Mild Deprotection of Dithioacetals by TMSCl / NaI Association in CH_3CN

Yunxin Yao,[a] Guangkuan Zhao,[a] Abdallah Hamze,[a] Mouad Alami,[a] and Olivier Provot[a]*

[a] Université Paris-Saclay, CNRS, BioCIS, 92290, Châtenay-Malabry, France. Phone: +33 (0)146835847. Email: olivier.provot@universite-paris-saclay.fr

Abstract. A mild process using a combination of TMSCl and NaI in acetonitrile is used to regenerate carbonyl compounds from a variety of dithiane and dithiolane derivatives. This easy to handle and inexpensive protocol is also efficient to deprotect oxygenated and mixed acetals as 1,3-dioxanes, 1,3-dioxolanes and 1,3-oxathianes quantitatively. As a possible extension of this method, it was also showed that nitrogenated-substrates as hydrazones, *N*-tosylhydrazones and ketimes reacted well under these conditions to give the expected ketones in high yields. The methodology proposed herein is a good alternative to the existing methods since it does not use metals, oxidants, reducing agents, acidic or basic media, and keto-products were obtained in high to excellent yields.

Keywords: dithioacetal; deprotection; trimethylsilylchloride; sodium iodide; ketone

Introduction

Dithianes are commonly used in organic chemistry to mask the electrophilic nature of carbonyl groups[1] in elaborated molecules but also serve as acyl anions in syntheses according to the Umpolung concept.[2]The main advantages of dithianes are their easy access from a carbonyl compound by using propane-1,3-dithiol and a Lewis acid and their stabilities in alkaline and acid conditions notably permitting their purification on silica columns. In counterparts to this stability, many procedures have been developed for their deprotection but generally require drastic conditions.[3] Most of the time, toxic metal salts as Hg(II),[4] Ag(I),[5] Zn(II),[6] Ga(III),[7] Cu(II),[8] Tl(V)[9] and others are used in excess in harsh conditions with some success. The use of hypervalent-iodine reagents for the removal of dithianes has been also reported as an efficient process using periodic acid,[10] diacetoxyiodobenzene,[11] *bis*(trifluoroacetoxy)iodo-benzene (BTI),[12] Dess-Martin periodinane[13] and *N*-halosuccinimides.[14] However, a large variety of the aforementioned methods require the use of toxic metals, the need of oxidizing species in large amounts sometimes accompanied with co-oxidants mainly in harsh reaction conditions. In this context, we believe that an alternative milder process is still needed using for example inexpensive and soft reagents to achieve this transformation at room temperature in the presence of various functional groups.

Recently, we reported the interesting reducing properties of the TMSCl/NaI association in CH_2Cl_2 towards various functional groups as unsymmetrical α-diketones,[15] α-ketoesters,[16] and hydrazones[**Error! Bookmark not defined.**] derivatives. Under similar reaction conditions, we next demonstrated that a variety of dithioacetals were cleanly desulfurized at room temperature[17] in CH_2Cl_2 using this metal-free process in a Mozingo-type reaction.[18]

By replacing CH_2Cl_2 by CH_3CN as the reaction solvent, we surprisingly observed that dithianes derivatives were not reduced into methylene substrates but were totally and cleanly deprotected into ketones. It seemed interesting to study in detail this method for the deprotection of thioacetals which does not use metal salts, nor oxidants, nor toxic or expensive reagents (Figure 1). Herein, we wish to report the mild deprotection conditions of a range of dithianes, dithiolanes and oxygenated derivatives using the TMSCl/NaI association in CH_3CN.

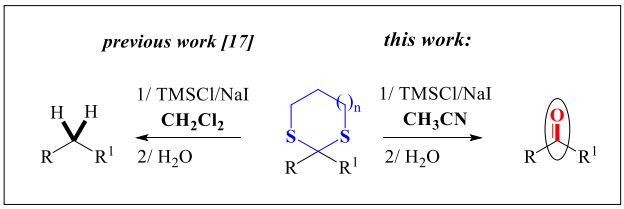
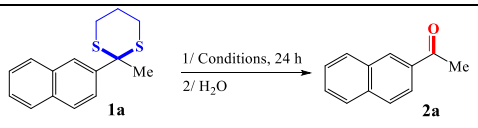


Figure 1. Properties of the TMSCl / NaI combination towards dithioacetals in CH_2Cl_2 and CH_3CN.

Results and Discussion

First, we have selected 2-methyl-2-(naphthalen-2-yl)-1,3-dithiane **1a** which was totally reduced into 2-ethylnaphtalene by TMSCl/NaI combination in

Table 1. Optimization of reaction conditions[a)]



Entry	Conditions	Yield %
1	TMSCl/NaI (10 eq), EtOH, rt	0[b)]
2	TMSCl/NaI (10 eq), TFE, rt	<10[b)]
3	TMSCl/NaI (10 eq), *t*BuOH, rt	0[b)]
4	TMSCl/NaI (10 eq), Et_2O, rt	24[b)]

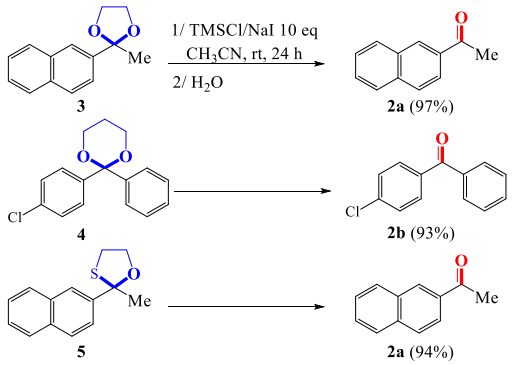
5	TMSCl/NaI (10 eq), THF, rt	25[b]
6	TMSCl/NaI (10 eq), acetone, rt	17[b]
7	**TMSCl/NaI (10 eq), MeCN**	**52**
8	TMSCl (10 eq), MeCN, rt	0
9	TMSCl/NaI (10 eq), MeCN/H_2O 85/15, rt	<10[b]
10	TMSCl/NaI (10 eq), wet MeCN, rt	38[b]
11	TMSCl/NaI (10 eq), $NaOH_{aq}$ (10 eq.) MeCN, rt	40[b]
12	TMSCl/NaI (10 eq), HCl_{aq} (10 eq.) MeCN, rt	36[b]
13	TMSCl/NaI (15 eq), MeCN, rt	67
14	TMSCl/NaI (20 eq), MeCN, rt	71[c]
15	TMSCl/NaI (10 eq), MeCN, 60 °C	68
16	TMSCl/NaI (15 eq), MeCN, 60 °C	78
17	**TMSCl/NaI (20 eq), MeCN, 60 °C**	**92**
18	TMSCl/NaI (20 eq), MeCN/CH_2Cl_2 (1/1), 60 °C	85
19	TMSI (10 eq), MeCN, rt	10[c]

[a] All trials were achieved using 100 mg of **1a**. [b] Most of **1a** remained intact. [c] Reaction time: 3 h.

CH_2Cl_2[**Error! Bookmark not defined.**] as our model substrate to herein examine the dithiane deprotection reaction by the same reagents under a variety of reaction conditions (Table 1). In view of using EtOH as a green solvent,[19] we firstly try to deprotect 1,3-dithiane **1a** in EtOH in the presence of 10 equiv. of TMSCl/NaI combination. However, EtOH and other alcohols of different nucleophilicity as trifluoroethanol (TFE) or *t*BuOH were found to be ineffective as **1a** was mainly found unchanged after 24 h of reaction at rt (entries 1-3). When the deprotection-reactions were done in Et_2O, THF or acetone (entries 4-6), a better trend was noticed since **2b** was isolated in low yields accompanied by a large part of unreacted **1a**. Longer reaction times or higher temperatures will probably be needed to complete this transformation in these solvents. In CH_3CN, in which the nitrogen atom is linked to the silicon atom of TMSCl,[20] we were pleased to isolate **2a** with a promising yield of 52 % (entry 7) with no trace of the reduced 2-ethylnaphtalene obtained in CH_2Cl_2.[**Error! Bookmark not defined.**] Under same reaction conditions but without NaI, **1a** was found unchanged thus showing the essential role of NaI (entry 8). Addition of water, $NaOH_{aq}$ or HCl_{aq} had a deleterious effect on the reaction since a large part of **1a** was recovered after 24 h of reaction (entries 9-12). The amount of TMSCl/NaI and the temperature of the reaction were next examined (entries 13-17) and the best result was obtained by achieving the deprotection reaction at 60 °C in the presence of 20 eq of TMSCl/NaI leading to ketone **2a** in an excellent yield of 92% (entry 17). To examine the influence of solvents (deprotection *vs* reduction), **1a** was reacted with TMSCl/NaI in CH_3CN/CH_2Cl_2 (1/1) for 24 h at 60 °C (entry 18). In this mixture of solvents, we have isolated only ketone **2a** (85 %) with no trace of the 2-ethylnaphtalene (reduced compound) showing the predominant role of CH_3CN when linked to TMSCl[20] (see plausible mechanism in Scheme 4). Last, the reaction was also run in CH_3CN in the presence of TMSI (10 eq) at rt (entry 19) for comparison. After only 3 h of reaction, we observed by TLC the total disappearance of **1a** but **2a** was isolated, beside a large number of unidentified by-products, with a poor yield of 10%[21] thus showing the superiority of the TMSCl/NaI association compared to TMSI for carrying out these deprotection reactions in CH_3CN.

Next, we were interested to evaluate this mild protocol with 1.3-dioxolane **3**, 1,3-dioxane **4**, and with 1,3-oxathiane **5**.

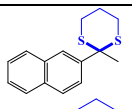
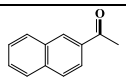
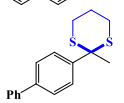
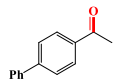
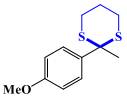
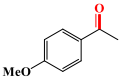
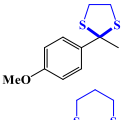
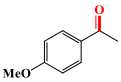
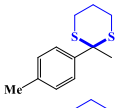
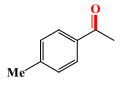
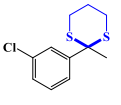
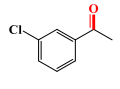
Scheme 1. Deprotection of cyclic ketals **3**,**4** and oxathiane **5** by TMSCl/NaI in MeCN

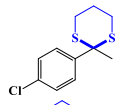
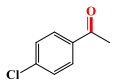
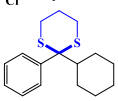
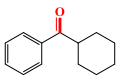
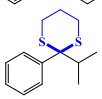
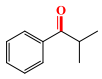
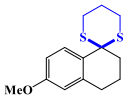
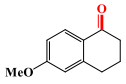
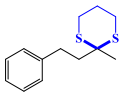
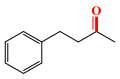
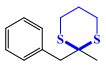
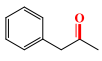
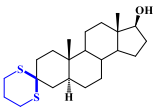
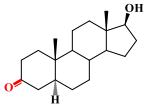
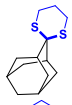
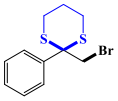
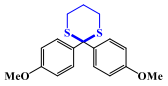
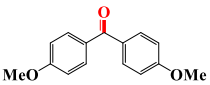
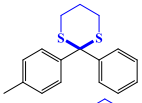
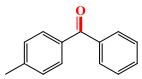
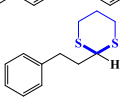
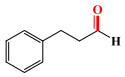
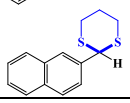
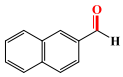


As it could be seen in Scheme 1, by using TMSCl/NaI in CH_3CN under conditions A (seen in entry 7 of Table 1), we observed a clean and complete deprotection of ketals **3** and **4** as well as 1.3-oxathiane **5** into ketones (93 to 97%). For comparison, Jung reported that TMSI in $CHCl_3$ deprotected ethylene ketals into ketones but with very low yields (20 %) and that TMSI did not react with thioketals after 24 h of mixing at 75 °C.[22]

Encouraged by these results and by the simplicity of this process, the deprotection of a variety of thioacetals **1** was carried out with the TMSCl/NaI association in CH_3CN for 24 h. Table 2 summarizes the results of this study achieved using 10 eq of TMSCl/NaI at rt (conditions A) or 20 eq of TMSCl/NaI at 60 °C (conditions B) for less cooperative substrates.

Table 2. Deprotection of **1a-u** by TMSCl/NaI in MeCN

Substrate[a]	TMSCl/NaI(eq)	T °C	t (h)	Product[b]	Yield (%)
	**1a** 20	60	24		**2a** 92
	**1b** 10	rt	24		**2c** 89
	**1c** 10	rt	24		**2d** 94
	**1d** 20	60	24		**2d** 83
	**1e** 10	rt	24		**2e** 86
	**1f** 10	rt	24		**2f** 76

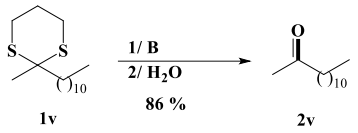
	**1g**	20	60	24		**2g**	54
	**1h**	20	rt	48		**2h**	90
	**1i**	10	rt	24		**2i**	87
	**1j**	10	rt	24		**2j**	83
	**1k**	10	rt	24		**2k**	85
	**1l**	20	60	24		**2l**	64
	**1m**	10	rt	24		**2m**	90
	**1n**	10	rt	24		**2n**	95
	**1o**	10	rt	24		**2o**	76
	**1p**	20	60	24		**2p**	88
	**1q**	20	60	24		**2q**	73
	**1r**	10	rt	24		**2r**	43[c]
		30	60	96			87[d]
	**1s**	30	60	48		**2s**	54[d]
	**1t**	10	rt	24		**2t**	93
	**1u**	10	rt	12		**2u**	40

[a] Dithioacetals were prepared from the corresponding ketones with dithiols in the presence of BF_3-Et_2O. [23] [b] All purified ketones had ^1H and ^{13}C NMR data identical to those of authentic samples. [c] 1-Benzyl-4-methoxybenzene (40%) resulting from the dithioketal reduction was also isolated. [d] NaBr replaced NaI.

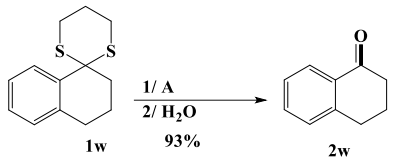
As observed 1,3-dithianes and 1,2-dithiolanes of acetophenones **1a-g** were deprotected into their parent ketones with good yields ranging from 54 to 94%. It is of note that, 1,3-dithianes **1b**,**c**, and **1f**,**g** were more cooperative substrates than our model substrate **1a** since the deprotection reaction required half quantity of TMSCl/NaI and was achieved at rt under conditions A. Examination of these results also shows that 1,3-dithianes seem easier to deprotect using TMSCl/NaI in CH_3CN than their 1,2-dithiolane counterparts (compare **1c** and **1d**) and that electron-donating groups on the aromatic nucleus allowed more efficient deprotection reactions (compare **1c** and **1g**). As expected, 1,3-dithianes prepared from aliphatic aryl (cyclic or not) ketones **1h-l** reacted well with the TMSCl/NaI combination and furnished ketones **2h-l** in good to excellent isolated yields (64 to 91%). The case of dialkyldithiane derivatives was next examined with compounds **1m-p** and showed that these compounds were also cooperative substrates as they were rapidly and cleanly deprotected to give the desired ketones **2m-p** with satisfactory yields (76 to 95%). When α-bromo dithiane **1q** was reacted with TMSCl/NaI, acetophenone **2q** was obtained indicating that, besides the expected deprotection reaction, a α-debromination reaction occurred too in agreement with a previous report of Olah.[24] Then, the case of diaryldithianes was examined. Under A classical conditions (TMSCl/NaI 10 equiv, rt, 24 h), we observed that 1,3-dithiane **1r** having no Hα, reacted with TMSCl/NaI to give a mixture composed in almost equal parts of the expected ketone **2r** (43%) accompanied by the reduction [Error! Bookmark not defined.] product 1-benzyl-4-methoxybenzene (40%). To avoid the formation of the reduction by-product, we successfully replaced NaI by NaBr, increased the quantity of TMSCl/NaBr and heated the solution at 60 °C for a prolonged time (TLC monitoring). By using these conditions, diarylketones **2r** and **2s** were then obtained with acceptable yields and without any traces of the reduced diarylmethane by-products. Next, 1,3-dithianes of aldehydes were also studied with compounds **1t** and **1u**. It is of note that these 1,3-dithianes reacted rapidly under A mild conditions to give the corresponding aldehydes in variable yields. For the deprotection of dithioketals of aldehydes, it is very important to examine carefully the course of the deprotection reaction by TLC monitoring because prolonged reaction times resulted in a severe decrease in yields. Indeed, it has been reported that, at rt, aldehydes reacted rapidly with TMSI to give iodosilyl ethers and diiodoethers.[25] This suggests that, as soon as aldehydes are formed after thioacetal deprotection, they add nucleophilic iodides which may arise from TMSI very slowly generated in the media according to an exchange Finkelstein reaction.[26]

To show the interest of this process with respect to other previously reported methods using for examples HgO associated with BF_3-Et_2O,[27] 2,6-dicarboxy pyridinium chlorochromate (DCPCC)[28] or $SbCl_5$[29] we have deprotected dithiolanes **1v** and **1w** by TMSCl/NaI in CH_3CN (Scheme 2). The comparison of the yields obtained using the TMSCl/NaI mild association in CH_3CN *vs* toxic oxidizing agent as HgO (86 % vs 65%), DCPCC (93% vs 70%) or $SbCl_5$ (93% vs 77%) supports well that this novel metal-free process is welcome since the yields in desired ketones are significantly higher and the reagents used for the deprotection are inexpensive, not toxic and very easy to handle.

Scheme 2. Deprotection of dithianes **1v** and **1w** by TMSCl/NaI in CH_3CN.



[26]: HgO 2 eq, BF_3-Et_2O 2 eq, THF/H_2O, rt, **65 %**



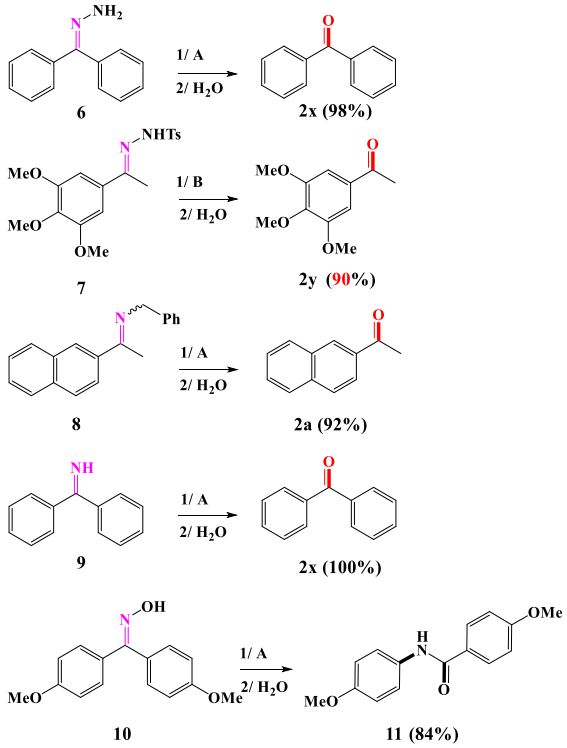
[27]: 2,6-dicarboxypyridinium chlorochromate 2.5 eq, CH_3CN, rt, **70 %**

[28]: $SbCl_5$ 1.5 eq, N_2, DCM, 0 °C then $NaHCO_3$, **77 %**

A : TMSCl/NaI 10 eq, CH_3CN, 24 h, rt. **B** : TMSCl/NaI 20 eq, CH_3CN, 24 h, 60 °C.

Next, as dithioacetals, the regeneration of carbonyl compounds from nitrogen-derivatives as hydrazones, *N*-tosylhydrazones, ketimines and oximes required most of the time harsh reaction conditions including oxidative or reducing process, acidic or alkaline media, expensive reagents or hazardous experimental protocols.[30] In order to find a milder process, we next examined if the TMSCl/NaI combination in CH_3CN process could be applied successfully to these robust nitrogen substrates.

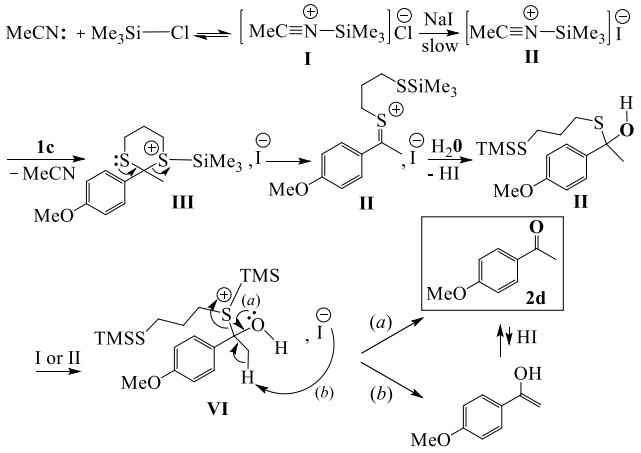
Scheme 3. Reaction of **6-10** by TMSCl/NaI in MeCN



A : TMSCl/NaI 10 eq, CH_3CN, 24 h, rt. **B** : TMSCl/NaI 20 eq, CH_3CN, 24 h, 60 °C.

In Scheme 3 were presented the results of the regeneration of carbonyl functions of diphenylhydrazone **6**, *N*-tosylhydrazone **7**, *N*-benzylimine **8**, ketimine **9** and diphenylmethanone oxime **10,** using TMSCl/NaI in CH_3CN. We were pleased to observe that the TMSCl/NaI combination in CH_3CN was able to transform imines and hydrazones into ketones with good yields (90 to 100%) as well as *N*-tosylhydrazone **7** which required the use of stronger reaction conditions. On the contrary, imine **8** and ketimine **9** were easily transformed into their ketones with high yields using the TMSCl/NaI association in CH_3CN at rt. When diphenylmethanone oxime **10** was reacted with the TMSCl/NaI association (10 eq), we isolated, after 24 h of reaction achieved at rt, 4-methoxy-*N*-(4-methoxyphenyl)benzamide **11** in a good yield (84%) accompanied by only 4 % of the *bis*(4-methoxyphenyl)methanone **2r**. The scope of this interesting Beckmann rearrangement, using the TMSCl/NaI combination, is currently under investigation in our lab with a range of oxime substrates.[31]

Scheme 4. Plausible mechanism



A plausible reaction mechanism is indicated in (Scheme 4). First, CH_3CN activates the TMSCl/NaI association as mentioned previously by Olah[**Error! Bookmark not defined.**] to promote intermediate **I** and **II** after halide exchange in the presence of NaI. Then, **II** reacts with a sulfur atom of dithiolane **1c** to give a sulfonium species of type **III**. Further assistance from the neighboring dithiane sulfur atom possibly leads to a fragmented sulfonium intermediate **IV** which added H_2O (from reagents, CH_3CN or during hydrolysis) to promote hemithioketal **V** which is then activated into a sulfonium intermediate **VI** (having or not Hα). With no Hα as in **1r** or **1s**, **VI** finally rearranges into the desired ketone **2d**.[32] For dithiolanes prepared from enolizable ketones as **1c**, the same (*a*) pathway could be followed but it is also reasonable to consider an additional pathway (*b*) in which an iodide deprotonates intermediate **VI** to furnish an enol species which tautomerizes into ketone **2d**. Since dithioacetals having Hα can evolve according to two different pathways, this can explain that these entities are easier to deprotect than diarylthioketals counterparts. It is of note that a similar mechanism has been previously proposed by Nicolaou for the deprotection of S,S-acetals and ketals using IBX.[33]

Conclusion

In this article we showed for the first time, the fundamental role of CH_3CN associated to TMSCl/NaI combination to deprotect S,S-ethylene- and S,S-propylene-ketals into ketones. Indeed, if the mild TMSCl/NaI association leads to the reduction of dithioketals in CH_2Cl_2, we have demonstrated that this association can be used to deprotect a large variety of various dithioketals into ketones in CH_3CN. Otherwise, under mild experimental conditions, O,O-acetals as well as O,S-oxathianes were cleanly deprotected with high yields. It is also possible to easily regenerate the carbonyl function of various hydrazones and imines using this novel protocol. We believe that this metal-free process is a good alternative to other known methodologies used to deprotect dithioketals into ketones.

Experimental Section

A general experimental procedure is described as following: a mixture of thioketal (100 mg) and NaI (10 eq) was stirred in MeCN for 5 min. Then, 10 eq of TMSCl were added to the solution which was stirred for 24 h at rt. The reaction was then hydrolyzed for 5 min. with H_2O (5 mL) and extracted with CH_2Cl_2. Organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to give a residue which was purified by chromatography on silica gel to give the expected carbonyl compound which have identical NMR spectra with starting ketones.

Acknowledgements

Authors gratefully acknowledge support of this project by CNRS and Univ. Paris-Saclay. Yunxin Yao and Guangkuan Zhao thank the Chinese Scholarship Council for Ph.D. funding.

References

[1] a) T. W.Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis* John Wiley: New York, NY, 2006, pp 477–500. b) P. J. Kocienski, *Protecting Groups*, 3 rd ed., Thieme, Stuttgart, 2003.

[2] D. Seebach, E. J. Corey, *J. Org. Chem.* **1975**, *40*, 231–237.

[3] T. E. Burghardt, *J. Sulfur Chem*. **2005**, *26*, 411–427.

[4] E. J. Corey, M. G. Bock, *Tetrahedron Lett*. **1975**, *26*, 2643–2647.

[5] K. Nishide, K. Yokota, D. Nakamura, T. Sumiya, M. Node, M. Ueda, Fuji, *Tetrahedron Lett*. **1993**, *34*, 3425–3428.

[6] A. Vakalopoulos, H. M. R. Hoffmann, *Org. Lett*. **2001**, *3*, 2185–2188.

[7] K. Saigo, Y. Hashimoto, N. Kihara, N. Urmehara, M. Hasegawa, *Chem. Lett*. **1990**, 831–834.

[8]T. Mukaiyama, K. Narasaka, M. Furusato, *J. Am. Chem. Soc.* **1972**, *94*, 8641–8642.

[9] M. Kirihara, T.Noguchi, N.; Okajima, S. Naito, Y. Ishizuka, A. Harano, H. Tsukiji, R. Takizawa, *Tetrahedron* **2012**, *68*, 1515–1520.

[10] X. X. Shi, S. P. Khanapure, J. Rokash, *Tetrahedron Lett*. **1996**, *37*, 4331–4334.

[11] X. X. Shi, Q.-Q. Wu, *Synthetic Commun*. **2000**, *30*, 4081–4086.

[12] G. Stork, K. Zhao, *Tetrahedron Lett*. **1989**, *30*, 287–290.

[13] N. F. Langille, L. A. Dakin, J. S. Panek, *Org. Lett*. **2003**, *5*, 575–578.

[14] a) E. J. Corey, B. W. J. Erickson, *J. Org. Chem*. **1971**, *36*, 3553–3560. b) P. V. Ramachanchandran, M. T. Rudd, T. E. Burghardt, M. V. R. Reddy, *J. Org. Chem*. **2003**, *68*, 9310–9316.

[15] L. Z. Yuan, D. Renko, I. Khelifi, O. Provot, J.-D. Brion, A. Hamze, M. Alami, *Org. Lett*. **2016**, *18*, 3238–3241.

[16] L. Z. Yuan, G. Zhao, A. Hamze, M. Alami, O. Provot, *Adv. Synth. Catal.*, **2017**, *359*, 2682–2691.

[17] G. Zhao, L. Z. Yuan, M. Alami, O. Provot, *Adv. Synth. Catal*., **2018**, *360*, 2522–2536.

[18] For a review see: G. Zhao, L. Z. Yuan, M. Alami, O. Provot, *ChemSelect*, **2017**, *2*, 10951–10959.

[19] See for exemple: G. Zhao, C. Roudaut, V. Gandon, M. Alami, O. Provot, *Green Chem*., **2019**, *21*, 4204–4210.

[20] G. A. Olah, S. C. Narang, *Tetrahedron* **1982**, *38*, 2225-2277.

[21] 2-(1-Iodoethyl)naphthalene resulting from the half-reduction of **1a** was also identified in the crude mixture (< 10%).

[22] M. E. Jung, W. A. Andrus, P. L. Ornstein, *Tetrahedron Lett*. **1977**, *48*, 4175-4178.

[23] To a solution of ketone or aldehyde (1 mmol) in 20 mL of DCM was added the thiol derivative (1,2-ethanedithiol or 1,3-propanedithiol; 5 mmol), followed by 1 mL of BF_3-Et_2O. The solution was stirred at rt until disappearance of starting material (judged by TLC). Then, H_2O (20 mL) and DCM (30 mL) were added to the solution. The organic layer was separated, washed with H_2O (2 x 10 mL) and saturated NaCl solution (2 x 10 mL), dried over $MgSO_4$, and concentrated under reduced pressure to give a dithioacetal which was purified by chromatography on silica gel.

[24] G. A. Olah, M. Arnavaghi, Y. D. Yankar, *J. Org. Chem*. **1980**, *45*, 3531-3532.

[25] M. E. Jung, A. B. Mossman, Lyster, M. A. *J. Org. Chem*. **1978**, *43*, 3698-3701.

[26] H. Finkelstein, *Ber. Dtsch. Chem. Ges*. **1910**, *43*, 1528-1532.

[27] M. Kirihara, T. Noguchi, N. Okajima, S. Naito, Y. Ishizuka, A. Harano, H. Tsukiji, R. Takizawa, *Tetrahedron* **2012**, *68*, 1515-1520.

[28] R. Hosseinzadeh, M. Tajbakhsh, A. Shakoori, M. Y. Niaki, *Monatsh. Chem.* **2004**, *135*, 1243–1249).
[29] M. Kamata, H. Otogawa, E. Hasegawa, *Tetrahedron Lett.* **1991**, *32*, 7421-7424.
[30] D. Enders, L. Wortmann, R. Peters, *Acc. Chem. Res*. **2000**, *33*, 157–169.
[31] To our knowledge, only one paper reported the use of TMSCl in CH_3CN to achieve at a high temperature of 100 °C, the Beckmann rearrangement of the cyclododecanone oxime into ω–laurolactam (a single example having no functional groups was described in this letter; no isolated yield is mentioned), see: S. Sato, S.Hoshino, T.; Sugimoto, K. Kashiwagi, *Chem. Lett*. **2010**, *39*, 1319-1320.
[32] With a dithioketal having no Hα as **1t**, an iodine may attack intermediate **IV** to give a mixed unstable S,I-ketal which evolves into the reduction product 1-benzyl-4-methoxybenzene (footnote c); Table 2).For a possible mechanism explaining the reduction process, see ref. [17].
[33] K. C. Nicolaou, C. J. N. Mathison, T. Montagnon, *J. Am. Chem. Soc*. **2004**, *26*, 5192-5201.