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Communication

Rearrangement

$LiAlH_4$-Induced Thia-Aza-Payne Rearrangement of Functionalized 2-(Thiocyanatomethyl)aziridines into 2-(Aminomethyl)thiiranes as an Entry to 5-(Chloromethyl)thiazolidin-2-ones

Jeroen Dolfen,[a] Kristof Van Hecke,[b] and Matthias D'hooghe*[a]

Abstract: Nonactivated 2-(thiocyanatomethyl)aziridines with diverse substitution patterns were deployed as substrates to effect a $LiAlH_4$-promoted thia-aza-Payne rearrangement to provide access to functionalized 2-(aminomethyl)thiiranes in good to excellent yields (78–94 %). The developed strategy involved hydride reduction of the thiocyanato moiety followed by intramolecular aziridine ring opening. Subsequent exposure of the obtained 2-(aminomethyl)episulfide intermediates to triphosgene resulted in the formation of 5-(chloromethyl)thiazolidin-2-ones.

Introduction

Since Payne's comprehensive research on the reorganization of 2,3-epoxy alcohols into their isomeric counterparts in 1962,[1] the "Payne rearrangement" has evolved into a powerful reaction in organic chemistry. Moreover, owing to its broad applicability, this elegant interconversion has become a widely used method in natural product synthesis.[2] Although the involved intramolecular ring-opening reactions occur in a stereospecific S_N2 fashion with inversion of configuration at the more-substituted carbon atom, the reversible character of the isomerization process still represents a significant drawback.

The "aza-Payne rearrangement", however, implying the conversion of a 2-(hydroxymethyl)aziridine into its isomeric oxirane or vice versa,[3] and the "thia-Payne rearrangement", referring to the equilibrium between a 2-(hydroxymethyl)thiirane and an epoxide,[4] can be tuned and controlled to a certain extent depending on the applied reaction conditions. Despite numerous papers reporting epoxide–aziridine and/or epoxide–thiirane migrations, only one article dealing with an aziridine-to-thiirane rearrangement has been published so far.[5] Moreover, the transformations in that particular study appeared to induce the formation of side products as well, as treatment of a variety of polysubstituted 1-tosyl-2-(tosyloxymethyl)aziridines with an excess amount of benzyltriethylammonium tetrathiomolybdate ($[BnEt_3N]_2MoS_4$) in CH_3CN afforded the corresponding thiiranes as the major products (75–80 %) and cyclic disulfides as the minor compounds (20–25 %).

In continuation of our research efforts concerning the $LiAlH_4$-induced regioselective ring rearrangement of 2-(cyanoethyl)-aziridines into either 2-(aminomethyl)pyrrolidines or 3-amino-piperidines,[6] and in light of the growing interest in sulfur-containing heterocycles,[7] the deployment of 2-(thiocyanatomethyl)aziridines as substrates for a hydride-promoted thia-aza-Payne rearrangement was envisaged. The feasibility of the premised aziridine-to-thiirane interconversion was assessed starting from nonactivated 2-(thiocyanatomethyl)aziridines **1**. These aziridines, bearing an electron-donating group on the nitrogen atom and differing in substitution patterns, can be prepared from corresponding 2-monosubstituted 2-(bromomethyl)aziridines **2**, 2,2-disubstituted aziridines **3**, or 2,3-disubstituted aziridines **4**, which have amply proven to be versatile precursors for further synthetic elaboration (Figure 1).[6,8]

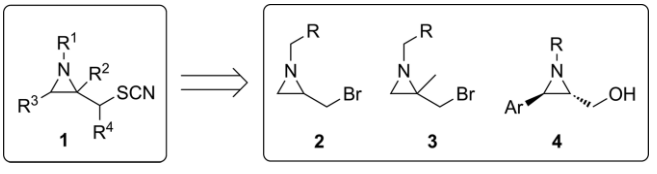


Figure 1. Diverse aziridine substrate classes.

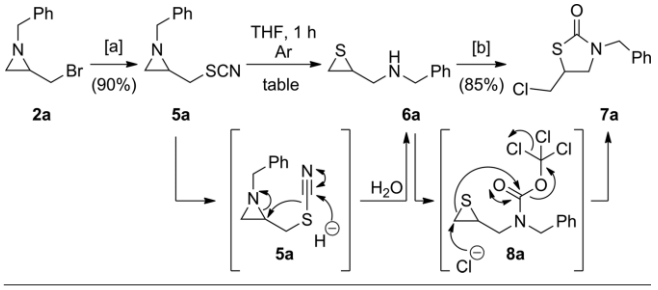
Results and Discussion

At the outset of this study, 2-(bromomethyl)aziridine **2a** was converted into 2-(thiocyanatomethyl)aziridine **5a** in 90 % yield upon treatment with KSCN (2 equiv.) in DMF at 70 °C,[8a] and then **5a** was used as a model substrate for the premised thia-aza-Payne rearrangement (Table 1). In a first attempt, aziridine **5a** was treated with $LiAlH_4$ (2 equiv.) and indium(III) trifluoromethanesulfonate ($In(OTf)_3$, 0.3 equiv.] at reflux temperature,[6] but these reaction conditions resulted in intermolecular dimer formation instead of intramolecular ring rearrangement (Table 1, entry 1). Next, an equimolar amount of $LiAlH_4$ and

[a] SynBioC Research Group, Department of Sustainable Organic Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, 9000 Ghent, Belgium
E-mail: Matthias.Dhooghe@UGent.be
http://www.synbioc.ugent.be
[b] XStruct, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281-S3, 9000 Ghent, Belgium
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejoc.201700549.

$In(OTf)_3$ was used, which led to complete conversion into desired thiirane **6a** (Table 1, entry 2). However, upon standing for a few hours, the reaction product appeared to be unstable, probably as a result of the presence of residual $In(OTf)_3$. Lowering the reaction temperature from reflux temperature to 0 °C in the absence of $In(OTf)_3$ again resulted in dimer formation (Table 1, entry 3), whereas increasing the amount of $LiAlH_4$ (1.7 equiv.) in combination with a reaction temperature of –78 °C afforded desired thiirane **6a** in an acceptable yield of 78 % (Table 1, entry 4). As isolated 2-(aminomethyl)thiirane **6a** still appeared to be unstable upon standing for a few days, it was trapped through treatment with triphosgene (1 equiv.) in THF to furnish 5-(chloromethyl)thiazolidin-2-one **7a** in 85 % yield. Mechanistically, the thia-aza-Payne rearrangement of 2-(thiocyanatomethyl)aziridine **5a** can be rationalized by hydride addition across the thiocyanato moiety with concomitant release of HCN. The in situ formed sulfide anion effects intramolecular aziridine ring opening, and this results in 2-(aminomethyl)thiirane **6a** after aqueous workup. Although nonactivated aziridines generally require activation of the ring system prior to ring opening (in contrast to activated aziridines),[9] the ring opening of 1-benzylaziridine **5a** can be attributed to the Lewis acid activity of $LiAlH_4$ (through coordination of aluminum with nitrogen).[10] Subsequent treatment of obtained 2-(aminomethyl)thiirane **6a** with triphosgene resulted in N-acylation to give carbamate **8a**, and this was followed by regioselective chloride-induced ring opening of the thiirane core at the less-substituted carbon atom[7d,11] and ring transformation into corresponding 5-(chloromethyl)thiazolidin-2-one **7a**. Initial attack of the amino group in **6a** across triphosgene was corroborated by reaction of thiirane **6a** with methyl chloroformate and Boc_2O (Boc = *tert*-butoxycarbonyl) on an analytical scale, which afforded the *N*-acylated products without thiirane ring opening.

Table 1. Optimization of the reaction conditions for the thia-aza-Payne rearrangement of 1-benzyl-2-(thiocyanatomethyl)aziridine (**5a**).

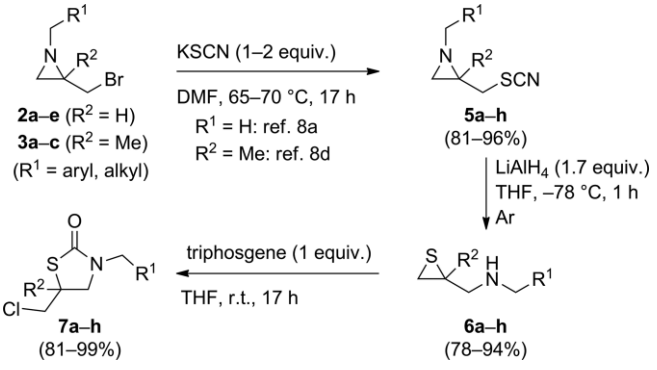


Entry	$LiAlH_4$ [equiv.]	$In(OTf)_3$ [equiv.]	Temp. [°C]	Yield [%] of **6a**
1	2	0.3	reflux	–[c]
2	1	1	reflux	45[d]
3	1.2	0	0	–[c]
4	1.7	0	–78	78

[a] Reaction conditions: KSCN (2 equiv.), DMF, 70 °C, 17 h.[8a] [b] Reaction conditions: Triphosgene (1 equiv.), THF, r.t., 17 h. [c] Dimer formation. [d] Thiirane **6a** appeared to be unstable in the presence of residual $In(OTf)_3$.

Having the optimal reaction conditions for the conversion of aziridine **5a** into thiirane **6a** in hand, other 2-(thiocyanatomethyl)aziridines were prepared next to trigger the observed thia-aza-Payne rearrangement. In a first approach, monosubstituted 2-(thiocyanatomethyl)aziridines **5b**–**e** (R^2 = H) were synthesized from corresponding 2-(bromomethyl)aziridines **2b**–**e** (2 equiv. KSCN, DMF, 70 °C, 17 h), which were subsequently confronted with $LiAlH_4$ (1.7 equiv.) at –78 °C under an argon atmosphere to furnish 2-(aminomethyl)thiiranes **6b**–**e** in good to excellent yields (79–92 %; Table 2, entries 2–5). Owing to the unstable nature of obtained thiiranes **6b**–**e** upon storing and during purification on silica gel, these intermediates were immediately treated with triphosgene (1 equiv.) in THF to produce stable 5-(chloromethyl)thiazolidin-2-ones **7b**–**e** in 81–99 % yield.

Table 2. Scope of the thia-aza-Payne rearrangement of 2-(thiocyanatomethyl)aziridines **5** and subsequent ring transformation with the use of triphosgene.



Entry	R^1	R^2	Product (yield[a] [%])		
			5	**6**	**7**
1	Ph	H	**5a** (90)	**6a** (78)	**7a** (85)
2	4-MeC_6H_4	H	**5b** (87)	**6b** (82)	**7b** (89)
3	4-ClC_6H_4	H	**5c** (95)	**6c** (79)	**7c** (81)
4	*i*Pr	H	**5d** (83)	**6d** (92)	**7d** (85)
5	cyclohexyl	H	**5e** (81)	**6e** (86)	**7e** (99)
6	Ph	Me	**5f** (86)	**6f** (94)	**7f** (97)
7	4-MeC_6H_4	Me	**5g** (96)	**6g** (91)	**7g** (99)
8	4-$MeOC_6H_4$	Me	**5h** (91)	**6h** (93)	**7h** (92)

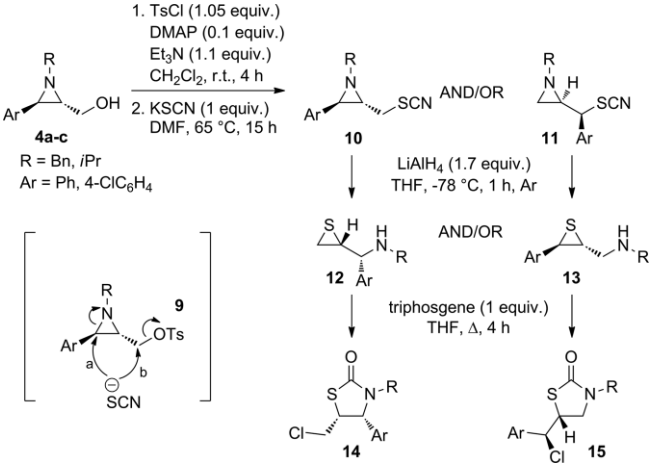
[a] Yield of isolated product.

The effect of an additional substituent at the aziridine C2 position on the thia-aza-Payne rearrangement was investigated next. In that respect, 2-methyl-2-(thiocyanatomethyl)aziridines **5f**–**h** (R^2 = Me) were synthesized in excellent yields (86–96 %) starting from 2-bromomethyl-2-methylaziridines **3a**–**c** upon treatment with an equimolar amount of KSCN in DMF at 65 °C (Table 2, entries 6–8).[8d] Subsequent addition of an excess amount of $LiAlH_4$ (1.7 equiv.) in THF at –78 °C induced the desired aziridine-to-thiirane reorganization, and 2-(aminomethyl)thiiranes **6f**–**h** were isolated in high yields (91–94 %). As a consequence, it can be concluded that the presence of a quaternary carbon center in aziridines **5** does not have a negative impact on the thia-aza-Payne rearrangement. On the contrary, 2-aminomethyl-2-methylthiiranes **6f**–**h** were isolated in slightly higher yields (91–94 %) than 2-(aminomethyl)thiiranes **6a**–**e** (78–92 %) and appeared to be more stable upon prolonged storage at 4 °C and during purification on silica gel. Subsequently, obtained 2,2-disubstituted thiiranes **6f**–**h** were treated with triphosgene (1 equiv.) in THF at room temperature

to afford corresponding 5-chloromethyl-5-methylthiazolidin-2-ones **7f**–**h** in almost quantitative yields (92–99 %; Table 2, entries 6–8). Notably, also in the case of *gem*-disubstituted thiiranes **6f**–**h**, ring opening of the thiirane core by chloride proceeded regioselectively at the less-substituted carbon atom.[12]

For aziridine substrate class **4** (Figure 1) featuring a *vic*-disubstitution pattern, the preparation of the corresponding 3-(thiocyanatomethyl)aziridines appeared to be highly dependent on the nature of the substituents of the involved aziridines. Tosylation of 2-(4-chlorophenyl)-3-(hydroxymethyl)aziridine **4a** with 4-toluenesulfonyl chloride (TsCl, 1.05 equiv.) in the presence of 4-(dimethylamino)pyridine (DMAP, 0.1 equiv.) and Et_3N (1.1 equiv.) in CH_2Cl_2, followed by nucleophilic substitution upon the addition of KSCN (1 equiv.) in DMF at 65 °C, afforded 3-(thiocyanatomethyl)aziridine **10a** in 52 % yield as a single reaction product (Table 3). Surprisingly, by applying the same reaction conditions to 2-phenyl-3-(hydroxymethyl)aziridine **4b**, 3-(thiocyanatomethyl)aziridine **10b** and 2-[phenyl(thiocyanato)-methyl]aziridine **11b** were obtained in a 55:45 ratio. Despite intensive efforts, structural isomers **10b** and **11b** could not be separated, and – as a consequence – this mixture was used as such in the next step. In addition to the unexpected influence of the 2-aryl substituent on the thiocyanate-induced tosyloxy displacement, the effect of the N-substituent in *vic*-disubstituted aziridines **4** was also studied by tosylation and subsequent treatment with KSCN of 1-isopropyl-2-phenylaziridine **4c**. Again, a mixture of isomers **10c** and **11c** was obtained in a ratio of 30:70, although in favor of 2-[phenyl(thiocyanato)methyl]-aziridine **11c** in this case. Subsequent purification of the reaction mixture by column chromatography (silica gel) allowed the isolation of major isomer **11c** in 44 % yield. Notably, analysis of intermediates **10a** and **10b** by NMR spectroscopy ($CDCl_3$) appeared to be impossible owing to unclear resolution of the corresponding signals. On the basis of the obtained experimental results, the addition of KSCN to in situ formed 3-(tosyloxymethyl)aziridines **9** seems to provoke a competition between ring opening at the benzylic position (route a) and the expected direct tosyloxy group displacement (route b) (Table 3).[8c] Remarkably, aziridines **4a**–**c** gave rise to a different

Table 3. Thia-aza-Payne rearrangement of (thiocyanatomethyl)aziridines **10** and **11**, followed by ring transformation upon treatment with triphosgene.



Conversion of 3-aryl-2-(hydroxymethyl)aziridines **4** into (thiocyanatomethyl)aziridines **10** and **11**					
Substrate	R	Ar	Ratio (**10**/**11**)[a]	Product (yield[b] [%])	
4a	Bn	4-ClC_6H_4	**10a**/**11a** (100:0)	**10a** (52)	**11a** (–)[c]
4b	Bn	Ph	**10b**/**11b** (55:45)	**10b** (–)[d]	**11b** (–)[d]
4c	*i*Pr	Ph	**10c**/**11c** (30:70)	**10c** (0)	**11c** (44)
Conversion of (thiocyanatomethyl)aziridines **10** and **11** into 2-(aminomethyl)thiiranes **12** and **13**					
Substrate(s)	R	Ar	Ratio (**12**/**13**)[a]	Product (yield[b] [%])	
10a	Bn	4-ClC_6H_4	–	**12a** (88)	**13a** (–)[c]
10b + **11b**	Bn	Ph	**12b**/**13b** (55:45)	**12b** (–)[e]	**13b** (–)[e]
11c	*i*Pr	Ph	–	**12c** (–)[c]	**13c** (90)
Conversion of 2-(aminomethyl)thiiranes **12** and **13** into thiazolidin-2-ones **14** and **15**					
Substrate(s)	R	Ar	Ratio (**14**/**15**)[a]	Product (yield[b] [%])	
12a	Bn	4-ClC_6H_4	–	**14a** (71)	**15a** (–)[c]
12b + **13b**	Bn	Ph	**14b**/**15b** (53:47)	**14b** (33)	**15b** (22)
13c	*i*Pr	Ph	–	**14c** (–)[c]	**15c** (95)

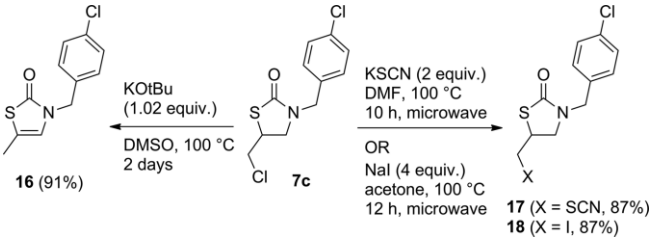
[a] Determined by analysis of the crude reaction mixture by ^1H NMR spectroscopy ($CDCl_3$). [b] Yield of isolated product. [c] Not applicable. [d] Aziridines **10b** and **11b** were isolated as a mixture in a combined yield of 28 %, and this mixture was used as such in the next step. [e] Thiiranes **12b** and **13b** were isolated as a mixture in a combined yield of 93 %, and this mixture was used as such in the next step.

reactivity profile, which pointed to the fact that the observed thiocyanate-induced nucleophilic attack across 1-alkyl-2-aryl-3-(tosyloxymethyl)aziridines **9** is governed by a subtle interplay between the different substituents present at the aziridine scaffold.

In a next step, obtained (thiocyanatomethyl)aziridines **10** and **11** were treated with $LiAlH_4$ (1.7 equiv.) in THF at –78 °C, which evoked a thia-aza-Payne rearrangement to afford thiirane(s) **12** and/or **13** in excellent yield(s) (88–93 %, Table 3). The relative *trans* stereochemistry of thiiranes **13b** and **13c** was confirmed by the vicinal coupling constants between the 2H and 3H protons on the thiirane ring (J_{trans} = 5.2–5.4 Hz), which is in accordance with the literature.[13] Separation of thiiranes **12b** and **13b**, obtained from aziridine mixture **10b** and **11b**, appeared to be inconvenient, and as a consequence, the mixture was used as such in the ring-transformation reaction with triphosgene (1 equiv.) in THF. After heating at reflux temperature for 4 h, corresponding thiazolidin-2-ones **14b** and **15b** were produced, and they could eventually be separated and isolated by means of preparative TLC (silica gel) in yields of 33 and 22 %, respectively. Aminomethylated thiiranes **12a** and **13c** (obtained from aziridines **10a** and **11c**, respectively) were also treated with triphosgene (1 equiv.) in THF under reflux conditions, and they afforded 5-(chloromethyl)thiazolidin-2-ones **14a** and **15c** in yields of 71 and 95 %, respectively. The molecular identity of thiazolidin-2-one **15c** was unequivocally established by means of single-crystal X-ray analysis (see the Supporting Information), which provided clear evidence for the regioselective chloride-induced ring opening of thiiranes **13b** and **13c** at the benzylic position.[11b,11c]

From the above-described results, it is clear that nonactivated 2-(thiocyanatomethyl)aziridines **1**, derived from corresponding aziridines **2**–**4**, represent valuable substrates for an unprecedented and efficient thia-aza-Payne rearrangement, as shown by the synthesis and characterization of 12 2-(aminomethyl)thiiranes. Furthermore, the involved experiments show that the aziridine-to-thiirane migrations are irreversible and occur with inversion at the stereogenic center. Moreover, subsequent treatment of the obtained 2-(aminomethyl)thiiranes with triphosgene resulted in the formation of chloromethyl-substituted thiazolidin-2-ones by regioselective thiirane ring opening by chloride at the less-substituted or benzylic position, which is in accordance with the literature concerning the ring opening of thiiranes.[7d,11,12] Notably, this report discloses the first method for an aziridine-to-thiirane conversion in a selective and straightforward manner, and it should therefore be considered as a powerful strategy in modern organic chemistry.

In a final stage of this study, additional synthetic efforts were made to explore briefly the reactivity of the obtained 5-chloromethyl-substituted thiazolidin-2-one building blocks. To that end, treatment of thiazolidin-2-one **7c** as a representative example with KO*t*Bu (1.02 equiv.) in DMSO afforded 5-methylthiazolin-2-one **16** in 91 % yield after 2 days at 100 °C through base-induced dehydrochlorination and subsequent prototrophic rearrangement toward a more stable endocyclic double bond (Scheme 1).[8a] Reaction of same thiazolidin-2-one **7c** with KSCN (2 equiv.) in DMF or NaI (4 equiv.) in acetone under microwave irradiation resulted in the formation of substitution products **17** and **18**, both in 87 % yield. The use of benzylamine, NaOAc, and KCN as nucleophiles, however, appeared to be less straightforward and resulted in more complex reaction mixtures.



Scheme 1. Reactivity of thiazolidin-2-one **7c** with respect to KO*t*Bu, KSCN, and NaI.

Conclusions

In conclusion, an efficient and reliable thia-aza-Payne rearrangement of nonactivated 2-(thiocyanatomethyl)aziridines toward 2-(aminomethyl)thiiranes was developed. The deployment of different classes of aziridine substrates showed that diverse substitution patterns did not impose any restrictions on the desired aziridine-to-thiirane migrations. In addition, the obtained 2-(aminomethyl)thiiranes were easily converted into 5-(chloromethyl)thiazolidin-2-one building blocks, which points to a regioselective thiirane ring opening by chloride.

CCDC 1536450 (for **15c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

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Keywords: Heterocycles · Rearrangement · Reduction · Regioselectivity · Small ring systems

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