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Unexpected conversion of vinyl sulfoxides into carbonyl compounds by means of iodotrimethylsilane

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Abstract

The unexpected and previously unknown TMSI-promoted conversion of α,β-unsaturated sulfoxides into carbonyl compounds and disulfides is described. It occurs in good yields under mild conditions. The examples provided support the generality and efficiency of this procedure which acts as a good method for removing the sulfinyl group with the advantage of transforming the vinyl sulfoxides into carbonyl compounds.

Keywords: carbonyl compounds; desulfurization; iodotrimethylsilane; sulfoxides.

1-Methoxy-3-alkylsulfinylbuta-1,3-dienes such as **1** (Scheme 1) have shown their efficiency as enantiopure partners in asymmetric Diels–Alder cycloadditions.[1] The high control exerted by the sulfoxide chirality on the stereochemistry of the final adducts such as **2**, and the easy isolation of the cycloaddition products in high yields, prompted us to explore their usefulness in asymmetric synthesis of target molecules. During this work, we observed an unexpected behaviour of iodotrimethylsilane (TMSI) which seems to be of general synthetic interest: TMSI was able to convert α,β-unsaturated sulfoxides into carbonyl compounds in good yields under mild conditions. To the best of our knowledge, this conversion is without precedent in the literature and we wish to present herein our first results on this subject.

With the aim of obtaining enantiopure polyhydroxylated molecules from (3*R*,4*S*,R_S)-4-(hydroxymethyl)-1-[(1*S*)-isoborneol-10-sulfinyl]-3-methoxycyclohexene (**3**) (Scheme 1) we decided to use TMSI to cleave the O–Me bond following a well-assessed literature procedure.[2] The reaction, which could be performed in an NMR tube and followed by ^{1}H NMR spectroscopy,[2] started with prompt formation of iodine, as indicated by brown colouring of the solution. Compound **3** had

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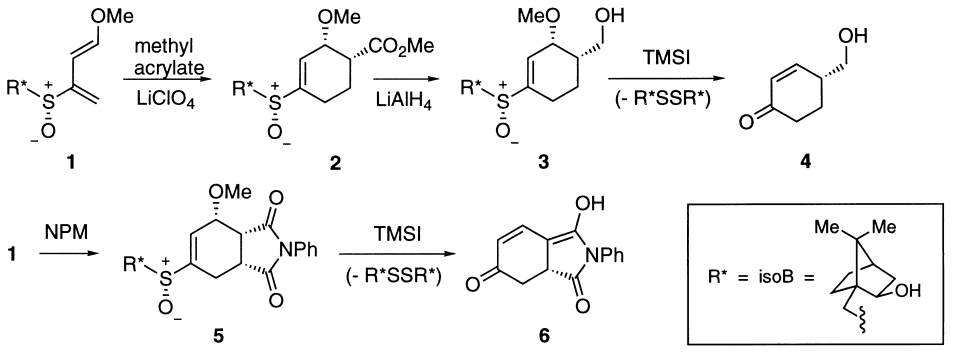


Scheme 1.

disappeared after 1.5 hours (TLC monitoring). MeOH work-up, followed by column chromatography, afforded (*R*)-4-(hydroxymethyl)cyclohex-2-ene-1-one (**4**)[3] and the more mobile bis-{(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]hept-1-ylmethyl}disulfide (R*SSR*),[4] as the major products of the reaction. In contrast to the disappointing result of losing the unmasked hydroxy substituent from the cyclohexene skeleton, the presence of a carbonyl function, which had taken the place of the alkylsulfinyl moiety, appeared to be an unexpected but remarkable outcome of the TMSI-induced reaction. It must be noted that alkyl(vinyl)sulfinyl cycloadducts frequently suffer the problem of ineffective removal of the chiral auxiliary by classical procedures, such as Raney nickel desulfurization.[5] All these considerations prompted us to explore the reactivity of TMSI with 1-sulfinylcyclohexene adducts different from **2** and/or its derivative **3**. Moreover we studied the behaviour of simple open-chain vinylsulfoxides in the presence of TMSI, owing to our interest in testing the generality and efficiency of the procedure. Reaction times and yields in products obtained by TMSI-promoted conversion of vinylsulfoxides into carbonyl compounds are shown in Table 1.

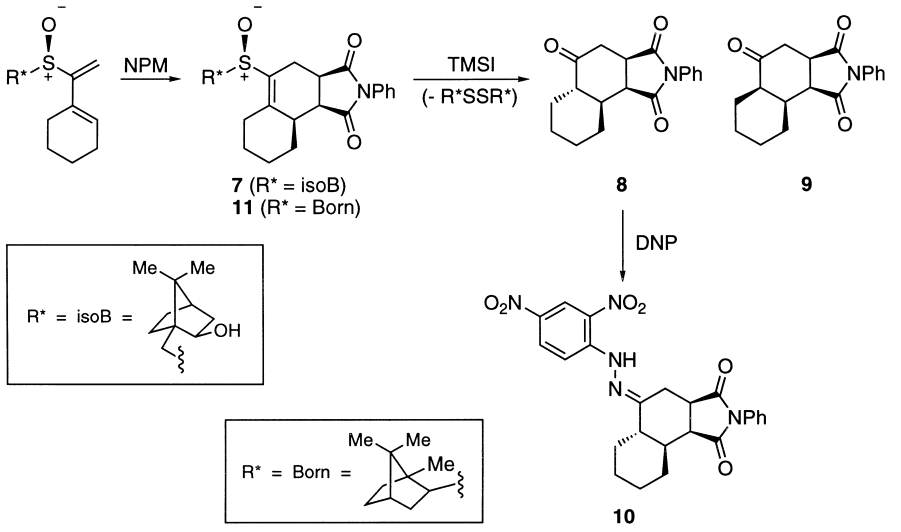
Table 1
TMSI-promoted conversion of α,β-unsaturated sulfoxides into carbonyl compounds at rt in chloroform

Entry	Substrate	Desulfurated Products	Time (hr)	Yield (%)
1	**3**	**4**	1.5	70
2	**5**	**6**	3	50
3	**7**	**8 + 9**	1.5	55 + 27
4	**11**	**8 + 9**	144	50 + 23
5	$PhS(O)C(Ph)=CH_2$ (**12**)	**acetophenone**	96	70
6	$PhS(O)CH=CH_2$ (**13**)	**acetaldehyde**	96	[a]

[a] This yield was not measured, because the experiment was performed on an NMR scale.

The reaction of cycloadduct **5**[6] with TMSI (Scheme 1) led to compound **6**,[7] at room temperature (rt) (entry 2 in Table 1)[8] while the polycyclic adduct **7**[9] afforded a 2:1 diastereomeric mixture of cyclohexanones **8** and **9**[10,11] under the same conditions (Scheme 2, entry 3 in Table 1). The crystalline **8** and **9** were easily isolated by column chromatography. In our hands their crystals were not

suitable for X-ray diffraction analysis, but the 2,4-dinitrophenylhydrazone derivative **10** gave X-ray quality crystals by slow evaporation of chloroform solvent, and the results of its diffraction study are shown in Fig. 1.[12,13] When the bornyl group was linked to the sulfinyl function, the reaction of **11**[9] with TMSI required longer reaction time (entry 4 in Table 1).



Scheme 2.

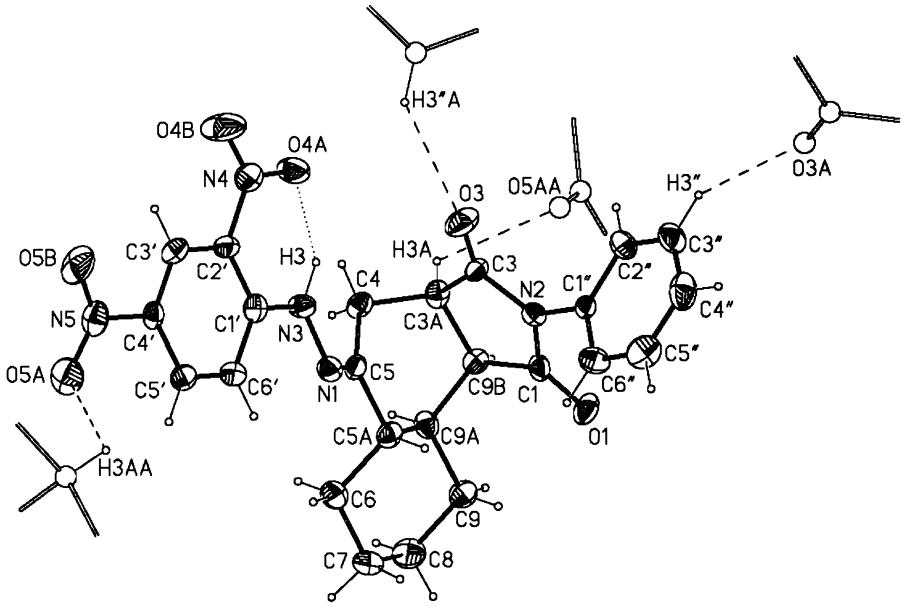


Figure 1. X-Ray structure (asymmetric unit) of 2,4-dinitrophenylhydrazone **10** showing 30% probability thermal ellipsoids for non-H atoms, and labelling scheme. The dotted line denotes the intramolecular H-interaction H(3)···O(4A) = 1.915(7) Å, while the dashed lines represent intermolecular interactions between H(3AA) [*0.5-x, -y, z-0.5*] and O(5A) [*0.5-x, -y, 0.5+z*] [2.55(1) Å], H(3″A) [*-x, 0.5+y, 0.5-z*] and O(3) [*-x, y-0.5, 0.5-z*] [2.58(1) Å, equivalent of the interaction between H(3″) and O(3A)]

Following the observed transformation of our alkyl(vinyl)sulfoxides **3**, **5**, **7, 11** into carbonyl compounds **4**, **6**, **8** and **9** (Schemes 1 and 2), we decided to test this unusual TMSI reactivity on substrates where sulfur is linked to a benzene ring, this structural feature being present in almost all the sulfur-based chiral auxiliaries.[14] 1-Phenylethenyl(phenyl)sulfoxide (**12**)[15,16] and phenyl(vinyl)sulfoxide (**13**) were chosen as substrates for different reasons. The reaction of **12** with TMSI would lead to acetophenone, which can be easily recognized by TLC and isolated. Phenyl(vinyl)sulfoxide (**13**) is commercially available together with the corresponding sulfide and sulfone, so we could perform the same reaction on analogous substrates containing sulfur in different oxidation states. 1-Phenylethenyl(phenyl)sulfoxide (**12**) was reacted with TMSI in anhydrous $CHCl_3$ at RT (entry 5 in Table 1). After MeOH work-up and column chromatography, the expected acetophenone was obtained together with diphenyldisulfide. The experiments regarding phenyl(vinyl)-sulfoxide (**13**), -sulfide and -sulfone were performed on NMR scale in deutero-chloroform. The phenyl(vinyl)sulfoxide (**13**) turned completely to acetaldehyde in 96 hours, no reaction was observed with the sulfone, which remained unchanged even after consecutive additions of further amounts of TMSI (up to a TMSI/substrate molar ratio 3:1), while the phenyl(vinyl)sulfide, analogously treated with the same reagent, showed a mixture of products among which acetaldehyde could not be identified.

The results obtained deserve some comment:

(i) Both nucleophilic sulfur and a sulfinyl oxygen are needed in these conversions of vinyl sulfoxides into carbonyl compounds. If the former (in sulfones) or the latter (in sulfides) are absent, the reaction does not occur.

(ii) The steric requirements of the alkyl or aryl substituents directly linked to the sulfinyl vinyl moiety only affect the conversion rate.

In conclusion, we have discovered a mild, efficient and seemingly general method of converting vinyl sulfoxides into aldehydes or ketones with the advantage of transforming the C–S cleavage of vinyl sulfoxides, generally not easy to achieve, into the functionalization of the molecule with a carbonyl group which can be subjected to numerous synthetic transformations. All of these considerations allow us to anticipate many applications to be developed around this reaction, and further studies in this direction are now in progress.

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7. Analytical and spectroscopic data were fully consistent with the assigned structure. NMR studies of the isolated compound **6** showed only the enol form, as depicted in Scheme 1.
8. Typical experimental procedure: To a solution of sulfoxide (0.53 mmol) in anhydrous $CHCl_3$ (3 ml), TMSI 97% (0.8 mmol) was added at rt. The reaction was monitored by TLC. After disappearance of the starting product, MeOH (30 ml) was added and the reaction mixture stirred for 0.5 h, concentrated under reduced pressure, and column chromatographed. The disulfide was eluted first in all cases, followed by the carbonyl compound.
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11. The analytical data obtained for our sample of **9** were consistent with those previously reported for its racemic form in Ref. 12.
12. X-Ray data: orange crystals of **10**, orthorhombic $P2_12_12_1$, $a = 8.492(2)$ Å, $b = 11.899(3)$ Å, $c = 22.350(4)$ Å, $V = 2258.2(9)$ Å^3, data collection at rt, $Z = 4$, R (*obs*/*all*) = 0.0603/0.1487, R_w (*obs*/*all*) = 0.0416/0.0494, GOF (*obs*) = 1.1803 [*obs* = 1725 for $F \leq 4\sigma(F)$ on 3974 unique reflections with $R_{int} = 0.0161$; 318 parameters]. Selected bond distances (Å) and angles (deg): C(1)–N(2) = 1.405(8), C(1)–C(9B) = 1.52(1), C(1′)–N(3) = 1.346(9), C(1″)–N(2) = 1.451(8), C(3)–C(3A) = 1.50(1), C(3)–N(2) = 1.395(9), C(3A)–C(4) = 1.536(9), C(3A)–C(9B) = 1.552(9), C(4)–C(5) = 1.515(9), C(5)–C(5A) = 1.521(9), C(5)–N(1) = 1.275(9), C(5A)–C(6) = 1.54(1), C(5A)–C(9A) = 1.547(9), C(6)–C(7) = 1.52(1), C(7)–C(8) = 1.53(1), C(8)–C(9) = 1.53(1), C(9)–C(9A) = 1.530(9), C(9A)–C(9B) = 1.527(9), N(1)–N(3) = 1.393(8), C(1)–C(9B)–C(9A) = 115.2(6), C(1)–N(2)–C(1″) = 121.7(5), C(1)–N(2)–C(3) = 113.6(6), C(1′)–N(3)–N(1) = 119.1(5), C(1″)–N(2)–C(3) = 124.7(6), C(2′)–C(1′)–N(3) = 122.8(6), C(3)–C(3A)–C(4) = 108.1(5), C(4)–C(5)–C(5A) = 116.0(5), C(4)–C(5)–N(1) = 128.3(6), C(5)–N(1)–N(3) = 116.4(6), C(5A)–C(5)–N(1) = 115.7(6), C(6′)–C(1′)–N(3) = 120.3(7), C(1′)–N(3)–N(1)–C(5) = 159.3(6), C(2′)–C(1′)–N(3)–N(1) = 177.9(6), C(3)–N(2)–C(1″)–C(6″) = 119.7(8).
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