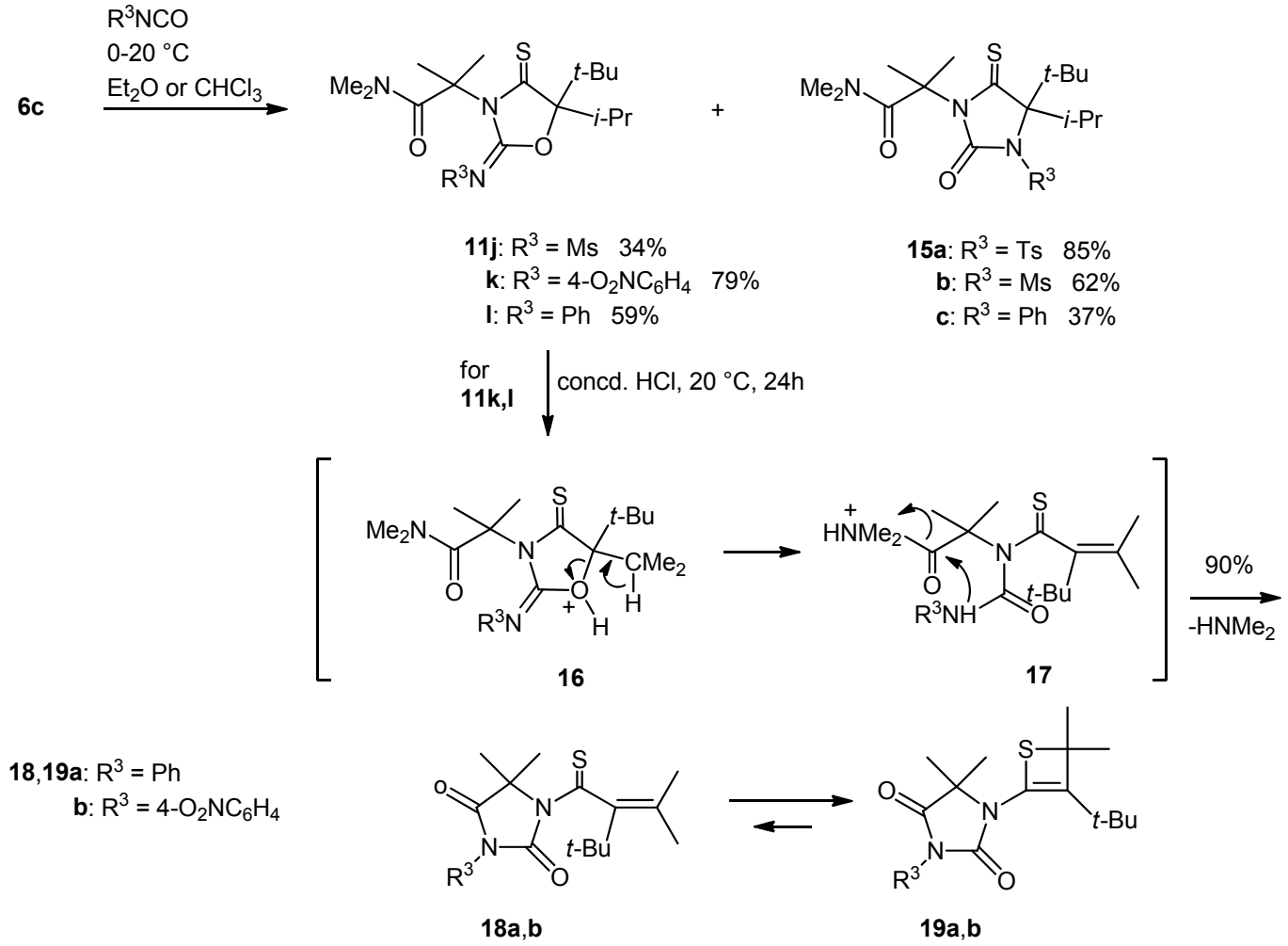


Scheme 3. Cycloaddition of thiiranimines **6a,b** to isocyanates **10** and hydrolysis products

The sterically less hindered thiiranimine **6c** gives two isomeric 1:1 cycloadducts with isocyanates **10**. One and the only one starting from **10c** is again a 2-imino-oxazolidine-4-thione **11** (Scheme 4). The second product is the corresponding product **15** of cycloaddition across the C=N bond of the isocyanate as finally confirmed by an X-ray study (Figure 5).[17] It appears that due to the smaller substituent on C-5 of the five-membered ring Pitzer tension is reduced and allows the C-5 substituents to be accommodated next to the substituted ring nitrogen N1. However, a relatively long N1-C5 bond of 151.6 pm should be noted.

Acid-catalyzed hydrolysis of cycloadducts **11k**,**l** with R^2 = *i*-Pr should be expected to give again oxazolidinones **14**. However, in striking contrast to expectation, the reaction mixture turns immediately orange and work-up leads to an orange-colored oil with a complex ^{1}H-NMR spectrum. From this oil, colorless crystals can be isolated which allowed an X-ray structural investigation to reveal thiete structure **19a** (Figure 6).[18] Now the color of the oil can be explained by the thione unit in valence tautomer **18** (Scheme 4). We see here an amazing β-elimination involving an alkyl CH bond from **16** to **17** and then an enethione/thiete (**18**/**19**) equilibrium. Such equilibria have been seen before,[19] but the present case is unusual as it involves the thiocarbonyl of a thioamide moiety other than the usual stabilization of thietes

by aryl substituents. In previous studies, this type of thiete has only been invoked as an intermediate.[20]



Scheme 4. Cycloaddition of thiiranimine **6c** to isocyanates **10** and hydrolysis products **18/19**

The noteworthy generation of a thiete from the vicinal thione/isopropyl units in **11k**,**l** motivated to search for the same effect in related structures such as in **15**. But when **15c** is treated with aqueous hydrochloric acid just as it had been done for **11k**,**l**, there is no orange color at all. From the complex product mixture, a compound lacking the dimethylamino unit can be isolated. But the ^{13}C NMR spectrum shows three quaternary aliphatic carbons which is not compatible with **18** or other compounds found earlier. The solution is again brought by an X-ray structural investigation (Figure 7).[21] We are dealing with a tricyclic compound **21** where the original isopropyl group shows up as annulated cyclopropane (Scheme 5). Our rational is the unusual insertion of the thiocarbonyl group into the isopropyl CH bond to give intermediate **20**. This may look like a light-induced process rather than acid-catalyzed,[22] but in a control experiment the conversion of **15c** into **21** could not be induced photochemically. The thiol in **20** finally attacks the amide unit, displaces the dimethylamino group and leads to formation of a γ-thiolactone.

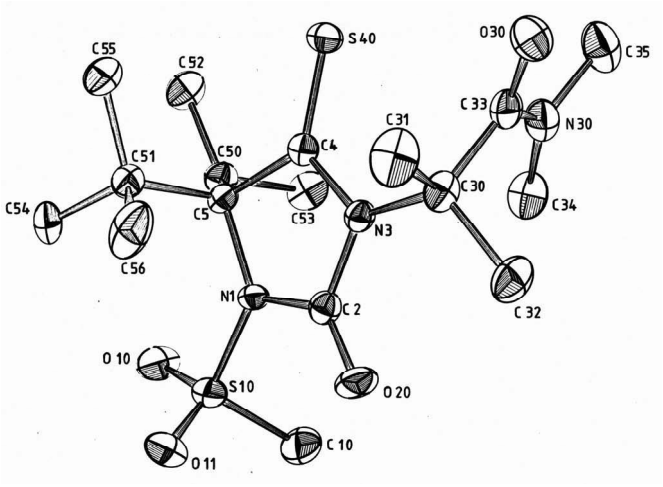


Figure 5. Perspective ORTEP presentation of the molecular structure of 4-thioxo-imidazolidin-2-one **15b** (hydrogen atoms not shown)

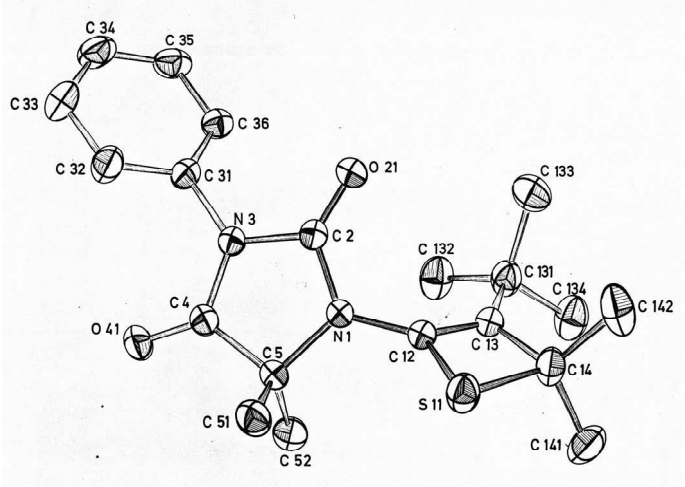
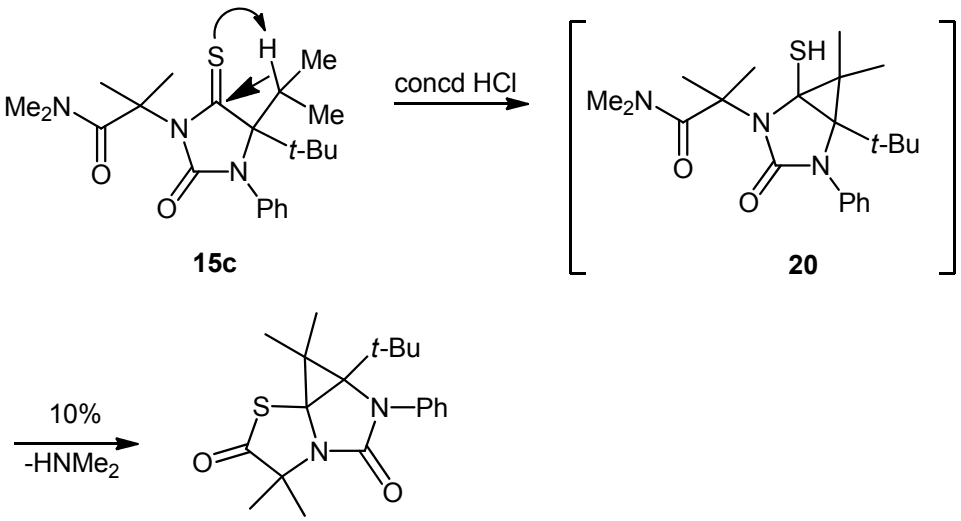
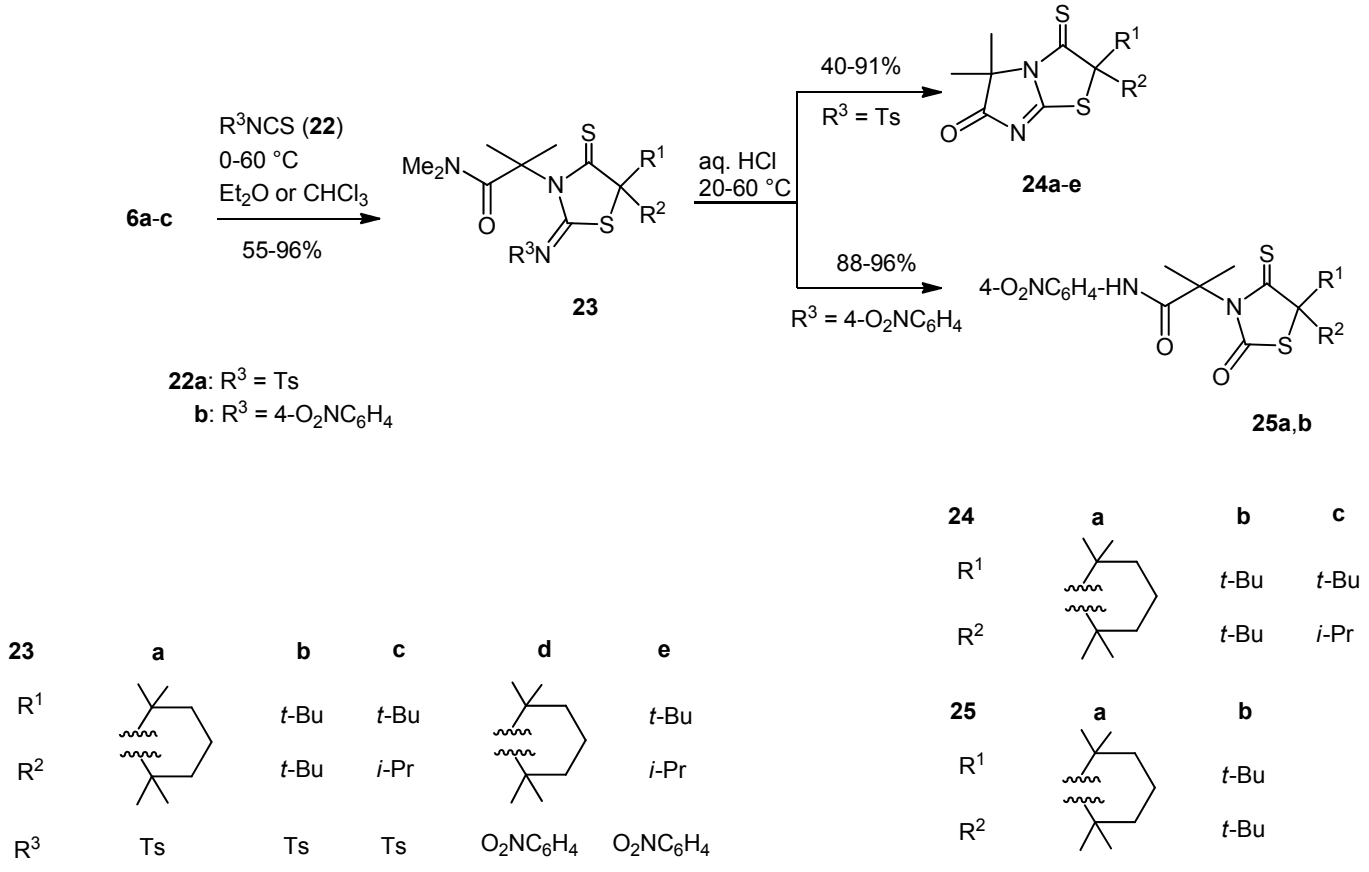


Figure 6. Perspective ORTEP presentation of the molecular structure of thiete **19a** (hydrogen atoms not shown)



Scheme 5. Hydrolysis of imidazolinone **15c** to give tricycle **21**



Scheme 6. Cycloaddition of thiiranimines **6a,b** to isothiocyanates **22** and hydrolysis products

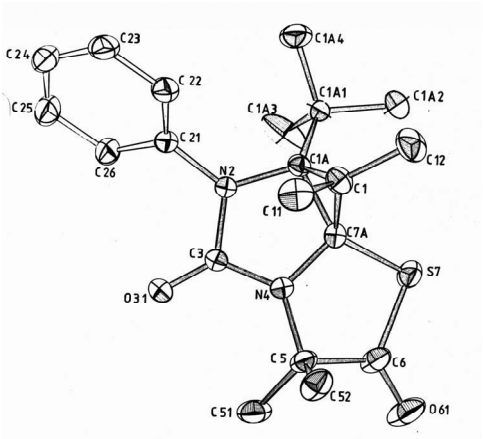


Figure 7. Perspective ORTEP presentation of the molecular structure of tricycle **21** (hydrogen atoms not shown)

Isothiocyanates are known to be less reactive than isocyanates,[23] but cycloadduct formation with thiiranimines **6** is possible, though for 4-nitrophenyl isothiocyanate (**22b**) heating to 60 °C is required. After isocyanates **10** show the preference for cycloaddition across the C=O bond, it is no surprise that isothiocyanates also enter into the reaction *via* their *C*-chalcogen bond to give [3+2] cycloadducts **23**

(Scheme 6). Structure assignment is suggested by the similarity of spectroscopic data, especially ^{13}C NMR shifts, to those of isocyanate cycloadducts **11** (vide supra). In some cases trace amounts of hydrolysis products are detected and hydrolysis can also be induced deliberately. Thus, the action of hydrochloric acid on *N*-tosyl derivatives **23a-c** yields bicycles **24a-c** as suggested by the similarity of spectroscopic data with those of **12a,b** and also the analogous reaction mechanism is invoked (cf. Scheme 3). Starting from 4-nitrophenyl derivatives **23d**,**e**, products **25** are formed by analogy with hydrolysis products **14** and again an intermediate of type **13** is plausible.

CONCLUSION

Thiiranimines **6** with their alkyl type *N*-substituent show a widely different reaction pattern from their *N*-sulfonyl congeners **2** though except for the trifluoroacetic acid-catalyzed hydrolysis of **6** both types of thiiranimines enter into reactions *via* cleavage of the C(sp^3)-S bond which is also the longest bond in the molecular structures.[5,8] However, the contrasting reactivity toward iso(thio)cyanates demonstrates that *N*-sulfonyl-thiiranimines **2** are mainly electrophilic while the thiiranimines **6** of the present study are in the first place nucleophilic. Thus, a wealth of heterocyclic structures is provided by the cycloaddition reactions and the subsequent hydrolysis experiments. A limitation is the need for bulky substituents to make thioketene *S*-oxides **3** isolable and use them in the synthesis of **6**. However, the different bond selectivity of **6a,b** vs. **6c** toward isocyanates shows that even with the presently possible substitution pattern different steric effects are seen. Moreover, it should not be underestimated that the bulky substituents certainly increase the stability of the products and e. g. may be crucial in the formation and stabilization of thietes **19** or to allow the highly unusual thermal insertion reaction in the formation of **21**.

EXPERIMENTAL

Melting points were determined on a Leitz hot-stage microscope and are uncorrected. IR spectra were recorded as KBr pellets or for oils as films between NaCl plates on Perkin-Elmer instruments 257, 299, and 399. ^1H- and ^{13}C-NMR spectra were recorded on Bruker spectrometers WH 270 and WM 400 with TMS as internal reference at $\delta = 0.00$ and using $CDCl_3$ as solvent. For ^{13}C-NMR spectra, only the significant shifts with $\delta > 50$ are given for characterization and all are inactive in the DEPT mode (quaternary carbons). MS spectra were obtained with a Varian CH7 with ionization energy 70 eV. X-ray measurements were carried out using a single-crystal CAD 4 (Enraf-Nonius; Cu-K_α radiation) or a Hilger & Watts instrument (Mo-K_α radiation). Preparative TLC (layer ca. 2 mm) was performed using silica PF_{254} (Merck). Isolated products were recrystallized from dichloromethane/*n*-hexane or diethyl ether/*n*-hexane unless noted otherwise. Petroleum ether (PE) had boiling point range 60-70 °C. Thiiranimines **6** were synthesized as reported before.[8] Isocyanates **10** were commercially available.

Isothiocyanate **22a**[24] and **22b**[25] were obtained using literature procedures.

Trifluoroacetic Acid-catalyzed Hydrolysis of Thiiranimines 6a,b.

A suspension of **6** (1 mmol) in CF_3COOH (1 mL) and H_2O (10 mL) was stirred at rt for 5 h when TLC showed no more **6**. The reaction mixture was extracted with $CHCl_3$. The extract was shaken with sat. aq. $NaHCO_3$ and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the product purified by preparative TLC (PE/EtOAc 1:2 v/v) to give **7a** (96%) and **7b** (99%).

***N,N*,2-Trimethyl-2-(2,2,6,6-tetramethyl-1-thio-cyclohexanecarbonyl)aminopropionamide (7a):** mp 132 °C; IR 3320, 2560, 1640, 1450, 1005 cm^{-1}; ^1H NMR δ 0.93, 1.28 (each s, 6H, ring-CMe_2), 1.66 (s, 6H, CMe_2), 1.77 (s, 1H, SH), 2.6-1.6 (br, 6H, 3 CH_2), 3.06 (s, 6H, NMe_2), 9.0 (br, 1H, NH); ^{13}C NMR δ 57.7(C-NH), 70.8 (C-SH), 171.9 (C=O), 173.6 (C=O). Anal. Calcd for $C_{17}H_{32}N_2O_2S$; C, 62.14; H, 9.84; N, 8.53; S, 9.76. Found: C, 62.18; H, 9.77; N, 8.36; S, 9.69.

2-(1-*tert*-Butyl-2,2-dimethyl-1-thio-butyryl)amino-*N,N*-2-trimethylpropionamide (**7b**): mp 102 °C; IR 3300, 1630, 1400 - 1500 cm^{-1}; ^1H NMR δ 1.27 (s, 18H, *t*-Bu_2), 1.65 (s, 6H, CMe_2), 2.00 (s, 1H, SH), 3.06 (s, 6H, NMe_2), 8.57 (br,1 H, NH); ^{13}C NMR δ 57.5, 73.6 (C-SH), 171.0 , 173.5. Anal. Calcd for $C_{16}H_{32}N_2O_2S$; C, 60.70; H, 10.21; N, 8.85; S, 10.13. Found: C, 60.88; H, 10.01; N, 8.59; S, 9.86.

Hydrochloric Acid-catalyzed Hydrolysis of Thiiranimines 6a-c.

6 (1 mmol) in Et_2O (5 mL) and 2 M HCl (2 mL) were mixed at rt. Control by TLC showed immediate reaction. The mixture was washed with sat. aq. $NaHCO_3$ and dried (Na_2SO_4). After preparative TLC (PE/EtOAc 1:2 v/v) gave **9a** (86%), **9b** (50%), and **9c** (85%).

2-(1-Chloro-2,2,6,6,-tetramethylcyclohexyl)-4,4-dimethyl-2-thiazolin-5-one (9a): mp 98 °C; IR 1700, 1600 cm^{-1}; ^1H NMR δ 1.08, 1.32, 1.42 (each s, 6H, CMe_2), 2.63 – 1.63 (br, 6H, 3 CH_2); ^{13}C NMR δ 86.6, 91.1, 169.6 (C=N), 213.0 (C=O); MS *m/z* 273 (M^+ - CO, 20), 237 (M^+ - CO - HCl, 100). Anal. Calcd for $C_{15}H_{24}ClNOS$; C, 59.67; H, 8.03; N, 4.64; S, 10.64, Cl 11.74. Found: C, 59.43; H, 8.00; N, 4.55; S, 10.68, Cl 11.41.

2-(1-*tert*-Butyl-1-chloro-2,2-dimethylpropyl)-4,4-dimethyl-2-thiazolin-5-one (9b): mp 66 °C; IR 1700, 1600 cm^{-1}; ^1H NMR δ 1.32 (s, 18H, *t*-Bu_2), 1.42 (s, 6H, ring-CMe_2). Anal. Calcd for $C_{14}H_{24}ClNOS$; C, 58.00; H, 8.36; N, 4.83; S, 11.06, Cl 12.24. Found: C, 58.21; H, 8.31; N, 4.58; S, 10.56, Cl 12.12.

2-(1-Chloro-1-isopropyl-2,2-dimethylpropyl)-4,4-dimethyl-2-thiazolin-5-one (9c): oil; IR (film) 1710, 1600 cm^{-1}; ^1H NMR δ 1.01, 1.13 (each d, *J* = 7 Hz, 6H, *i*-Pr), 1.20 (s, 9H, *t*-Bu), 1.38 (s, 6H, CMe_2), 2.83 (septet, *J* = 7 Hz, 1H, *i*-Pr). Anal. Calcd for $C_{13}H_{22}ClNOS$; C, 56.60; H, 8.06; N, 5.08; S, 11.62, Cl 12.85. Found: C, 57.05; H, 8.46; N, 4.81; S, 11.40, Cl 12.72.

General Procedure for the Reaction of Thiiranimines 6 with Iso(thio)cyanates 10, 22.

6 (1 mmol) in dry Et_2O (5 mL) or dry $CHCl_3$ (5 mL) and **10** or **22** (1.1 mmol) were mixed at 0 °C. Sulfonyl iso(thio)cyanates reacted at this temperature, while aryl derivatives required gentle heating up to 60 °C in $CHCl_3$. The reaction was monitored by TLC. In some cases, yellow crystals separated from the reaction mixture which were nevertheless purified by preparative TLC (PE/EtOAc 1:2 v/v) as were, after evaporation, the crude reaction mixtures. Solid products **11**, **15**, and **23** were further purified by recrystallization from PE/EtOAc. By chromatography of the *N*-sulfonyl derivatives of **11a-c**, traces of hydrolysis products **12** or **14** were detected (vide infra); starting from chlorosulfonyl isocyanate (**10e**), considerable hydrolysis to **12a,b** occurred and, starting from **10f**, only products **12** were isolated. Also the reaction products from isothiocyanate **22a** gave considerable hydrolysis to **24**.

2-(6,6,10,10-Tetramethyl-4-thioxo-2-tosylimino-1-oxa-3-azaspiro[4,5]decan-3-yl)-*N,N*-2-trimethyl-propionamide (11a): yield 87% from **6a** and **10a**; mp 131 °C; IR 1655 (br) cm^{-1}; ^1H NMR δ 0.77, 1.22, (each s, 6H, CMe_2), 1.52 (br s, 6H, $(CH_2)_3$), 1.83 (s, 6H, CMe_2), 2.38 (s, 3H, Ar-Me), 2.83 (s, 6H, NMe_2), 7.50 (mc, 4H, Ar); ^{13}C NMR δ 67.9, 106.0, 126.9, 129.3, 139.1, 143.2, 156.9 (C=O), 169.7 (C=N), 202.9 (C=S). Anal. Calcd for $C_{25}H_{37}N_3O_4S_2$; C, 59.14; H, 7.35; N, 8.28; S, 12.63. Found: C, 58.99; H, 7.37; N, 8.15; S, 12.47.

2-(5,5-Di-*tert*-butyl-4-thioxo-2-tosylimino-oxazolidin-3-yl)-*N,N*-2-trimethylpropionamide (11b): yield 96% from **6b** and **10a**; mp 152-3 °C; IR 1640 (br) cm^{-1}; ^1H NMR δ 1.08 (s, 18 H, *t*-Bu_2), 1.83 (s, 6H, CMe_2), 2.35 (s, 3H, Ar-Me), 2.80 (s, 6H, NMe_2), 7.43 (mc, 4H, Ar-Me); ^{13}C NMR δ 68.1, 106.6, 126.8, 129.2, 138.9, 143.2, 157.4 (C=O), 169.8 (C=N), 204.6 (C=S). Anal. Calcd for $C_{24}H_{37}N_3O_4S_2$; C, 58.15; H, 7.52; N, 8.48; S, 12.94. Found: C, 58.02; H, 7.65; N, 8.44; S, 12.66.

2-(2-Mesylimino-6,6,10,10-tetramethyl-4-thioxo-1-oxa-azaspiro[4,5]decan-3-yl)-*N,N*-2-trimethyl-propionamide (11c): yield 86% from **6a** and **10b**; mp 144 °C; IR 1640 (br) cm^{-1}; ^1H NMR δ 0.95, 1.32 (each s, 6H, CMe_2), 1.15 (br, 6H, $(CH_2)_3$), 1.87 (s, 6H, CMe_2), 2.90 (s, 6H, NMe_2), 3.17 (s, 3H, Ms); ^{13}C NMR δ 67.6, 105.9, 157.1 (C=O), 169.7 (C=N), 203 (C=S). Anal. Calcd for $C_{19}H_{33}N_3O_4S_2$; C, 52.86; H, 7.72; N, 9.74; S 14.85. Found: C, 52.47; H, 8.02; N, 9.87; S, 14.98.

2-(6,6,10,10-Tetramethyl-2-*p*-nitrophenylimino-4-thioxo-1-oxa-3-azaspiro[4,5]decan-3-yl)-*N,N*-2-tri-methylpropionamide (11d): yield 98% from **6a** and **10c**; mp 129-130 °C; IR 1710, 1630, 1600, 1330, 1580 cm^{-1}; ^1H NMR δ 0.97, 1.30 (each s, 6H, CMe_2), 1.60 (s, br, 6H, $(CH_2)_3$), 2.00 (s, 6H, CMe_2), 3.00 (s, 6H, NMe_2), 7.70 (mc, 4H, Ar); ^{13}C NMR δ 67.5, 102.00, 123.5, 124.6, 143.8, 150.6, 151.1 (C=O), 170.6 (C=N), 202.4 (C=S). Anal. Calcd for $C_{24}H_{34}N_4O_4S$; C, 60.74; H, 7.22; N, 11.80; S, 6.76. Found: C, 60.51; H, 7.64; N, 11.76; S, 6.87.

2-(5,5-Di-*tert*-butyl-2-phenylimino-4-thioxo-oxazolidin-3-yl)-*N,N*-2-trimethylpropionamide (11e): yield 62% from **6b** and **10d**; mp 139 °C; IR 1695, 1640, 1580 cm^{-1}; ^1H NMR δ 1.22 (s, 18H, *t*-Bu_2), 2.00 (s, 6H,

CMe_2), 2.90 (s, 6H, NMe_2), 7.10 (s, 5H, Ph); ^{13}C NMR δ 67.5, 102.4, 123.4, 123.9, 128.7, 144.2, 148.8 (C=O), 171.2 (C=N), 203.7 (C=S). Anal. Calcd for $C_{23}H_{35}N_3O_2S$; C, 66.14; H, 8.36; N, 10.06; S, 7.68. Found: C, 66.13; H, 8.20; N, 9.86; S, 8.08.

2-(3-Chlorosulfonylimino-6,6,10,10-tetramethyl-4-thioxo-1-oxa-3-azaspiro[4,5]-decan-3-yl)-*N,N*-2-trimethylpropionamide (11f): yield 59% from **6a** and **10e**; mp 92 °C; IR 1650, 1580, 1450, 1180 cm^{-1}; ^1H NMR δ 0.98, 1.32 (each s, 6H, CMe_2), 1.70 (br, 6H, $(CH_2)_3$), 1.88 (s, 6H, CMe_2), 2.91 (s, 6H, NMe_2); ^{13}C NMR δ 68.5, 108.7, 161.3 (C=O), 169.0 (C=N), 202.6 (C=S). Anal. Calcd for $C_{18}H_{30}ClN_3O_4S_2$; C, 47.82; H, 6.70; N, 9.30; S, 14.18; Cl, 8.33. Found: C, 47.68; H, 6.52; N, 9.23; S, 14.05, Cl, 8.33.

2-(5,5-Di-*tert*-butyl-3-chlorosulfonylimino-4-thioxo-oxazolidin-3-yl)-*N,N*-2-trimethylpropionamide (11g): yield 16% from **6b** and **10e**; mp 99 °C; IR 1660, 1640, 1360, 1300 cm^{-1}; ^1H NMR δ 1.30 (s, 18H, *t*-Bu_2), 1.95 (s, 6H, CMe_2), 2.98 (s, 6H, NMe_2). Anal. Calcd for $C_{17}H_{30}ClN_3O_4S_2$; C, 46.40; H, 6.88; N, 9.55. Found: C, 46.68; H, 6.78; N, 5.57.

2-(5-*tert*-Butyl-5-isopropyl-2-mesylimino-4-thioxo-oxazolidin-3-yl)-*N,N*-2-trimethylpropionamide (11j): yield 34% from **6c** and **10b**; mp 105 °C; IR 1700, 1600 cm^{-1}; ^1H NMR δ 0.94, 1.18 (each d, *J* = 6 Hz, 6H, *i*-Pr), 1.18 (s, 9H, *t*-Bu), 1.88 (s, 6H, CMe_2), 2.65 (sept, 1H, *i*-Pr), 2.92 (s, 6H, NMe_2), 3.02 (s, 3H, Ms); ^{13}C NMR δ 67.9, 106.07, 157.6 (C=O), 169.7 (C=N), 206.2 (C=S). Anal. Calcd for $C_{17}H_{31}N_3O_4S_2$; C, 50.35; H, 7.70; N, 10.36; S, 15.81. Found: C, 50.03; H, 7.77; N, 10.27; S, 16.30.

2-(5-*tert*-Butyl-5-isopropyl-2-*p*-nitrophenylimino-4-thioxo-oxazolidin-3-yl)-*N,N*-2-trimethylpropionamide (11k): yield 79% from **6c** and **10c**; mp 132 °C; IR 1690, 1650, 1600, 1580, 1330 cm^{-1}; ^1H NMR δ 0.93, 1.11 (each d, *J* = 6 Hz, 6H, *i*-Pr), 1.18 (s, 9H, *t*-Bu), 2.00 (s, 6H, CMe_2), 2.70 (sept, 1H, *i*-Pr), 2.98 (s, 6H, NMe_2), 7.60 (mc, 4H, Ar); ^{13}C NMR δ 67.5, 103.4, 123.6, 124.5, 143.8, 150.7, 150.8 (C=O), 170.5 (C=N), 205.3 (C=S). Anal. Calcd for $C_{22}H_{32}N_4O_4S$; C, 58.89; H, 7.20; N, 12.49; S, 7.15. Found: C, 58.92; H, 7.41; N, 12.32; S, 7.40.

2-(5-*tert*-Butyl-5-isopropyl-2-phenylimino-4-thioxo-oxazolidin-3-yl)-*N,N*-2-trimethylpropionamide (11l): yield 59% from **6c** and **10d,** mp 144-145 °C; IR 1700, 1640, 1580 cm^{-1}; ^1H NMR δ 0.91, 1.11 (each d, *J* = 9 Hz, 6H, *i*-Pr), 1.17 (s, 9H, *t*-Bu), 2.00 (s, 6H, CMe_2), 2.70 (sept, 1H, *i*-Pr), 2.95 (s, 6H, NMe_2), 7.17 (s, 5H, Ph). Anal. Calcd for $C_{22}H_{33}N_3O_2S$; C, 65.47; N, 8.24; N, 10.41; S, 7.94. Found C, 65.66; H, 8.12; N, 10.15; S, 8.06.

2,2,5′,5′,6,6-Hexamethyl-3′-thioxo-3'*H*-spirocyclohexane-1,2′-(7′*H*)-imidazo[2,1-*b*]oxazol-6′(5'*H*)-one (12a): yield 8% from **6a** and **10e**, 47% from **6a** and **10f**; mp 135 °C; IR 1760, 1600, 1580, 1370, 1360 cm^{-1}; ^1H NMR δ 0.90, 1.20, 1.57, 1.60 (each s, 6H, CMe_2 and $Me_2C(CH_2)_3CMe_2$), ca. 1.7 (br, 6H, $(CH_2)_3$); ^{13}C NMR δ 68.2, 116.0, 176.7, 190.5 (C=O, C=N), 194.8 (C=S); MS *m/z* 308 (M^+, 43), 293 (M^+ - Me, 18), 182 (54), 167 (100). Anal. Calcd for $C_{16}H_{24}N_2O_2S$; C, 62.29; H, 7.86; N, 9.08; S, 10.39. Found: C, 62.49; H,7.97; N, 9.65; S, 10.59.

2,2-Di-*tert*-butyl-2,3,5,6-tetrahydro-5,5-dimethyl-3-thioxo-imidazo[2,1-*b*]oxazol-6-one (12b): yield 44% from **6b** and **10e**, 25% from **6b** and **10f**; mp 95 °C; IR 1760, 1600, 1360, 850 cm^{-1}; ^1H NMR δ 1.27 (s, 18H, *t*-Bu_2), 1.67 (s, 6H, CMe_2); ^{13}C NMR δ 68.3, 116.6, 177.3, 190.8 (C=O, C=N), 196.3 (C=S). Anal. Calcd for $C_{15}H_{24}N_2O_2S$; C, 60.77; H, 8.18; N, 9.45; S, 10.81. Found: C, 60.57; H, 8.34; N, 9.33; S, 10.51.

2-(5-*tert*-Butyl-5-isopropyl-2-oxo-4-thioxo-1-tosyl-imidazolidin-3-yl)-*N,N*-trimethylpropionamide (15a): yield 85% from **6a** and **10a**; mp 153-4 °C; IR 1750, 1675, 1600, 1275, 1170 cm^{-1}; ^1H NMR δ 1.08, 1.24 (each d, *J* = 5 Hz, 6H, *i*-Pr), 1.33 (s, 9H, *t*-Bu), 1.72, 1.80 (each s, 3H, CMe_2), 2.43 (s, 3H, Ts), 2.70 (s, 6H, NMe_2), 3.53 (m, 1H, *i*-Pr), 7.70 (mc, 4H, Ar); ^{13}C NMR δ 66.4, 93.3, 128.9, 129.4, 130.5, 145.3, 154.2 (C=O), 170.6 (C=O), 201.7 (C=S). Anal. Calcd for $C_{23}H_{35}N_3O_4S_2$; C, 57.35; H, 7.32; N, 8.72; S, 13.31. Found: C, 57.28; H, 7.32; N, 8.62; S, 13.35.

2-(5-*tert*-Butyl-5-isopropyl-1-mesyl-2-oxo-4-thioxo-imidazolidin-3-yl)-*N,N*-2-trimethylpropionamide (15b): yield 62% from **6c** and **10b**; mp 160-1 °C; IR 1740, 1630 cm^{-1}; ^1H NMR δ 1.23 (br, d, 6H, *i*-Pr), 1.87 (s, 6H, CMe_2), 2.92 (s, 6H, NMe_2), 3.52 (s, 3H, Ms); ^{13}C NMR δ 66.9, 92.8, 155.9 (C=O), 170.5 (C=O), 203.1 (C=S). Anal. Calcd for $C_{17}H_{31}N_3O_4S_2$; C, 50.35; H, 7.70; N, 10.36; S, 15.81. Found: C, 50.53; H, 8.03; N, 10.21; S, 15.43.

2-(5-*tert*-Butyl-5-isopropyl-2-oxo-1-phenyl-4-thioxo-imidazolidin-3-yl)-*N,N*-2-trimethylpropionamide (15c): yield 37% from **6c** and **10d**; mp 50 °C (decomp); IR 1730, 1650, 1590 cm^{-1}; ^1H NMR δ 1.2 (mc, 6H, *i*-Pr), 2.85, 2.92 (2s, br, 6H, CMe_2), 2.95 (s, 6H, NMe_2), 7.82 (s, 5H, Ph); ^{13}C NMR δ 65.8, 100.2, 120.3, 124.7, 129.1, 137.2, 155.4 (C=O), 169.0, 208.4 (C=S). Anal. Calcd for $C_{22}H_{33}N_3O_2S$; C, 65.47; H, 8.24; N, 10.41; S, 7.94. Found: C, 65.66; H, 8.12; N, 10.15; S, 8.06.

2-(6,6,10,10-Tetramethyl-4-thioxo-2-tosylimino-1-thia-3-azaspiro[4,5]decan-3-yl)-*N,N*-2-trimethyl-propionamide (23a): yield 96% from **6a** and **22a**; mp 162 °C; IR 1640, 1550 cm^{-1}; ^1H NMR δ 0.9 – 2.0 (br, 12H), 1.25 (s, 6H, CMe_2), 1.83 (s, 6H, CMe_2), 2.43 (s, 3H, Ts), 2.78 (s, 6H, NMe_2), 7.48 (mc, 4H, Ar); ^{13}C NMR δ 71.5, 82.8, 126.9, 129.2, 137.0, 143.6, 169.0, 170.6 (C=O, C=N), 207.8 (C=S). Anal. Calcd for $C_{25}H_{37}N_3O_3S_3$; C, 57.32; H, 7.14; N, 8.02; S 18.36,. Found: C, 57.38; H, 7.10; N, 7.80; S, 18.55.

2-(5,5-Di-*tert*-butyl-4-thioxo-2-tosylimino-thiazolidin-3-yl)-*N,N*-2-trimethylpropionamide (23b): yield 94% from **6b** and **22a**; mp 146 °C; IR 1645, 1590 cm^{-1}; ^1H NMR δ 1.27 (s, 18H, *t*-Bu_2), 1.87 (br, 6H, CMe_2), 2.43 (s, 3H, Ts), 2.80 (s, 6H, NMe_2), 7.53 (mc, 4H, Ar); ^{13}C NMR δ 71.6, 85.0, 127.0, 129.2, 137.3, 143.6, 169.1 (C=O), 170.8 (C=N), 207.7 (C=S). Anal. Calcd for $C_{24}H_{37}N_3O_3S_3$; C, 56.27; H, 7.30; N, 8.21; S, 18.79. Found: C, 56.19; H, 7.40; N, 8.00; S, 18.68.

2-(5-*tert*-Butyl-5-isopropyl-4-thioxo-2-tosylimino-thiazolidin-3-yl)-*N,N*-2-trimethylpropionamide (23c): yield 96% from **6c** and **22a**; mp 142 °C; IR 1640, 1550, 1600 cm^{-1}; ^1H NMR δ ca. 1.2 (br,mc, 6H, *i*-Pr), 1.22 (s, 9H, *t*-Bu), 2.42 (s, 3H, Ts), 2.80 (s, 6H, NMe_2), 7.50 (mc, 4H, Ar); ^{13}C NMR δ 71.2, 83.0,

127.0, 129.2, 137.0, 143.7, 168.7 (C=O), 170.6 (C=N), 210.9 (C=S). Anal. Calcd for $C_{23}H_{35}N_3O_3S_3$; C, 55.50; H, 7.10; N, 8.44; S, 19.32. Found: C, 55.50; H, 7.29; N, 8.44; S, 19.54.

2-(6,6,10,10-Tetramethyl-2-*p*-nitrophenylimino-4-thioxo-1-thia-3-azaspiro[4,5]decan-3-yl)-*N*,*N*-2-trimethylpropionamide (**23d**): yield 77% from **6a** and **22b**; mp 190 °C; IR 1640, 1590 cm^{-1}; ^1H NMR δ 0.87, 1.03, 1.20, 1.57 (each s, 3H, ring-Me_2C), 1.67 (s, 6H, $(CH_2)_3$), 2.00 (s, 6H, CMe_2), 2.97 (s, 6H, NMe_2), 7.57 (mc, 4H, Ar); ^{13}C NMR δ 70.7, 82.9, 121.1, 125.3, 144.4, 154.2, 158.3 (C=O), 171.7 (C=N), 207.0 (C=S). Anal. Calcd for $C_{24}H_{34}N_4O_3S_2$; C, 58.74; H, 7.00; N, 11.42; S, 13.07. Found: C, 58.64; H, 7.16; N, 11.23; S, 12.80.

2-(5-*tert*-Butyl-5-isopropyl-2-*p*-nitrophenylimino-4-thioxo-thiazolidin-3-yl)-*N*,*N*-2-trimethylpropionamide (**23e**): yield 55% from **6c** and **22b**; mp 158 °C; IR 1640, 1585 cm^{-1}; ^1H NMR δ 0.86, 1.08 (each d, J = 5 Hz, 6H, *i*-Pr), 1.20 (s, 9H, *t*-Bu), 2.00 and 2.10 (each s, br, 6H, CMe_2), 3.00 (s, 6H, NMe_2), 7.67 (mc, 4H, Ar); ^{13}C NMR δ 70.4, 83.3, 121.1, 125.3, 144.4, 154.2, 158.3 (C=O), 171.7 (C=N), 209.6 (C=S). Anal. Calcd for $C_{22}H_{32}N_4O_3S_2$; C, 56.86; H, 6.96; N, 12.06. Found: C, 56.83; H, 7.17; N, 11.76.

General Procedure for the Hydrochloric Acid-catalyzed Hydrolysis of Cycloadducts 11, 15, 23.

A compound **11**, **15**, or **23** including crude **11h**,**i** (0.5 mmol) in $CHCl_3$ (10 mL) and half-concentrated (5 M) aq. HCl (concd aq. HCl for **11k**,**l**) were mixed at rt and kept at this temperature for up to 24 h while the progress of the reaction was monitored by TLC. If required, the reaction mixture was refluxed till TLC showed no more starting material. The reaction mixture was washed with sat. aq. $NaHCO_3$, concentrated in vacuo and the crude product purified by preparative TLC (PE/EtOAc 1:2 v/v) to give the following products:

12a: yield 65% from **11a**, 36% from **11c**, 20% from **11d**, 20% from **11f,** 48% from **11h**. Data see above.

12b: yield 68% from **11b**, 60% from **11e**, 20% from **11g**, 20% from **11i**. Data see above.

2-(6,6,10,10-Tetramethyl-2-oxo-4-thioxo-1-oxa-3-azaspiro[4,5]decan-3-yl)-2-methyl-*N*-(4-nitrophenyl)-propionamide (**14a**): yield 80% from **11d**; mp 170 °C; IR 3400, 1770, 1700, 1600, 1590, 1530, 1500, 1340 cm^{-1}; ^1H NMR δ 1.00, 1.20 (each s, 6H, ring-Me_2C), 1.60 (s, 6H, $(CH_2)_3$), 1.90 (s, 6H, CMe_2), 7.73 (mc, 4H, Ar); ^{13}C NMR δ 65.8, 100.0, 119.3, 125.0, 143.2, 143.8, 154.6 (C=O), 169.3 (C=O), 205.4 (C=S); MS *m/z* 447 (M^+, 3), 310 (M^+ - Ar-NH, 100), 266 (76). Anal. Calcd for $C_{22}H_{29}N_3O_5S_2$; C, 59.03; H, 6.54; N, 9.39; S, 7.16. Found: C, 58.78; H, 6.47; N, 9.23; S, 7.20.

2-(5,5-Di-*tert*-butyl-2-oxo-4-thioxo-oxazolidin-3-yl)-2-methyl-*N*-phenylpropionamide (**14b**): yield 60% from **11e**; mp 207 °C; IR 3300, 1800, 1640, 1600, 1345, 1290 cm^{-1}; ^1H NMR δ 1.20 (s, 18H, *t*-Bu_2), 1.83 (s, 6H, CMe_2), 7.13 (m, 5H, Ph); ^{13}C NMR δ 65.7, 100.3, 120.3, 124.7, 129.1, 137.4, 155.4 (C=O), 169.1 (C=O), 206.5 (C=S). Anal. Calcd for $C_{21}H_{30}N_2O_3S$; C, 64.57; H, 7.84; N, 7.17; S, 8.21. Found: C, 63.62; H, 7.58; N, 6.94; S, 8.36.

1-(3-*tert*-Butyl-2,2-dimethyl-2*H*-thiet-4-yl)-5,5-dimethyl-3-phenyl-imidazolidine-2,4-dione (19a): yield 90% from **11k**; mp 103 °C; IR 1770, 1720, 1635, 1600, 1350–1390 cm^{-1}; ^1H NMR δ 1.20 (s, 9H, *t*-Bu), 1.63, 1.84 (each s, 6H, CMe_2), 7.40 (s, 5H, Ph); ^{13}C NMR δ 55.0, 63.2, 121.0, 126.0, 128.1, 128.9, 131.6, 151.1, 152.1 (C=O), 174.7 (C=O); MS *m/z* 358 (M^+, 94), 343 (M^+ - Me, 68), 301 (M^+ - *t*-Bu, 70), 196 (33), 139 (100). Anal. Calcd for $C_{20}H_{26}N_2O_2S$; C, 66.99; H, 7.32; N, 7.82; S, 8.94. Found: C, 67.10; H, 7.47; N, 7.76; S, 8.98.

1-(3-*tert*-Butyl-2,2-dimethyl-2*H*-thiet-4-yl)-5,5-dimethyl-3-(4-nitrophenyl)imidazolidine-2,4-dione (**19b**): yield 90% from **11l**; mp 129 °C; IR 1780, 1740, 1640, 1620, 1600, 1520, 1380 cm^{-1}; ^1H NMR δ 1.20 (s, 9H, *t*-Bu), 1.67, 1.87 (each s, 6H, CMe_2), 8.08 (mc, 4H, Ar); ^{13}C NMR δ 55.3, 63.3, 120.5, 124.2, 125.8, 137.3, 146.4, 151.2, 151.7 (C=O), 174.1 (C=O); MS *m/z* 403 (M^+, 84), 388 (M^+ - Me, 78), 346 (M^+ - *t*-Bu, 48), 196 (41), 139 (100). Anal. Calcd for $C_{20}H_{25}N_3O_4S$; C, 59.52; H, 6.26; N, 10.42; S, 7.95. Found: C, 59.52; H, 6.32; N, 10.13; S, 7.52.

6a-*tert*-Butyl-3,3,7,7-tetramethyl-6-phenyl-cyclopropa[4,5]imidazo[5,1-b]thiazol-2,5(3*H*,6*H*)-dione (21): yield 10% from **15c**; mp 105 °C; ^1H NMR δ 1.08 (s, 9H, *t*-Bu), 1.25 (s, 3H, Me), 1.50 (s, 6H, CMe_2), 2.85 (s, 3H, Me), 7.37 (s, 5H, Ph); ^{13}C NMR δ 55.7, 60.0, 66.0, 125.9, 126.1, 128.1, 138.6, 154.4 (C=O), 205.3 (C=O); MS *m/z* 358 (M^+, 1.8), 301 (100), 273 (48). Anal. Calcd for $C_{20}H_{26}N_2O_2S$; C, 66.99; H, 7.32; N, 7.82; S, 8.94. Found: C, 67.11; H, 7.28; N, 7.86; S, 8.88.

5′,6′-Dihydro-2,2,5′,5′,6,6-hexamethyl-7′-thioxo-spirocyclohexane-1,1′-(7′*H*)-imidazo[2,1-*b*]thiazol-4′-one (**24a**): yield 89% from **23a**; mp 146 – 7 °C; IR 1760, 1500, 1360, 1290, 1080 cm^{-1}; ^1H NMR δ 1.00, 1.33 (each s, 6H, cyclohexane-CH_3), 1.67 (s, 6H, CH_2), 2.13, 2.77 (each br s, 3H, Me); ^{13}C NMR δ 68.08, 92.8, 185.2, 191.3 (C=O, C=N), 200.5 (C=S); MS *m/z* 324 (M^+, 82), 242 (73), 200 (59), 167 (64), 91 (56), 41 (100). Anal. Calcd for $C_{16}H_{24}N_2OS_2$; C, 59.21; H, 7.47; N, 8.63; S, 19.76. Found: C, 59.14; H, 7.44; N, 8.37; S, 19.52.

2,2-Di-*tert*-butyl-2,3,5,6-tetrahydro-5,5-dimethyl-3-thioxo-imidazo[2,1-*b*]thiazol-6-one (**24b**): yield 40% from **23b**; mp 98 – 9 °C; IR 1760, 1600, 1380, 1360, 1295, 1250, 1185, 1080 cm^{-1}; ^1H NMR δ 1.33 (s, 18H, *t*-Bu_2), 1.67 (s, 6H, CMe_2). Anal. Calcd for $C_{15}H_{24}N_2OS_2$; C, 57.64; H, 7.76; N, 8.97; S, 20.52. Found: C, 57.72; H, 7.57; N, 8.91; S, 20.21.

2-*tert*-Butyl-2-isopropyl-2,3,5,6-tetrahydro-5,5-dimethyl-3-thioxo-imidazo[2,1-*b*]thiazol-6-one (24c): yield 91% from **23c**; mp 117 °C; ^1H NMR δ 0.92, 1.55 (each d, *J* = 5 Hz, 6H, *i*-Pr), 1.27 (s, 9H, *t*-Bu), 1.70 (s, 6H, CMe_2), 2.90 (sept, *J* = 5 Hz, 1H, *i*-Pr); ^{13}C NMR δ 67.7, 92.5, 186.3, 191.4 (C=N, C=O), 202.4 (C=S). Anal. Calcd for $C_{14}H_{22}N_2OS_2$; C, 56.33; H, 7.44; N, 9.39; S, 21.48. Found: C, 56.41; H, 7.64; N, 9.32; S, 21.65.

2-(6,6,10,10-Tetramethyl-2-oxo-4-thioxo-1-thia-3-azaspiro[4,5]decan-3-yl)-2-methyl-*N*-(4-nitrophenyl)-propionamide (25a): yield 83% from **23d**; mp 232 °C (decomp); IR 3400, 1700, 1615, 1530, 1500, 1480

cm^{-1}; ^1H NMR δ 1.50 – 2.80 (br, 6H, $(CH_2)_3$), 1.00, 1.30, 1.93 (3s, each 6H, CMe_2), 7.70 (mc, 4H, Ar); ^{13}C NMR δ 69.4, 81.2, 119.0, 125.1, 143.6, 143.7, 169.9 (C=O), 174.2 (C=O), 207.7 (C=S). Anal. Calcd for $C_{22}H_{29}N_3O_4S_2$; C, 56.99; H, 6.32; N, 9.06; S, 13.83. Found: C, 56.76; H, 6.27; N, 9.05; S, 13.89.

2-(5,5-Di-*tert*-butyl-2-oxo-4-thioxo-thiazolidin-3-yl)-2-methyl-*N*-(4-nitrophenyl)propionamide (25b): yield 96% from **6b** and **22b** by hydrolysis on work-up; mp 180 °C; IR 3400, 1700, 1620, 1600, 1535, 1500, 1400, 1340, 1300 cm^{-1}; ^1H NMR δ 1.33 (s, 18H, *t*-Bu_2), 1.93 (s, 6H, CMe_2), 7.07 - 8.10 (mc, 4H, Ar). Anal. Calcd for $C_{21}H_{29}N_3O_4S_2$; C, 55.84; H, 6.49; N, 9.31; S, 14.20. Found: C, 55.63; H, 6.48; N, 9.31; S, 14.53.

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