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An investigation of the behaviour of α,β-unsaturated sulfoxides in the presence of trimethylsilyl iodide

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Abstract—A mild, efficient and seemingly general method for converting α,β-unsaturated sulfoxides into carbonyl compounds by means of trimethylsilyl iodide (TMSI) is described. Experiments on different substrates and trimethylsilyl halides lead to the conclusion that the oxidation state of the sulfur atom, on one hand, and halogen kind in TMSX on the other, assume a determining role in the progression of the reaction. The ease of experimental procedure, the possibility of ^{1}H NMR monitoring, and good yields of final products constitute advantages of the TMSI-promoted conversion of α,β-unsaturated sulfoxides into carbonyl compounds.

1. Introduction

Trimethylsilyl iodide (TMSI) is a versatile synthetic reagent which interacts very readily with organic molecules containing oxygen and promotes the cleavage of carbon–oxygen bonds of compounds such as ethers, esters, ketals, acetals, lactones, carbamates, and epoxides.[1] It has also proved useful for the synthesis of alkyl iodides from alcohols,[2] for the silylation of carbonyl compounds,[3] allylic carbanions,[4] and for reducing azides to amines,[5] sulfoxides to sulfides, and sulfonyl halides to the corresponding disulfides. Recently, we have described a mild and efficient method for converting α,β-unsaturated sulfoxides into carbonyl compounds by means of TMSI.[6] The reaction starts with prompt formation of iodine, which indicates a redox process, and generally, within a few hours, the starting vinyl sulfoxides are transformed into precursors of carbonyl compounds, and disulfides, as shown in Eq. (1).

$$2CH_2{=}CH{-}S(O)R + 2TMSI = 2CH_2{=}CH{-}OTMS + RSSR + I_2 \quad (1)$$

The methodology offers some advantages: (i) TMSI-promoted reactions can be performed in NMR tubes and followed by ^{1}H NMR spectroscopy; (ii) yields of final products are generally good; (iii) the C–S cleavage in the α,β-unsaturated sulfoxides leads to functionalization of the substrates with a carbonyl group which can be easily involved into numerous synthetic transformations.

We now report extensions of our previous observation, for supporting the generality and efficiency of this procedure, even in the presence of sterically and electronically different substituents directly linked to the sulfinyl vinyl moiety. Some results support the reaction mechanism that we discuss below, others define the limits of this procedure, like for instance the use of trimethylsilyl halides different from iodide.

2. Results and discussion

Treatment of α,β-unsaturated sulfoxides with TMSI at room temperature in chloroform gives the corresponding carbonyl compounds. Substrates, final products, reaction times, and yields of the investigated reactions with TMSI are shown in Table 1 (entries 1, 4–14) together with experiments performed on phenyl vinyl sulfoxide (**1**) with trimethylsilyl bromide (TMSBr) (entry 2) and trimethylsilyl chloride (TMSCl) (entry 3). The substrates **2**–**4** come from $LiAlH_4$ reduction of esters obtained as enantiopure products of stereocontrolled Diels–Alder cycloadditions.[12,23]

All the reactions ended within 6 h, apart from the one involving the substrate **5** (entry 7). Entries 1 and 6 refer to reactions performed with TMSI in $CDCl_3$, inside a NMR tube, monitored by ^{1}H NMR experiments, and the desulfurated products were identified in situ as acetaldehyde (**6**) and (*S*)-2,3-dihydro-2-hydroxymethylpyran-4-one (**7**), together with disulfides **8** and **9**, respectively, (see footnote b in Table 1). Also the reactions of phenyl vinyl sulfoxide (**1**) with TMSBr and TMSCl (entries 2 and 3) were performed in NMR tube, and in both cases the final products still contained the sulfur atom. TMSBr promoted reduction of the sulfinyl moiety followed by electrophilic

Keywords: carbonyl compounds; cleavage reactions; desulfurisation; sulfoxides.

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Table 1. TMSX-promoted conversion of α,β-unsaturated sulfoxides at RT in chloroform

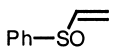
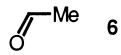
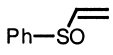
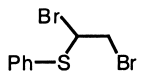
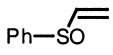
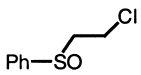
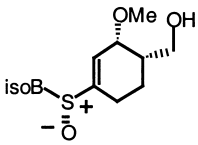
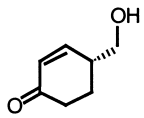
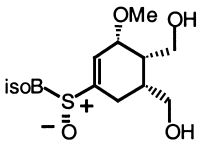
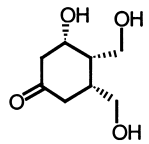
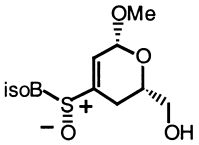
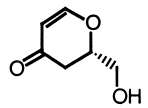
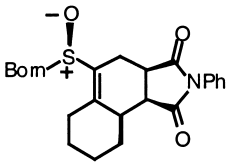
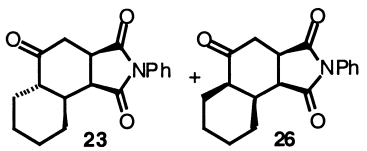
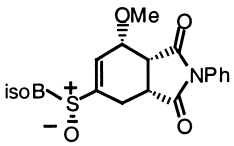
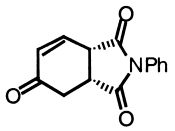
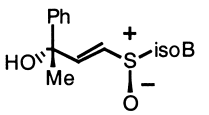
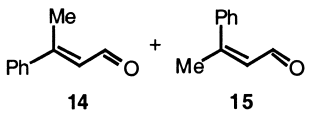
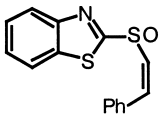
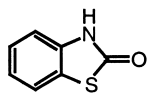
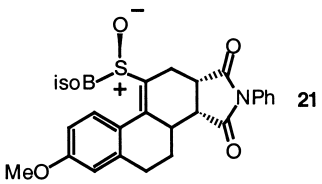
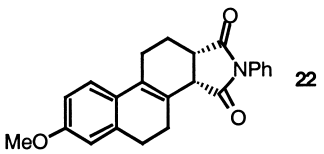
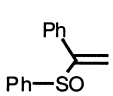
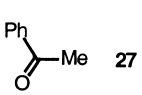
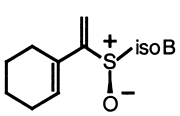
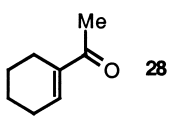
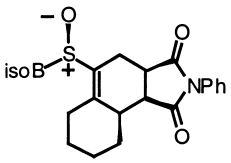
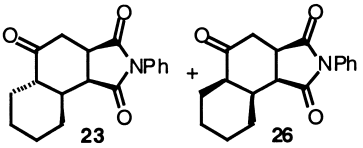
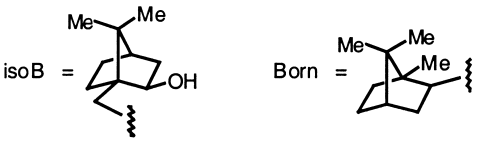
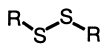
Entry	Substrate[a]	Ref. for substrate	Reagent	Products[b]	Ref. for products	Time (h)	Yield (%)
1	 **1**	Commercial	TMSI	 **6**	Commercial	4	>95[c]
2	 **1**	Commercial	TMSBr	 **24**	7	4	>95[c]
3	 **1**	Commercial	TMSCl	 **25**	Commercial	0.2	40[c]
4	 **2**	6	TMSI	 **12**	6,8	1	70
5	 **3**		TMSI	 **17**		1	80
6	 **4**		TMSI	 **7**	9	4	[d]
7	 **5**	6,10	TMSI	 **23** **26**	6,11	144	50+23
8	 **11**	6,12	TMSI	 **13**	6,13	3	50
9	 **16**	14	TMSI	 **14** **15**	15	0.3	63+32
10	 **18**	16	TMSI	 **19**	Commercial	5	60
11	 **21**	17	TMSI[e]	 **22**	17	1.5	50
12		6,18	TMSI	 **27**	Commercial	6	70
13		10,19	TMSI	 **28**	Commercial	5	>95

Table 1 (*continued*)

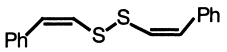
Entry	Substrate[a]	Ref. for substrate	Reagent	Products[b]	Ref. for products	Time (h)	Yield (%)
14		6,10	TMSI	 **23** + **26**	6,11	1.5	55+27

[a] 

[b] Disulfides **8** (entries 1, 12), **9** (entries 4–6, 8, 9, 13, 14),[20] **29** (entry 7),[21] and **30** (entry 10)[22] were also obtained.



8 (R = Ph), **9** (R = isob), **29** (R = Born)



30

[c] The experiment was performed on a NMR scale and the yield estimated by integration of significant proton resonances.

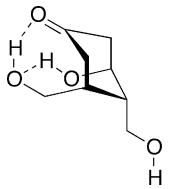
[d] The yield is not reported because of unstability of **7**.[9]

[e] The reaction required a 2.5:1 molar ratio of TMSI/substrate to be completed (see Section 4).

addition of bromine to the double bond, whereas TMSCl was unable to reduce the sulfinyl group, a predictable result on the basis of the redox potential of chlorine/chloride couple, and the HCl addition to the vinyl function was the unique reaction observed in this case. A comparison of the results reported in entries 1–3 clearly proves that TMSI was uniquely effective for promoting conversion of vinyl sulfoxides into carbonyl compounds.

The mechanism we suggest for explaining the outcome of these reactions with TMSI is depicted in Scheme 1. Formation of a strong oxygen–silicon bond[1] is followed by reduction of the sulfur function and oxidation of iodide to iodine, which precipitates in chloroform as a brown red solid. Trimethylsilyloxy anion attacks the unsaturated carbon linked to the sulfur function, which leaves the substrate, allowing the formation of trimethyl(vinyloxy)-silane **10**. Finally, water converts vinyl ether **10** into carbonyl compound.

Cleavage of the O–Me bond by means of TMSI and subsequent dehydration to form a double bond conjugated with the carbonyl function are proposed for substrates **2**, **4**, and **11** which were transformed into α,β-unsaturated ketones **12**, **7**, and **13** respectively (see entries 4, 6, and 8 in Table 1). This hypothesis is supported by a comparison of the results observed in the experiments involving the starting products **2** and **3** (entries 4 and 5): the hydroxymethyl α,β-unsaturated ketone **12**, in one case, and the triol **17**, in the other, have been obtained in the same reaction times and comparable yields. For the conversion of **3** in **17**, the TMSI-promoted cleavage of O–Me bond, not followed by dehydration, can be ascribed to intramolecular hydrogen bonding which stabilizes the reaction product **17** as depicted in **A**.

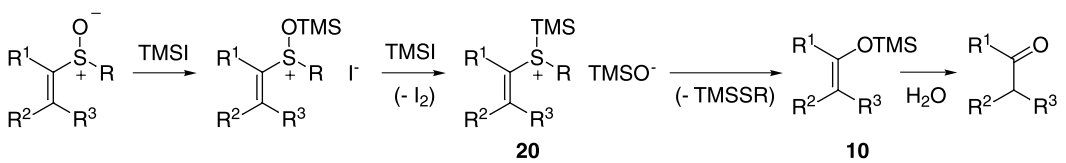


A

In line with previous results, α,β-unsaturated aldehydes **14** and **15** were the final desulfurated products of TMSI-promoted reaction on substrate **16** which lost a stereogenic carbon atom by dehydration (entry 9 in Table 1).

In the substrate **18**, S(O) is located between two unsaturations which show a different electronic nature. We assume that the formation of **19** in the reaction of **18** with TMSI (entry 10 in Table 1) is due to the attack of the trimethylsilyloxy anion onto the more electrophilic unsaturated carbon, the one linked to the nitrogen atom, in the cationic species analogous of **20** in Scheme 1.

The reaction of **21** with TMSI afforded the desulfurated 16-azasteroid derivative **22** (entry 11 in Table 1). The attribution of its structure is based mainly on NMR measurements, such as APT and homodecoupling (see Section 4) in comparison with corresponding experiments performed on the precursor **21**.[17] Noteworthy, no conversion of α,β-unsaturated sulfoxide moiety into a carbonyl function was observed when compound **21** underwent the



Scheme 1.

TMSI treatment, and the cleavage of the C–S bond was followed by reductive migration of the double bond from the 9(11) to the 8 position. The reaction required a 1:2.5 molar ratio of substrate/TMSI to be completed, and no formation of disulfide **9** was observed. These results lead us to believe that the mechanistic outcome of this reaction differs from the one proposed for the other α,β-unsaturated sulfoxides investigated (entries 1, 4–10, 12–14) possibly because of high conformational rigidity of the steroidal skeleton and consequent difficulty of $TMSO^-$ in approaching the electrophilic unsaturated C-11. This significant result holds a prospect of further investigation in a very near future.

3. Conclusion

In conclusion, we have demonstrated the validity of TMSI methodology for the cleavage of C–S bond in α,β-unsaturated sulfoxides, which in almost all the performed experiments resulted in the conversion of the sulfinyl moiety into a carbonyl, providing useful synthetic possibilities. Oxidation state of the sulfur atom, on one hand, and halogen kind in TMSX, on the other, assume a determining role in the progression of the reaction which can be performed on enantiopure substrates without any racemization of stereogenic centres. The ease of experimental procedure and the possibility of ^{1}H NMR monitoring constitute further advantages of this reaction.

4. Experimental

4.1. General

Solvents were purified according to standard procedures. Petroleum ether used refers to the fraction boiling at 30–50°C. All reactions were monitored by TLC on commercially available precoated plates (Aldrich silica gel 60 F 254) and the products were visualized with vanillin [1 g dissolved in MeOH (60 ml) and conc. H_2SO_4 (0.6 ml)]. Silica gel used for column chromatography was Aldrich 60. Melting points were recorded on a microscopic apparatus and are uncorrected. Optical rotations were measured for $CHCl_3$ solutions on a Jasco P-1030 polarimeter (concentrations *c* are in g/100 ml). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300 and 75 MHz respectively in $CDCl_3$ solutions with $SiMe_4$ as internal standard: *J* values are given in Hz; the attributions are supported by Attached Proton Test (APT) and homodecoupling experiments; proton and carbon nuclei, marked with ($'$), pertain to the isoborneol moiety in compounds **2**–**4** and phenyl group in compounds **22** and **23**. Mass spectra were measured by Electron Impact (EI, 70 eV) or Fast Atom Bombardment (FAB, *m*-nitrobenzyl alcohol as matrix) with a Finnigan MAT 90 instrument. IR spectra were recorded in $CHCl_3$ solutions on a Nicolet 410 D FTIR spectrometer. The analytical/spectral data collected for products **6**–**9**, **12**–**15**, **19**, **22**, **24**–**30** were consistent with those reported in the literature (see references in Table 1).

4.1.1. (3*R*,4*S*,*R*$_S$)-4-Hydroxymethyl-1-[(1*S*)-isoborneol-10-sulfinyl]-3-methoxycyclohexene (2). $LiAlH_4$ (83 mg, 2.19 mmol) was added in small subsequent amounts to a solution of (3*R*,4*R*,*R*$_S$)-1-[(1*S*)-isoborneol-10-sulfinyl]-3-methoxy-4-methoxycarbonylcyclohexene (404 mg, 1.09 mmol)[23a] in anhydrous Et_2O (30 ml) at −78°C, under stirring and argon atmosphere. The resulting mixture was allowed to reach room temperature, and the reaction monitored by TLC (eluant light petroleum/EtOAc 50:50) until the starting material had totally disappeared (1 h). The reaction was then quenched by careful addition of H_2O (15 ml). The organic layer was separated and the water phase extracted with Et_2O (2×20 ml) and EtOAc (2×20 ml). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford 365 mg (98% yield) of the expected alcohol **2** as a light yellow oil; ^{1}H NMR: δ 6.69 (dd, 1H, $J_{2,3}$=4.1 Hz, $J_{2,6}$=1.8 Hz, H-2), 4.12 (dd, 1H, $J_{2',3'}$=7.8 and 3.6 Hz, H-2′), 4.05 (t, 1H, $J_{3,4}$=4.1 Hz, H-3), 3.79 (m, 2H, C*H*$_2$OH), 3.48 (s, 3H, OMe), 3.14 and 2.42 (AB system, 2H, $J_{10'A,10'B}$=13.0 Hz, H_2-10′), 2.3–1.1 (m, 12H, H_2-3′,5,5′,6,6′, H-4,4′), 1.08 (s, 3H, H_3-8′), 0.83 (s, 3H, H_3-9′); ^{13}C NMR: δ 146.39 (C-1), 126.92 (C-2), 77.00 (C-2′), 75.44 (C-3), 64.20 (CH_2OH), 57.25 (OMe), 53.47 (C-10′), 51.42 (C-1′), 48.27 (C-7′), 45.09 (C-4′), 40.04 (C-4), 38.39 (C-3′), 30.88 and 27.13 (C-5′,6′), 22.33 (C-6), 21.12 (C-5), 20.52 and 19.88 (C-8′,9′); MS/FAB: *m/z* (%) 343 (M+1, 30), 155 (43), 138 (56), 137 (100), 107 (43), 89 (38), 77 (36); IR: ν_{max} 3415 (OH) cm^{-1}; Anal. calcd for $C_{18}H_{30}O_4S$: C, 63.12; H, 8.83; Found: C, 62.84; H, 8.72.

4.1.2. (3*R*,4*S*,5*R*,*R*$_S$)-4,5-Dihydroxymethyl-1-[(1*S*)-isoborneol-10-sulfinyl]-3-methoxycyclohexene (3). $LiAlH_4$ (26.6 mg, 0.70 mmol) was added in small subsequent amounts to a solution of (3*R*,4*R*,5*R*,*R*$_S$)-4,5-dimethoxycarbonyl-1-[(1*S*)-isoborneol-10-sulfinyl]-3-methoxycyclohexene (100 mg, 0.23 mmol)[12] in anhydrous Et_2O (10 ml) at −78°C, under stirring and argon atmosphere. The resulting mixture was allowed to reach the room temperature, and the reaction monitored by TLC (eluant EtOAc/light petroleum 80:20) until the starting material had totally disappeared (18 h). The reaction was then quenched by careful addition of H_2O (15 ml). The organic layer was separated and the water phase extracted with Et_2O (2×20 ml) and EtOAc (2×20 ml). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford the crude diol **3** which was purified by column chromatography first eluting with EtOAc/light petroleum 50:50 and gradually increasing the polarity of the eluant up to 90% EtOAc. The pure **3** was obtained (71% yield) as a light yellow oil; ^{1}H NMR: δ 6.48 (m, 1H, $J_{2,3}$=4.2 Hz, H-2), 4.15 (dd, 1H, $J_{2',3'}$=7.7 and 2.6 Hz, H-2′), 4.09 (dd, 1H, $J_{3,4}$=8.3 Hz, H-3), 3.9–3.6 (m, 4H, C*H*$_2$OH), 3.49 (s, 3H, OMe), 3.27 and 2.34 (AB system, 2H, $J_{10'A,10'B}$=13.0 Hz, H_2-10′), 2.5–1.2 (m, 11H, H_2-3′,5′,6,6′, H-4,4′,5), 1.09 (s, 3H, H_3-8′), 0.83 (s, 3H, H_3-9′); ^{13}C NMR: δ 143.43 (C-1), 130.10 (C-2), 78.42 (C-3), 76.97 (C-2′), 63.97 (4-CH_2OH), 57.86 (5-CH_2OH), 57.14 (OMe), 53.00 (C-10′), 51.32 (C-1′), 48.24 (C-7′), 44.98 (C-4′), 41.14 (C-4), 38.31 (C-3′), 37.57 (C-5), 30.74 and 27.04 (C-5′,6′), 21.15 (C-6), 20.44 and 19.83 (C-8′,9′); IR: ν_{max} 3432 (OH) cm^{-1}; Anal. calcd for $C_{19}H_{32}O_5S$: C, 61.26; H, 8.66; Found: C, 61.30; H, 8.72.

4.1.3. (2*R*,6*S*,*R*$_S$)-5,6-Dihydro-6-hydroxymethyl-4-[(1*S*)-isoborneol-10-sulfinyl]-2-methoxy-2*H*-pyran (4). The

alcohol **4** was obtained by $LiAlH_4$ reduction of (2*R*,6*S*,R_S)-5,6-dihydro-6-ethoxycarbonyl-4-[(1*S*)-isoborneol-10-sulfinyl]-2-methoxy-2*H*-pyran[23b] following the procedure above reported for the preparation of **2**. The reduction appeared complete after 5 h. The crude product **4**, purified by column chromatography eluting with $CHCl_3$/EtOAc 50:50, was obtained in 79% yield as a light yellow oil, $[\alpha]_D^{22}=-3.5$ (*c* 1.07); ^{1}H NMR: δ 6.33 (dt, 1H, $J_{2,3}=J_{3,5B}=1.9$ Hz, $J_{3,5A}=1.7$ Hz, H-3), 5.22 (dt, 1H, $J_{2,5A}=J_{2,5B}=2.2$ Hz, H-2), 4.1–3.7 (m, 4H, H-2′,6, CH_2OH), 3.56 (s, 3H, OMe), 3.36 and 2.32 (AB system, 2H, $J_{10'A,10'B}=13.0$ Hz, H_2-10′), 2.52 (AB dddd, 1H, $J_{5\ A,5B}=17.0$ Hz, $J_{5\ A,6}=4.3$ Hz, H_A-5), 2.37 (AB ddt, 1H, $J_{5B,6}=8.1$ Hz, H_B-5), 2.3–1.1 (m, 7H, H_2-3′,5′,6′, H-4′), 1.07 (s, 3H, H_3-8′), 0.81 (s, 3H, H_3-9′); ^{13}C NMR: δ 145.01 (C-4), 128.70 (C-3), 97.45 (C-2), 76.90 (C-2′), 64.94 (CH_2OH), 56.41 (OMe), 53.06 (C-10′), 51.34 (C-1′), 48.33 (C-7′), 44.99 (C-4′), 38.40 (C-3′), 30.74 and 27.08 (C-5′,6′), 21.04 (C-5), 20.46 and 19.85 (C-8′,9′); IR: ν_{max} 3400 (OH) cm^{-1}; Anal. calcd for $C_{17}H_{28}O_5S$: C, 59.27; H, 8.19; Found: C, 59.45; H, 8.35.

4.2. General procedure for the TMSI-promoted conversion of α,β-unsaturated sulfoxides into carbonyl compounds

To a solution of α,β-unsaturated sulfoxide (0.53 mmol) in anhydrous $CHCl_3$ (3 ml), TMSI (97%, 0.64 mmol) was added at RT. The reaction was monitored by TLC. After disappearance of the starting material, MeOH (30 ml) was added and the reaction mixture stirred for 0.5 h, concentrated under reduced pressure, and column chromatographed eluting with light petroleum/EtOAc mixture where the EtOAc percentage was gradually increased from 10 up to 80%. The disulfide was eluted first in all cases, followed by the carbonyl compounds.

4.2.1. (3*S*,4*S*,5*R*)-4,5-Dihydroxymethyl-3-hydroxycyclohexanone (17). Oil, $[\alpha]_D^{20}=+18.5$ (*c* 0.32); ^{1}H NMR: δ 4.45 (broad s, 1H, H-3), 3.98 (AB ddd, 1H, $J_{gem}=8.7$ Hz, $J_{vic}=5.3$ Hz, $J_{long\text{-}range}=1.8$ Hz, 5-C$H_A$$H_B$OH), 3.80 (AB d, 1H, 5-C$H_A$$H_B$OH), 3.76 (AB dd, 1H, $J_{gem}=11.4$ Hz, $J_{vic}=7.3$ Hz, 4-C$H_A$$H_B$OH), 3.69 (AB dd, 1H, $J_{vic}=7.2$ Hz, 4-C$H_A$$H_B$OH), 2.71 (AB dd, 1H, $J_{2\ A,2B}=17.6$ Hz, $J_{2\ A,3}=3.3$ Hz, H_A-2), 2.6–2.4 (m, 4H, H-4,5, H_2-6), 2.41 (AB dd, 1H, $J_{2B,3}=2.1$ Hz, H_B-2); ^{13}C NMR: δ 209.56 (C-1), 75.55 (C-3), 71.91 (5-CH_2OH), 61.93 (4-CH_2OH), 50.67 (C-4), 49.07 and 48.86 (C-2,6), 35.81 (C-5); IR: ν_{max} 3452 (OH), 1716 (CO) cm^{-1}.

4.2.2. (3a*R*,5a*S*,9a*S*,9b*S*)-Octahydro-2-phenyl-1*H*-benz[*e*]isoindole-1,3,5(2*H*,4*H*)-trione (23). White crystals, mp 233–235°C; ^{1}H NMR: δ 7.5–7.2 (m, 5H, H-2′,3′,4′,5′,6′), 3.49 (ddd, 1H, $J_{3a,4A}=2.2$ Hz, $J_{3a,4B}=8.0$ Hz, $J_{3a,9b}=9.8$ Hz, H-3a), 3.29 (dd, 1H, $J_{9a,9b}=5.7$ Hz, H-9b), 2.98 (AB dd, 1H, $J_{4\ A,4B}=16.2$ Hz, H_A-4), 2.79 (AB dd, 1H, H_B-4), 2.3–1.2 (m, 10H, H_2-6,7,8,9, H-5a,9a); ^{13}C NMR: δ 208.11 (C-5), 177.06 and 175.94 (C-1,3), 131.52 (C-1′), 129.20, 128.82, and 126.37 (C-2′,3′,4′,5′,6′), 49.11 (C-5a), 42.88 (C-9b), 38.85 (C-3a), 38.19 (C-9a), 37.03 (C-4), 29.05, 28.25, 25.95, and 25.29 (C-6,7,8,9); MS/EI: *m*/*z* (%) 297 (M, 100), 189 (10), 188 (73), 187 (10), 174 (10), 135 (22), 77 (10); IR: ν_{max} 1715 (CO), 1500, 1384 cm^{-1}; Anal. calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; Found: C, 72.59; H, 6.37.

4.2.3. (3a*S*,11a*S*)-7-Methoxy-2,3,3a,4,5,10,11,11a-octahydro-2-phenylnaphth[2,1-*e*]isoindole-1,3(1*H*)-dione (22). TMSI (97%, 0.40 mmol) was added to a solution of **21** (90 mg, 0.16 mmol) in $CHCl_3$ (1.5 ml) under argon atmosphere and stirring. The reaction, monitored by TLC, appeared complete after 90 min. Then MeOH (5 ml) was added and the stirring maintained for further 30 min. After evaporation of the solvent under reduced pressure, purification of the crude product by column chromatography with light petroleum/EtOAc 95:5 as eluant afforded **22**, low melting solid, 29 mg, 50% yield, $[\alpha]_D^{24}=+32.4$ (*c* 3.26); ^{1}H NMR: δ 7.5–6.7 (m, 5H, H-2′,3′,4′,5′,6′), 3.80 (s, 3H, OMe), 3.69 (d, 1H, $J_{3a,11a}=8.5$ Hz, H-3a), 3.33 (dt, 1H, $J_{11a,11A}=J_{11a,11B}=5.3$ Hz, H-11a), 2.9–2.3 (m, 7H, H_2-4,5,10, H_A-11), 1.94 (m, 1H, H_B-11); ^{13}C NMR: δ 178.18 and 175.50 (C-1,3), 158.72 (C-7), 137.41 (C-5a), 131.91 (C-1′), 131.24 and 128.31 (C-3b,9b), 129.04, 128.43, and 126.38 (C-2′,3′,4′,5′,6′), 124.23 (C-9a), 123.58 (C-9), 113.52 (C-6), 111.08 (C-8), 55.28 (OMe), 45.72 (C-3a), 40.07 (C-11a), 28.50, 27.33, 21.93, and 21.75 (C-4,5,10,11); MS/EI: *m*/*z* (%) 359 (M, 100), 213 (11), 212 (62), 211 (16), 197 (11), 165 (10); Anal. calcd for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.89; Found: C, 76.79; H, 5.90.

4.3. General procedure for the reaction of α,β-unsaturated sulfoxides with TMSBr and TMSCl

To a solution of α,β-unsaturated sulfoxide (0.13 mmol) in anhydrous $CDCl_3$ (0.7 ml), TMSBr 97% (0.16 mmol) [or TMSCl >99% (0.16 mmol)] was added at RT. The reaction was monitored and the products identified in situ by ^{1}H NMR.

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