Preparation of oxo-substituted α-chloro ethers and their reaction with samarium diiodide

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Abstract
Oxo-substituted α-chloro ethers have been prepared by cleavage of the corresponding *O,S*-acetals with sulfuryl dichloride. Some of these α-chloro ethers give hydroxysubstituted oxygen heterocycles when reacted with samarium diiodide.

Keywords: α-Chloro ethers**,** samarium diiodide, hydroxysubstituted oxygen heterocycles, intramolecular samarium Barbier reaction

Introduction

Oxo-substituted α-chloro ethers like 1 (Fig. 1) are hardly known in the literature. One of the few examples is the fluorinated α-chloro ether 2, which was prepared by chlorination of a methoxy group.[1]

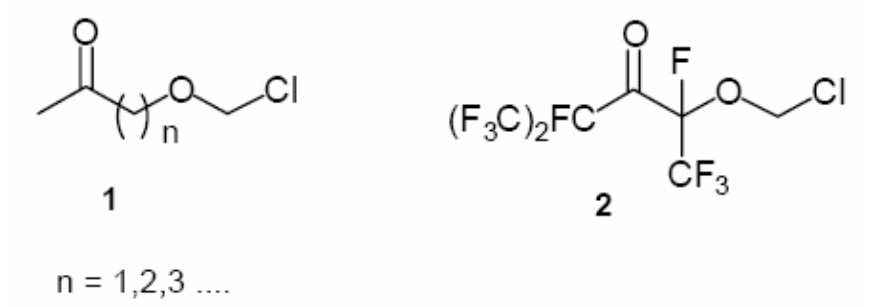
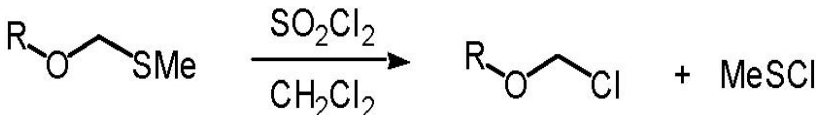


Figure 1

We have previously prepared a number of α-chloro ethers by cleavage of *O,S*-acetals with sulfuryl dichloride.[2] (Scheme 1)



Scheme 1

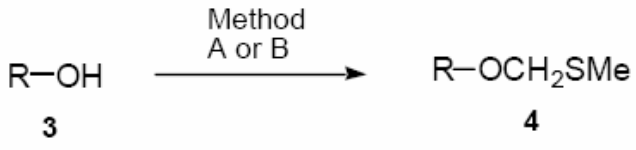
This method has also been used to prepare 4-acetyl- chloromethoxybenzene.[2a] We believed that the method could be useful in the synthesis of α-chloro ethers like **1**, since the requested *O,S*-acetals could in principle be accessible from readily available hydroxy ketones. α-Halo ethers react with samarium diiodide in the presence of ketones to give α-alkoxy alcohols.[3] To our knowledge an intramolecular version of this reaction has not been documented. Such a reaction would be an example of an intramolecular Samarium-Barbier reaction and would give hydroxysubstituted oxy-rings. The ring size being dependent on the chain lenght between the α-chloro ether function and the oxo-group. A number of oxygen heterocyles are important compounds; oxolanes and oxanes for instance occur in a wide variety of biologically active compounds.[4] In this paper we present our results in the preparation of oxy-substituted α-chloro ethers and in the investigation of the intramolecular Samarium-Barbier reaction of oxy-substituted α-chloro ethers.

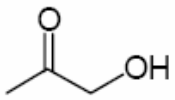
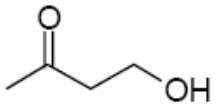
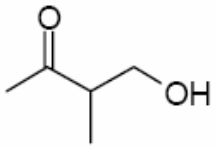
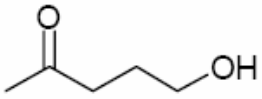
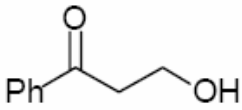
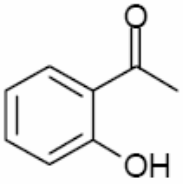
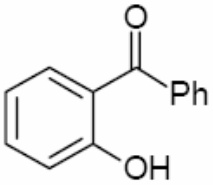
Results and Discussion

A convenient way to make *O,S*-acetals from alcohols, is to react the alcohol with chloromethyl methyl sulfide under basic conditions.[5] This method (Method A, Table 1) proved useful for the hydroxy ketones **3d, 3f** and **3g** (Table 1, entries 4, 6 and 7). In the case of **3a, 3b, 3c** and **3e**, however, the method was useless (entries 1, 2, 3 and 5).

O,S-acetals can also be formed from alcohols by a reacting the alcohol with DMSO in the presence of acetic anhydride and acetic acid.[6] This protocol (Method B, Table 1) gave mostly good yields where Method A had failed (entries 2 - 5).

Table 1. Preparation of hemithioacetals

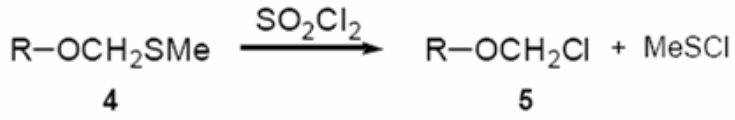


Entry	Compound	ROH	Method A[a] Yield of **4**[c]	Method B[b] Yield of **4**[c]
1	**3a**		0	23
2	**3b**		0	63
3	**3c**		0	72
3	**3d**		46	63
5	**3e**		0[7]	58
6	**3f**		89	-
7	**3g**		76	-

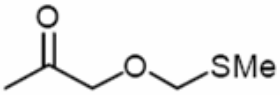
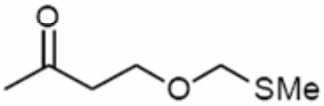
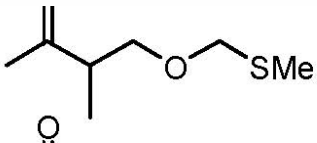
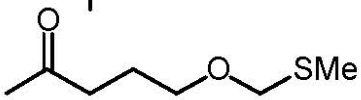
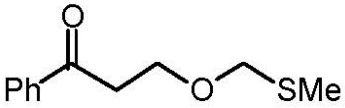
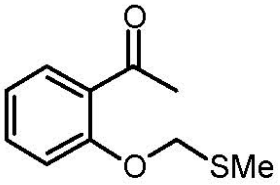
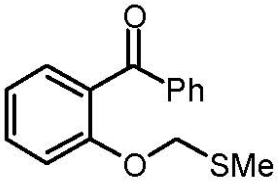
[a] Method A:[5] $ClCH_2Me$, NaH, NaI/DMF. [b] Method B:[6] DMSO/Ac2O/Ac OH. [c] Isolated

Cleavage of the *O,S*-acetals **4** with sulfuryl dichloride gave the corresponding α-chloro ethers **5** in almost quantitative yield (Table 2, entries 1-5 and 7) except in one case (**4f**, entry 6) where a mixture of products was obtained.

Table 2 Preparation of α-chloro ethers



4 5

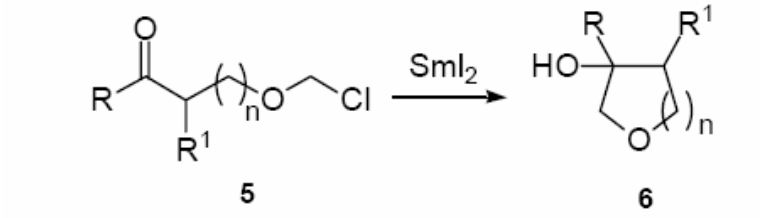
Entry	Compound	ROH	Yield of **5**[a]
1	**4a**		~quant.
2	**4b**		~quant.
3	**4c**		~quant.
4	**4d**		~quant.
5	**4e**		~quant.
6	**4f**		0[b]
7	**4g**		~quant.

[a] Crude product. [b] ^{1}H-NMR signal of the crude product indicated the presence of an α-chloro ether

The reason why the *O,S*-acetal **4f** does not cleanly give the corresponding α-chloro ether, must come from the position of the acetyl group and the fact that the acetyl group can enolize. This because the *para*-isomer 4-acetyl-chloromethoxybenzene has been synthesized in good yield by cleavage of an *O,S*-acetal with sulfuryl dichloride [2a] and the *O,S*-acetal **4g** , which does not have an enolizable keto group, is cleanly cleaved to the corresponding α-chloro ether. 2-Formyl-chloromethoxybenzene has also been prepared in good yield by cleavage of the corresponding *O,S*-acetal with sulfuryl dichloride.[8]

The cyclization of the α-chloro ether **5a** with samarium diiodide met with little success. No oxetane formation was observed (Table 3, entry 1). This was not surprising since formation of a 4-membered ring from a simple halide in a similar reaction gave only 5 % yield.[9] The formation five membered rings were easier and the 3hydroxyoxolanes **6b** and **6c** were obtained in moderate yields when the corresponding α-chloro ethers were treated with two equivalents of samarium diiodide in THF at - 78 ^{o}C (Table 3, entries 2 and 3). The diastereoselectivity in the cyclization of **5c** was 2.5 : 1. The phenyl ketone **5e** gave, however, no oxolane (entry 5). The 6-membered ring **6d** was formed in 47 % yield (entry 4).

Table 3. Preparation of 3-hydroxyoxolanes and 3-hydroxy-3-methyloxane



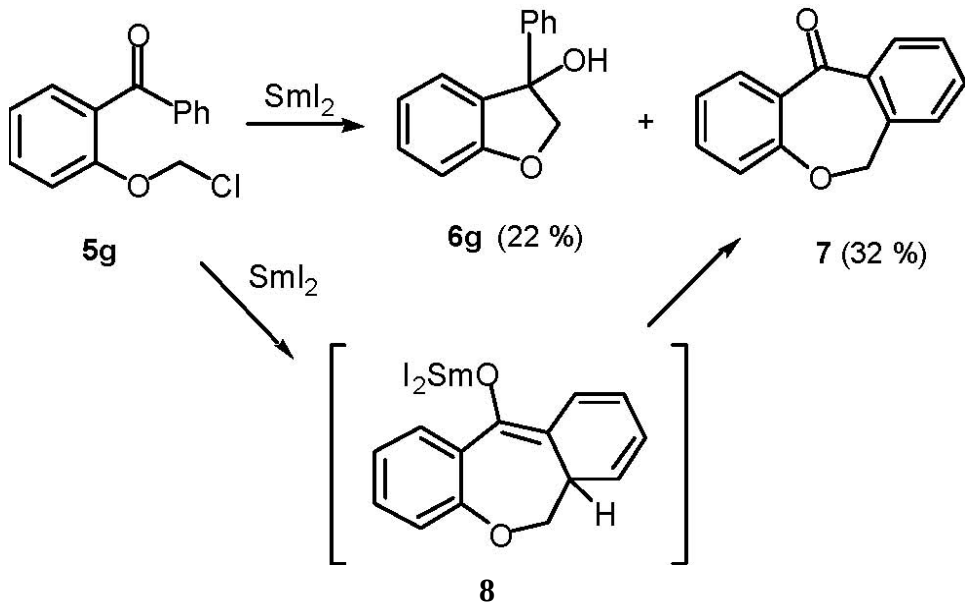
Entry	Compound	n	R	R1	Yield of **6***a*
1	**5a**	0	Me	H	0
2	**5b**	1	Me	H	54
3	**5c**	1	Me	Me	65
4	**5d**	2	Me	H	47
5	**5e**	1	Ph	H	0

[a] Isolated

When the α-chloro ether **5g** was treated with samarium diiodide the oxepinon **7** was formed together with the oxolane **6g** (Scheme 2). The oxepinon was the main product.

The oxepinon can be formed by hydride elimination from compound **8**, which may be formed by a nucleophilic attac by an organosamarium species *ortho* to the keto group. This would resemble an 1,4-addition by a nucleophile to an α,β-unsaturated ketone.

In summary oxy-substituted α-chloro ethers are readily made by cleavage of *O,S*-acetals by sulfuryl dichloride. α-Chloro ethers are readily reduced by samarium diiodide and oxo-substituted α-chloro ethers may be cyclized to five or six membered rings by samarium diiodide.



Scheme 2

Experimental Section

General Procedures. All reactions were conducted under an inert amosphere of either Ar or N_2. THF was distilled from sodium and benzophenone. Dichloromethane, acetonitrile and *N,N*-dimethylformamide (DMF) were dried with CaH_2 before distillation. NMR spectra were recorded at 300 MHz (^{1}H) and at 75 MHz (^{13}C) on a Bruker Avance DPX 300 instrument. Mass spectra, under electron impact conditions, were recorded at 70 eV ionizing energy on a Fision ProSpec instrument. The spectra are presented as *m/z* (% rel. int.). The melting points are uncorrected.

General procedures for the preparation of the *O,S*-acetals (4). Method A:[5] The alcohol 3 (10.0 mmol) in DMF (20 mL) was added to a mixture of sodium hydride (0.38 g 15.0 mmol, 95 % in paraffine) and NaI (1.5 g, 10 mmol) at 0 ^{o}C under N_2. After stirring for 15 min was chloromethyl methyl sulfide (1.10 mL, 13.0 mmol) added dropwise. The mixture was stirred for 10 h while reaching ambient temperature before ice/water was added, the product extracted into diethyl ether, dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude product was purified by distillation, recrystallization or flash chromatography on silica gel.

2-Acetyl-1-methylthiomethoxybenzene (4f). Eluent hexane-ethyl acetate 10:1; mp 33.5-34.5 ^{o}C (hexane); (Found: M^+, 196.0552. $C_{10}H_{12}O_2S$ requires 196.0558); ^{1}H-NMR δ (300 MHz, $CDCl_3$) 2.25 (3H, s, SCH_3), 2.62 (3H, s, CH_3), 5.22 (2H, s, CH_2), 6.96-7.05 (2H, m, Ar,), 7.40-7.43 (1H, m, Ar), 7.69-7.72 (1H, m, Ar); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 15.1 (SCH_3), 31.7 (CH_3), 72.9 (CH_2), 113.8 (CH), 121.5 (CH), 129.5 (C), 130.5 (CH), 133.2 (CH), 156.2 (C), 199.6 (CO);

m/z (EI) 196 (M^+, 7%), 149 (20), 61 (100).

2-Methylthiomethoxybenzophenone (4g). Mp. 65-66 ^oC (hexane) (Found: M^+, 258.0709. $C_{15}H_{14}O_2S$ requires 258.0715); ^{1}H-NMR δ (300 MHz, $CDCl_3$) 1.90 (3H, s, SCH_3), 5.02 (2H, s, CH_2), 7.01-7.07 (2H, m, Ar), 7.34-7.52 (5H, m, Ar), 7.79-7.81 (1H, m, Ar); ^{13}CNMR δ (75 MHz, $CDCl_3$) 14.3 (SCH_3), 72.7 (CH_2), 114.2 (CH), 121.5 (CH), 128.2 (CH), 129.5 (CH), 129.7 (CH), 130.3 (C), 131.4 (CH), 132.9 (CH), 137.7 (C), 154.3 (C), 196,1 (CO); m/z (EI) 258 (M^+, 6 %), 194 (6), 211 (21), 182 (6), 137 (8), 121 (10), 77 (18), 61 (100).

Method B:[6] A mixture of the alcohol **3** (10.0 mmol), DMSO (33 mL), acetic acid (6.5 mL), acetic anhydride (33 mL) and water (0.7 mL) was stirred for 48 h at ambient temperature before it was poured into a cold solution of 10 % Na_2CO_3 in water and extracted with chloroform. The organic phase was washed with water (5x), dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography on silica gel.

1-Methylthiomethoxy-2-propanone (4a). Eluent hexane-ethyl acetate 5:1 (Found: M^+, 134.0394. $C_5H_{10}O_2S$ requires 134.0402); ^{1}H-NMR δ (300 MHz, $CDCl_3$) 2.04 (3H, s, CH_3), 2.05 (3H, s, CH_3), 4.08 (2H, s, CH_2), 4.61 (2H, s, CH_2); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 13.7 (CH_3S), 26.2 (CH_3), 72.2 (CH_2), 75.3 (CH_2), 205.3 (C); m/z (EI) 134 (M^+, 0.7 %), 87 (29), 61 (100), 58 (45), 57 (25), 43 (40).

4-Methylthiomethoxy-2-butanone (4b). Eluent hexane-ethyl acetate 5:1 (Found: M^+, 148.0562. $C_6H_{12}O_2S$ requires 148.0558); δH (300 MHz, $CDCl_3$) 2.03 (3H, s, CH_3S), 2.09 (3H, s, CH_3S), 2.60 (2H, t, CH_2, *J* 6.1), 3.68 (2H, t, CH_2, *J* 6.1), 4.52 (2H, s, CH_2); δC (75 MHz, $CDCl_3$) 13.7 (CH_3S), 30.1 (CH_3), 43.1 (CH_2), 62.8 (CH_2), 75.2 (CH_2), 206.5 (C); m/z (EI) 148 (M^+, 2 %), 101 (59), 71 (27), 61 (22), 43 (100).

4-Methylthiomethoxy-3-methyl-2-butanone (4c). Eluent hexane-ethyl acetate 12:1 (Found: M^+, 162.0720. $C_7H_{14}O_2S$ requires 162.0715); ^{1}H-NMR δ(300 MHz, $CDCl_3$) 1.03 (3H, d, CH_3, *J* 7.1), 2.04 (3H, s, SCH_3), 2.11 (3H, s, CH_3), 2.75 (1H, ddq, CH, *J* 7.5, 7.1 and 5.3), 3.50 (1H, dd, CH, *J* 9.3 and 5.3), 3.60 (1H, dd, CH, *J* 9.3 and 7.5), 4.52 (2H, s, OCH_2S); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 13.2 (CH_3), 13.8 (CH_3), 28.6 (CH_3), 46.7 (CH), 69.5 (CH_2), 75.3 (CH_2), 210.4 (CO); m/z (EI) 162 (M^+, 0.5 %), 115 (55), 85 (23), 61 (30), 43 (100).

5-Methylthiomethoxy-2-pentanone (4d). Eluent hexane-ethyl acetate 5:1 (Found: M^+, 162.0726. $C_7H_{14}O_2S$ requires 162.0715); ^{1}H-NMR δ (300 MHz, $CDCl_3$) 1.75 (2H, tt, CH_2, *J* 6.2 and 7.2), 2.03 (3H, s, CH_3), 2.04 (3H, s, CH_3), 2.43 (2H, t, CH_2, *J* 7.2), 3.41 (2H, t, CH_2, *J* 6.2), 4.49 (2H, s, OCH_2S); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 13.8 (CH_3S), 23.3 (CH_3), 29.7 (CH_2), 40.1 (CH_2), 66.9 (CH_2), 75.0 (CH_2), 208.0 (CO); m/z (EI) 162 (M^+, 0.2 %), 115 (69), 101 (15), 85 (100), 43 (29).

3-Methylthiomethoxy-1-phenyl-1-propanone (4e). Eluent hexane-ethyl acetate 9:1 (Found: M^+- SCH_3, 163.0764. $C_{10}H_{11}O_2$ requires 163.0759); ^{1}H-NMR δ (300 MHz, $CDCl_3$) 2.09 (3H, s, SCH_3), 3.23 (2H, t, CH_2, *J* 6.3), 3.94 (2H, t, CH_2, *J* 6.3), 4.62 (2H, s, OCH_2S), 7,40 - 7.56 (3H, m, Ar), 7.91 - 7.94 (2H, m, Ar); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 13.8 (SCH_3), 38,3 (CH_2), 63.3 (CH_2), 75.4 (OCH_2S), 128.0 (2 x CH), 128.5 (2 x CH), 133.1 (CH), 136.8 (C) 197.9 (CO).

General procedure for the synthesis of the α-chloro ethers (5). Sulfuryl dichloride (0.16 mL, 2.0 mmol) in dichloromethane (4 mL) was added to a solution of the *O,S*-acetal **4** (2.0 mmol) in dichloromethane (6 mL) at 0 ^{o}C under N_2. The mixture was stirred for 10 min before it was evaporated under reduced pressure. The crude product could be used in the next step without further purification. *Note*: The α-chloro ethers **5** are reactive compounds and thus potentially toxic. Care should be taken to avoid exposure.

1-Chloromethoxy-2-propanone (5a). ^{1}H-NMR δ (300 MHz, $CDCl_3$) 2.13 (3H, s, CH_3), 4.24 (2H, s, CH_2), 5.47 (2H, s, CH_2); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 26.4 (CH_3S), 73.7 (CH_2), 81.9 (CH_2), 203.8 (C).
4-Chloromethoxy-2-butanone (5b). ^{1}H-NMR δ (300 MHz, $CDCl_3$) 2.13 (3H, s, CH_3), 2.69 (2H, t, CH_2, *J* 6.1), 3.89 (2H, t, CH_2, *J* 6.1), 5.42 (2H, s, CH_2); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 30.2 (CH_3S), 42.6 (CH_2), 65.2 (CH_2), 82.9 (CH_2), 205.9 (C).
4-Chloromethoxy-3-methyl-2-butanone (5c). ^{1}H-NMR δ(300 MHz, $CDCl_3$) 1.03 (3H, d, CH_3, *J* 7.2), 2.10 (3H, s, CH_3), 2.76 (1H, ddq, CH, *J* 7.5, 7.2 and 5.4), 3.65 (1H, dd, CH, *J* 9.5 and 5.4), 3.73 (1H, dd, CH, *J* 9.5 and 7.5), 5.35 (1H, d, CH, *J* 5.5), 5.39 (1H, d, CH, *J* 5.5); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 13.1 (CH_3), 28.6 (CH_3), 46.2 (CH), 71.5 (CH_2), 82.8 (CH_2), 209.7 (C).
5-Chloromethoxy-2-pentanone (5d). ^{1}H-NMR δ (300 MHz, $CDCl_3$) 1.79 (1H, tt, CH, *J* 7.1 and 6.1), 2.05 (3H, s, CH_3), 2.45 (2H, d, CH_2, *J* 7.1), 3.60 (2H, d, CH_2, *J* 6.1), 5.38 (2H, s, CH_2); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 22.8 (CH_3), 29.8 (CH_2), 39.5 (CH_2), 69.3 (CH_2), 82.9 (CH_2), 207.7 (C).
3-Chloromethoxy-1-phenyl-1-propanone (5e). ^{1}H-NMR δ (300 MHz, $CDCl_3$) 3.29 (2H, t, CH_2, *J* 6.3), 4,13 (2H, t, CH_2, *J* 6.3), 5.53 (2H, s, OCH_2Cl), 7,44 - 7.58 (3H, m, Ar), 7.94 - 7.97 (2H, m, Ar); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 37,8 (CH_2), 65.8 (CH_2), 83.2 (CH_2), 128.0 (2 x CH), 128.7 (2 x CH), 133.3 (CH), 136.8 (C) 197.4 (CO).
2-Chloromethoxybenzophenone (5g). ^{1}H-NMR δ (300 MHz, $CDCl_3$) 5.73 (2H, s, CH_2), 7.16-7.80 (9H, m, Ar); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 76.8 (CH_2), 114.5 (CH), 123.2 (CH), 129.0 (2 x CH), 129.7 (2xCH), 129.8 (CH), 130.3 (C), 131.7 (CH), 133.2 (CH), 137.2 (C), 152.9 (C), 195.3 (C).
General procedure for the synthesis of 3-hydroxyoxolanes and 3-hydroxy-3-methyloxane. The α-chloro ether **5** (2.0 mmol) in dry THF (4 mL) was added to a solution of SmI_2 (4.0 mmol) in THF (10 mL) at - 78 ^{o}C under N_2. The mixture was stirred for 6 h while slowly reaching ambient temperature before it was poured into a saturated solution of K_2CO_3. The product was extracted into diethyl ether and the organic phase washed with a saturated solution of K_2CO_3 and a saturated solution of NaCl before it was dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography on silica gel.

3-Hydroxy-3-methyloxolane (6b).[10] Eluent hexane-ethyl acetate 1:2. (Found: M^+, 102.0690. $C_5H_{10}O_2$ requires 102.0681); ^{1}H-NMR δ(300 MHz, $CDCl_3$) 1.36 (3H, s, CH_3), 1.85 - 1.93 (2H, m, CH_2), 2.55 (1H, s, OH), 3.47 (2H, d, CH_2, *J* 9.1), 3.64 (2H, d, CH_2, *J* 9.1), 3.83 - 3.87 (1H, m,

CH_2), 3.94 - 3.99 (1H, m, CH_2); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 24.0 (CH_3), 41.0 (CH_2), 67.6 (CH_2), 78.0 (CH), 79.4 (CH_2); m/z (EI) 102 (M^+, 100 %), 87 (56), 72 (76), 57 (22).

3-Hydroxy-3,4-dimethyloxolane (6c). Eluent hexane-ethyl acetate 1:2. Diastereomer 1: (Found: M^+, 116.0829. $C_6H_{12}O_2$ requires 116.0837); ^{1}H-NMR δ (300 MHz, $CDCl_3$) 0.91 (3H, d, CH_3, *J* 6.8), 1.22 (3H, s, CH_3), 1.96 (1H, ddq, CH, *J* 10.2, 8.1 and 6.8), 2.18 (1H, s, OH), 3.47 (1H, dd, CH, *J* 10.2 and 8.1), 3.60 (1H, d, CH, *J* 9.2), 3.70 (1H, d, CH, *J* 9.2), 3.70 (1H, dd, CH, *J* 8.1 and 8.1); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 8.8 (CH_3), 21.9 (CH_3), 43.1 (CH), 73.9 (CH_2), 78.0 (C), 80.1 (CH_2). Diastereomer 2: (Found: M^+, 116.0838. $C_6H_{12}O_2$ requires 116.0837); ^{1}H-NMR δ(300 MHz, $CDCl_3$) 0.93 (3H, d, CH_3, *J* 7.2), 1.23 (3H, s, CH_3), 2.01 (1H, s, OH), 2.10 (1H, ddq, CH, *J* 8.5, 7.2 and 5.4), 3.39 (1H, dd, CH, *J* 7.1 and 5.4), 3.55 (1H, d, CH, *J* 9.1), 3.66 (1H, d, CH, *J* 9.1), 4.20 (1H, dd, CH, *J* 8.5 and 7.1); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 14.6 (CH_3), 19.8 (CH_3), 44.5 (CH), 74.9 (CH_2), 78.3 (C), 81.4 (CH_2); m/z (EI) 116 (M^+, 2 %), 101 (3), 84 (6), 75 (88), 71 (80), 57 (15), 43 (100).

3-Hydroxy-3-methyloxane (6d).[11] Eluent hexane-ethyl acetate 1:1 (Found: M^+, 116.0851. $C_6H_{12}O_2$ requires 116.0837); ^{1}H-NMR δ (300 MHz, $CDCl_3$) 1.08 (3H, s, CH_3), 1.41-1.52 (2H, m, CH_2), 1.61-1.70 (1H, m, CH), 1.74-1.88 (1H, m, CH), 2.60 (1H, s, OH), 3.25 (1H, d, CH, *J* 11.4), 3.34 (1H, dt, CH, *J* 11.1 and 2.7), 3.70 (1H, dd, CH, *J* 11.4 and 2.3), 3.78 (1H, dt, CH, *J* 11.1 and 3.3); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 22.4 (CH_3), 24.9 (CH_2), 35.8 (CH_2), 67.1 (C), 67.9 (CH_2), 76.9 (CH_2); m/z (EI) 116 (M^+, 21 %), 84 (33), 74 (17), 71 (72), ,58 (93), 43 (100).

3-Phenyl-3-hydroxy-2,3-dihydrobenzofuran (6g). Eluent hexane-ethyl acetate 10:1 (Found: M^+, 212.0838. $C_{14}H_{12}O_2$ requires 212.0837); ^{1}H-NMR δ (300 MHz, $CDCl_3$) 2.36 (1H, s, OH), 4.49 (1H, d, CH, *J* 10.3), 4.68 (1H, d, CH, *J* 10.3), 6.93-7.50 (9H, m, Ar); ^{13}C-NMR δ (75 MHz, $CDCl_3$) 82.5 (C), 86.1 (CH_2), 110.7 (CH), 121.4 (CH), 124.4 (CH), 126.0 (2 x CH), 127.5 (CH), 128.2 (2 x CH), 130.6 (CH), 132.2 (C), 142.6(C), 160.6(C); m/z (EI) 212 (M^+, 100 %), 195 (48), 194 (53), 181 (29), 165 (43), 152 (26), 135 (48), 121 (39), 105 (25), 77 (41), 51 (17).

6,11-Dihydrobenzo[b,e]oxepin-11-on (7).[12,13] Eluent hexane-ethyl acetate 10:1(Found: M^+, 210.0682. $C_{14}H_{10}O_2$ requires 210.0681); ^{1}H-NMR δ_H (300 MHz, $CDCl_3$) 5.16 (2H, s, CH_2), 7.01 - 7.09 (2H, m, Ar), 7.33 (1H, d, Ar, *J* 7.3), 7.43 - 7.52(3H, m, Ar), 7.88 (1H, d, Ar, *J* 7.3), 8.21 - 8.24 (1H, m, Ar); ^{13}C-NMR δ(75 MHz, $CDCl_3$) 73.5 (CH_2), 120.6 (CH), 122.0 (CH), 125.3 (C), 127.7 (CH), 129.1 (CH), 129.4 (CH), 131.9 (CH), 132.6 (CH), 135.2 (CH), 135.6 (CH), 140.5 (CH), 161.2 (C), 191.0 (CO); m/z (EI) 210 (M^+, 100 %), 181 (61), 153 (16), 152 (20), 89 (11), 76 (9), 63 (12).

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