Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 8393–8398

TETRAHEDRON

New odorless method for the Corey–Kim and Swern oxidations utilizing dodecyl methyl sulfide (Dod-S-Me)

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Received 24 July 2003; revised 27 August 2003; accepted 28 August 2003

Abstract—Development of the odorless dodecyl methyl sulfide (Dod-S-Me, **1**) as an alternative for dimethyl sulfide (DMS) and new odorless methods for the Corey–Kim and Swern oxidations are described. These reactions have been developed with a view toward green chemistry, utilizing Dod-S-Me (**1**) and common solvents instead of dichloromethane.

1. Introduction

Thiols and sulfides are useful reagents for organic syntheses.[1] However, because of their general malodorous nature, they are widely known to contribute to environmental pollution as well as to the physical stress of the researchers working with them. Development of odorless substitutes for commonly used foul-smelling thiols and sulfides would greatly improve or, in some cases, eliminate these objectionable features. Demethylations of phenyl methyl ethers[2a] and methyl phosphates[2b] using either an odorless bulky thiol or an odorless sodium dithiocarboxylate have been reported. Studies of a novel reaction using chiral 1,3-mercapto alcohols (odorless)[3] prompted us to exploit odorless thiol substitutes for ethanethiol,[4] benzyl mercaptan,[4,5] benzenethiol[5] and hydrogen sulfide,[6] which we have applied to dealkylation and the Michael addition. Dimethyl sulfide (DMS) is also commonly used for organic reactions, e.g. dealkylation[7] and the Corey–Kim oxidation[8] (NCS–DMS, Et_3N). However, due to its foul smell, industrial use of DMS is regulated by the offensive odor control law. Recently, odorless versions of the Corey–Kim oxidation[9] and the Swern oxidation[10,11] have been published. We report herein the development of dodecyl methyl sulfide[12] (Dod-S-Me, **1**), which was easily prepared as an odorless alternative for DMS, and new odorless versions of the oxidations mentioned above in an application of green chemistry.[13]

2. Result and discussion

2.1. Odor of alkyl methyl sulfides

We tested the odor of a number of alkyl methyl sulfides. The relative odor index of these sulfides compared to foul-smelling dimethyl sulfide perceived by the human nose[4] of three test subjects is listed in Table 1, with 5 being the most malodorous and 0 an odorless sulfide. All the alkyl methyl sulfides were commercially available except for undecyl methyl sulfide and Dod-S-Me (**1**), which were synthesized from the corresponding 1-undecanethiol and 1-dodecanethiol, respectively (Scheme 1).

These sulfides were purified by distillation and HPLC on

Table 1. Odor scale for alkyl methyl sulfides

Entry	Sulfides	Carbon length	Odor scale		
			A	B	C
1	CH_3SCH_3	1	5	5	5
2	$CH_3CH_2SCH_3$	2	5	5	5
3	$CH_3(CH_2)_2SCH_3$	3	4	4	4
4	$CH_3(CH_2)_3SCH_3$	4	4	4	4
5	$CH_3(CH_2)_4SCH_3$	5	4	3	4
6	$CH_3(CH_2)_6SCH_3$	7	2	2	3
7	$CH_3(CH_2)_7SCH_3$	8	2	2	2
8	$CH_3(CH_2)_9SCH_3$	10	1	1	2
9	$CH_3(CH_2)_{10}SCH_3$	11	1	1	0
10	$CH_3(CH_2)_{11}SCH_3$ (**1**)	12	0	0	0
11	$CH_3(CH_2)_{13}SCH_3$	14	0	0	0
12	$CH_3(CH_2)_{15}SCH_3$	16	0	0	0
13	$C_6H_{13}SC_6H_{13}$	6+6	1	1	1

Odor scale: stench 5↔0 odorless.

Keywords: odorless Corey–Kim oxidation; dodecyl methyl sulfide; odorless Swern oxidation; dodecyl methyl sulfoxide.

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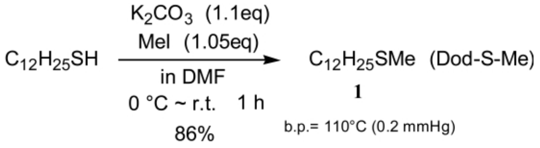
doi:10.1016/j.tet.2003.08.055



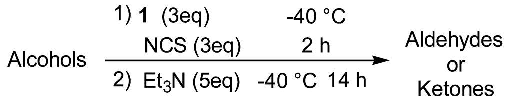
Scheme 1. Synthesis dedecyl methyl sulfide (**1**).

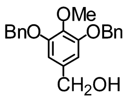
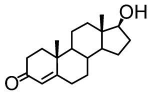
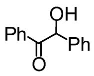
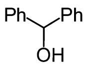
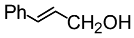
GPC columns. Among the alkyl methyl sulfides, Dod-S-Me (**1**) was found to be odorless, while lower carbon-chain sulfides were malodorous. These results suggest that the alkyl methyl sulfides with longer chains have lower volatility than DMS and that the sulfides having more than 12 carbons become odorless due to their lower volatility.

2.2. Odorless Corey–Kim oxidation using dodecyl methyl sulfide (Dod-S-Me)

We next used Dod-S-Me (**1**) as an odorless substitute for foul-smelling DMS in the Corey–Kim oxidation,[8] which is a useful method for oxidation of alcohols to aldehydes or ketones. Oxidation of benzhydrol was carried out first under the original Corey–Kim oxidation conditions (−20°C to room temperature, 6 h after addition of triethylamine) to give benzophenone (50%). Benzophenone was obtained in high yield under optimized reaction conditions, while maintaining the reaction temperature at −40°C for longer reaction times (14 h after addition of triethylamine). This result suggested that it was necessary to generate a sufficient amount of the sulfur ylide intermediate and to prevent the undesired Pummerer rearrangement.[11a] The results of the new odorless Corey–Kim oxidation using the sulfide **1** are summarized in Table 2. Toluene was also tested as a solvent instead of dichloromethane, following the original Corey–Kim oxidation[8] from the standpoint of industrial chemistry. The yields of the corresponding aldehydes or ketones were excellent in both solvents.

Table 2. Odorless Corey–Kim oxidation using dodecyl methyl sulfide (**1**)

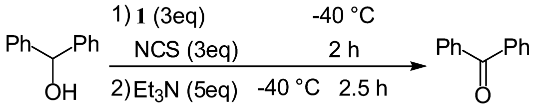


Entry	Alcohols	Yield in CH_2Cl_2	Yield in toluene
1		99	95
2		91	97
3		99	–[a]
4		95	98
5		91	90

[a] No reaction.

Applying this new odorless Corey–Kim oxidation to industrial scale experiments, we considered using common solvents instead of dichloromethane and toluene (Table 3). All the solvents tested were applied to the new Corey–Kim oxidation and gave excellent yields, with acetone being the most suitable solvent for industrial use.

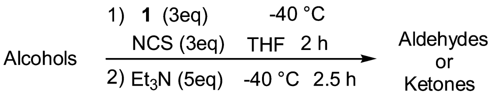
Table 3. Odorless Corey–Kim oxidation using **1**

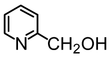
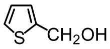
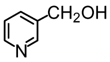
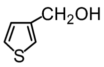
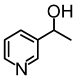
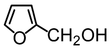


Solvent	Yield (%)	Solvent	Yield (%)
Toluene	83	THF	99
CH_2Cl_2	96	CH_3CN	93
AcOEt	97	Acetone	100

The new odorless Corey–Kim oxidation of alcohols having a heteroaromatic substituent also proceeded in good to excellent yields (Table 4). Tetrahydrofuran (THF) was found to be the best solvent for oxidation of these alcohols.

Table 4. Odorless Corey–Kim oxidation of heteroaromatics using dodecyl methyl sulfide (**1**)



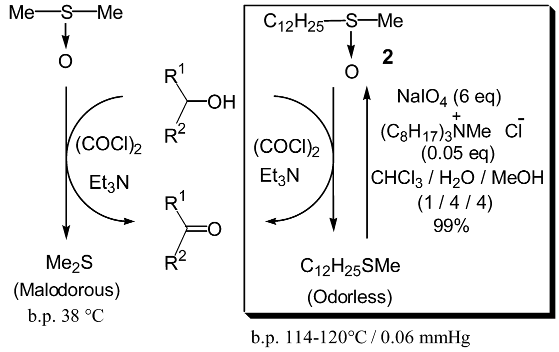
Entry	Alcohols	Yield[a]	Entry	Alcohols	Yield[a]
1		77	4		86
2		71	5		85
3		99	6		92

[a] Yield was determined by GC.

2.3. Odorless Swern oxidation using dodecyl methyl sulfoxide

The Swern oxidation[14] (DMSO–oxalyl chloride, Et_3N) is also a useful method for oxidation of alcohols to aldehydes or ketones. However, one serious drawback is the foul odor of the volatile DMS which is produced during the reaction. In order to overcome this problem, we planned a new odorless Swern oxidation using dodecyl methyl sulfoxide (**2**), as illustrated in Scheme 2.

Dodecyl methyl sulfoxide (**2**) could be prepared in high yield from Dod-S-Me (**1**) by oxidation with sodium periodate. In our strategy, Dod-S-Me was recovered as an odorless byproduct instead of DMS, and was reused by re-oxidation to the sulfoxide **2**. The optimized reaction conditions of the new Swern oxidation for benzhydrol (−60 to −40°C for 200 min after addition of triethylamine, then warming to room temperature for 40 min) gave benzophenone (95%) along with the recovered Dod-S-Me (**1**,



Scheme 2. Strategy of a new odorless Swern oxidation.

98%). The reaction in other solvents such as THF,[15] toluene, and ether afforded benzophenone in moderate to low yields (49, 53 and 10%, respectively). The results of the new odorless Swern oxidation using the sulfoxide **2** and oxalyl chloride are summarized in Table 5. All benzylic, allylic, and aliphatic primary and secondary alcohols were oxidized smoothly to aldehydes or ketones in high yields.

The two protocols described for the oxidation of alcohols were carried out without creating a foul smell in the laboratory. Since Dod-S-Me (**1**) has a higher boiling point than the volatile DMS, the products of the oxidations were isolated by column chromatography in the case of neutral products.[16] However, chromatographic isolation of the product could be avoided in large scale reactions in the case of acidic alcohols. For example, odorless Swern oxidation of mandelic acid gave phenylglyoxylic acid in 96% yield by sequential extraction[17] of the reaction mixture after basification and acidification.

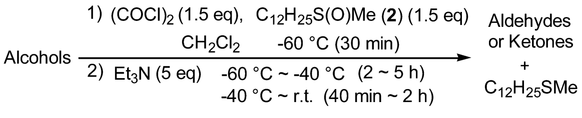
In conclusion, we were able to provide new odorless methods for the Corey–Kim and Swern oxidations using Dod-S-Me (**1**)[18] or dodecyl methyl sulfoxide (**2**)[18] as substitutes for the foul-smelling DMS and the sulfoxide DMSO. These protocols furnish the products under odorless conditions at minimal cost. The starting material, 1-dodecanethiol, for the synthesis of the odorless sulfide **1** and the sulfoxide **2** is inexpensive (about $20/kg) because it is used in bulk as a vulcanizing agent for rubber. The odorless compounds **1** and **2** can therefore be prepared at a moderate price without using a foul-smelling reagent (MeSSMe and MeSH are regulated by the offensive odor control law). We anticipate that the odorless feature of these methods will be important for green chemistry as well as for organic chemistry in general. Further studies utilizing odorless sulfides and sulfoxides are underway in our laboratory.

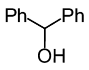
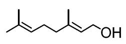
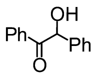
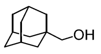
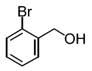
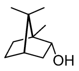
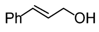
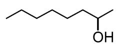
3. Experimental

3.1. General

^{1}H NMR spectra were obtained with a VARIAN GEMINI 2000/200, XL-300, INOVA-400NB or JEOL JNM-AL300 spectrometer with tetramethylsilane as the internal standard. Infrared spectra were measured with a SHIMADZU FTIR-8300 spectrometer. Low and high-resolution mass spectra were determined on either a JEOL JMS GC-mate (EI) or a JEOL JMX SX 102A QQ (FAB) mass spectrometer. Gas chromatographic analyses were performed on a DB-1 column (0.25 mm×30 m J & W Scientific) with SHIMADZU GS-2010 and FID. High performance liquid chromatography was performed on a SHIMADZU LC-10A series, chiral column (Chiralcel OD, OJ). Wakogel C-200 (Wako Pure Chemical Industries), Silica gel 60N (Kanto Chemical) was used for column chromatography. Silica gel F254 plates (Merck) were used for TLC. Visualization was performed using UV light, iodine and 12-molybdo(VI) phosphoric acid *n*-hydrate in EtOH. Sulfides were further purified by a recycle HPLC (LC-908, Japan Analytical Industry Co., Ltd.) on GPC columns (JAIGEL 1H and 2H) after purification by distillation. Dichloromethane was distilled from CaH_2,

Table 5. Odorless Swern oxidation using dodecyl methyl sulfoxide



Entry	Alcohols	Isolated yield (%)		Entry	Alcohols	Isolated yield (%)	
		Aldehydes or ketones (lit.)[a]	Recovery of **1**			Aldehydes or ketones (lit.)[a]	Recovery of **1**
1		95 (98)	100	5		93 (95)	99
2		91 (95)	94	6		93 (99)	99
3		95	95	7		91 (95)	91
4		93 (98)	93	8		81 (98[b])	95

[a] Swern et al. *Synthesis* **1980**, 165.
[b] GC yield.

after washing with water. Other solvents were dried by general methods.

3.1.1. Dodecyl methyl sulfide (1). To a DMF (3 ml) suspension of potassium carbonate (751 mg, 5.43 mmol) was added a DMF solution of 1-dodecanethiol (1000 mg, 4.94 mmol) and methyl iodide (736 mg, 5.19 mmol) at 0°C, and the resulting mixture was stirred at room temperature for 1 h. The reaction mixture was filtered, then 1N HCl was added to the solution, which was concentrated in vacuo. The residue was added to distilled water, then extracted with ethyl acetate. The organic layer was washed with sodium thiosulfate solution, dried (Na_2SO_4), filtered and concentrated in vacuo. Purification of the residue by silica gel column chromatography gave dodecyl methyl sulfide (**1**) (922 mg, 86%).

The scale-up reaction under the above conditions using a DMF (300 ml) solution of potassium carbonate (75.1 g, 543.5 mmol) and a DMF (200 ml) solution of 1-dodecanethiol (100 g, 494.1 mmol) and methyl iodide (73.6 g, 518.8 mmol), gave dodecyl methyl sulfide (**1**) (91.4 g, 81%) by distillation in vacuo.

Colorless oil; bp 110°C (0.2 mm Hg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.49 (t, J=7.4 Hz, 2H), 2.10 (s, 3H), 1.59 (sextet, J=7.4 Hz, 2H), 1.43–1.19 (m, 15H), 0.88 (t, J=6.9 Hz, 3H); MS (20 eV) m/z: 216 (M^+, 60), 201 (100), 125 (11), 111 (30), 103 (24), 97 (50), 83 (51), 71 (25), 70 (36), 69 (38), 61 (12), 57 (35); HRMS calcd for $C_{13}H_{28}S$ (M^+): 216.1912, found 216.1914.

3.1.2. Dodecyl methyl sulfoxide (2). To a $CHCl_3$/MeOH/H_2O (1/4/4, 9 ml) solution of dodecyl methyl sulfide (50 mg, 0.23 mmol) was added trioctylmethylammonium chloride (20 ml, 0.04 mmol) and sodium periodate (296 mg, 1.38 mmol) at 0°C, and the resulting mixture was stirred at room temperature for 10 min. The reaction mixture was added to distilled water (10 ml) and stirred for 2 h. The reaction mixture was concentrated in vacuo then extracted with ethyl acetate. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated in vacuo. Purification of the residue by silica gel column chromatography gave dodecyl methyl sulfoxide (**2**) (53 mg, 99%).

White powder; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.81–2.57 (m, 2H), 2.52 (s, 3H), 1.76 (quintet, J=7.9 Hz, 2H), 1.57–1.19 (m, 15H), 0.88 (t, J=6.7 Hz, 3H); IR ($CHCl_3$): 3550–3150 (br), 2997, 2928, 2855, 1466, 1408, 1034, 934 cm^{-1}; MS (20 eV) m/z: 233 (M^++H, 1), 232 (M^+, 1), 216 (43), 215 (100), 201 (40), 187 (2), 168 (3), 140 (3), 125 (4), 111 (13), 97 (24), 85 (19), 83 (30), 71 (32), 69 (25), 57 (52); HRMS calcd for $C_{23}H_{23}SO$ (M^+): 232.1861, found 232.1865.

3.2. A typical procedure for the new method of the Corey–Kim oxidation using dodecyl methyl sulfide (1)

To a dichloromethane or toluene solution (10 ml) of *N*-chlorosuccinimide (108 mg, 0.81 mmol) was added a dichloromethane or toluene solution (2 ml) of dodecyl methyl sulfide (**1**) (176 mg, 0.81 mmol) dropwise at −40°C, and the resulting mixture was stirred for 30 min. A dichloromethane or toluene solution (2 ml) of an alcohol (0.27 mmol) was added dropwise at −40°C. After the mixture was stirred for 2 h, triethylamine (0.19 ml, 1.36 mmol) was added dropwise at −40°C. After stirring for 14 h, water (20 ml) was added to the reaction mixture. The mixture was neutralized with 1N HCl (0.5 ml), followed by extraction of the aqueous layer with chloroform (40 ml×3) or ethyl acetate (40 ml×3). The combined organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated in vacuo. Silica gel chromatography of the residue (hexane/ethyl acetate=40/1) gave an aldehyde or a ketone. The resulting products were analyzed by comparing their NMR spectra and TLC with those of authentic samples.

3.2.1. 3,5-Dibenzyloxy-4-methoxybenzaldehyde (Table 2, entry 1). *Using CH_2Cl_2 as a solvent.* According to the general procedure, the reaction was performed using 3,5-dibenzyloxy-4-methoxybenzyl alcohol (50 mg, 0.14 mmol), dodecyl methyl sulfide (94 mg, 0.43 mmol), *N*-chlorosuccinimide (58 mg, 0.43 mmol), triethylamine (0.10 ml, 0.72 mmol), and dichloromethane (10 ml) to give 3,5-dibenzyloxy-4-methoxybenzaldehyde (49 mg, 99%).

Using toluene as a solvent. According to the general procedure, the reaction was performed using 3,5-dibenzyloxy-4-methoxybenzyl alcohol (50 mg, 0.14 mmol), dodecyl methyl sulfide (94 mg, 0.43 mmol), *N*-chlorosuccinimide (58 mg, 0.43 mmol), triethylamine (0.10 ml, 0.72 mmol), and toluene (10 ml) to give 3,5-dibenzyloxy-4-methoxybenzaldehyde (47 mg, 95%).

3.2.2. 4-Androsten-3,17-dione (Table 2, entry 2). *Using CH_2Cl_2 as a solvent.* According to the general procedure, the reaction was performed using testosterone (50 mg, 0.17 mmol), dodecyl methyl sulfide (113 mg, 0.52 mmol), *N*-chlorosuccinimide (69 mg, 0.52 mmol), triethylamine (0.12 ml, 0.86 mmol), and dichloromethane (14 ml) to give 4-androsten-3,17-dione (45 mg, 91%).

Using toluene as a solvent. According to the general procedure, the reaction was performed using testosterone (50 mg, 0.17 mmol), dodecyl methyl sulfide (113 mg, 0.52 mmol), *N*-chlorosuccinimide (69 mg, 0.52 mmol), triethylamine (0.12 ml, 0.86 mmol), and toluene (14 ml) to give 4-androsten-3,17-dione (48 mg, 97%).

3.2.3. Benzil (Table 2, entry 3). *Using CH_2Cl_2 as a solvent.* According to the general procedure, the reaction was performed using benzoin (50 mg, 0.24 mmol), dodecyl methyl sulfide (153 mg, 0.71 mmol), *N*-chlorosuccinimide (94 mg, 0.70 mmol), triethylamine (0.16 ml, 1.18 mmol), and dichloromethane (14 ml) to give benzil (49 mg, 99%).

3.2.4. Benzophenone (Table 2, entry 4). *Using CH_2Cl_2 as a solvent.* According to the general procedure, the reaction was performed using benzhydrol (50 mg, 0.27 mmol), dodecyl methyl sulfide (176 mg, 0.81 mmol), *N*-chlorosuccinimide (108 mg, 0.81 mmol), triethylamine (0.19 ml, 1.35 mmol) and dichloromethane (14 ml) to give benzophenone (47 mg, 95%).

Using toluene as a solvent. According to the general procedure, the reaction was performed using benzhydrol

(50 mg, 0.27 mmol), dodecyl methyl sulfide (176 mg, 0.81 mmol), *N*-chlorosuccinimide (108 mg, 0.81 mmol), triethylamine (0.19 ml, 1.35 mmol) and toluene (14 ml) to give benzophenone (48.5 mg, 98%).

3.2.5. Cinnamaldehyde (Table 2, entry 5). *Using CH_2Cl_2 as a solvent*. According to the general procedure, the reaction was performed using cinnamyl alcohol (50 mg, 0.37 mmol), dodecyl methyl sulfide (242 mg, 1.12 mmol), *N*-chlorosuccinimide (149 mg, 1.12 mmol), triethylamine (0.26 ml, 1.86 mmol), and dichloromethane (14 ml) to give cinnamaldehyde (45 mg, 91%).

Using toluene as a solvent. According to the general procedure, the reaction was performed using cinnamyl alcohol (50 mg, 0.37 mmol), dodecyl methyl sulfide (242 mg, 1.12 mmol), *N*-chlorosuccinimide (149 mg, 1.12 mmol), triethylamine (0.26 ml, 1.86 mmol), and toluene (14 ml) to give cinnamaldehyde (44.5 mg, 90%).

3.3. A typical procedure for the new method of the Corey–Kim oxidation using dodecyl methyl sulfide for heteroaromatic alcohols

To a tetrahydrofuran solution (30 ml) of *N*-chlorosuccinimide (324 mg, 2.43 mmol) was added a tetrahydrofuran solution (6 ml) of dodecyl methyl sulfide (**1**) (526 mg, 2.43 mmol) dropwise at −40°C, and the resulting mixture was stirred for 30 min. A tetrahydrofuran solution (6 ml) of an alcohol (0.81 mmol) was added dropwise at −40°C. After the mixture was stirred for 2 h, triethylamine (410 mg, 4.05 mmol) was added dropwise at −40°C. After stirring for 14 h, the reaction mixture gave an aldehyde or a ketone. The resulting products were analyzed by comparing their GC with those of authentic samples.

3.3.1. 2-Pyridinecarboxaldehyde (Table 4, entry 1). According to the general procedure, the reaction was performed using 2-pyridinemethanol (88 mg, 0.81 mmol). Yield: 77%.

3.3.2. 3-Pyridinecarboxaldehyde (Table 4, entry 2). According to the general procedure, the reaction was performed using 3-pyridinemethanol (88 mg, 0.81 mmol). Yield: 71%.

3.3.3. 3-Acetylpyridine (Table 4, entry 3). According to the general procedure, the reaction was performed using 2-(1-hydroxyethyl)pyridine (100 mg, 0.81 mmol). Yield: 99%.

3.3.4. 2-Thiophenecarboxaldehyde (Table 4, entry 4). According to the general procedure, the reaction was performed using 2-thiophenemethanol (92 mg, 0.81 mmol). Yield: 86%.

3.3.5. 3-Thiophenecarboxaldehyde (Table 4, entry 5). According to the general procedure, the reaction was performed using 3-thiophenemethanol (92 mg, 0.81 mmol). Yield: 85%.

3.3.6. Furfral (Table 4, entry 6). According to the general procedure, the reaction was performed using furfuryl alcohol (79 mg 0.81 mmol). Yield: 92%.

3.4. A typical procedure for the new method of the Swern oxidation using dodecyl methyl sulfoxide (2)

To a dichloromethane (4 ml) suspension of dodecyl methyl sulfoxide (**2**) (95 mg, 0.41 mmol) was added dropwise oxalyl chloride (41 μl, 0.41 mmol) at −60°C, and the resulting mixture was stirred for 15 min. A dichloromethane (1 ml) solution of an alcohol (0.27 mmol) was added dropwise at −60°C. The mixture was stirred for 30 min, triethylamine (0.19 ml, 1.36 mmol) was added dropwise and the resultant mixture was gradually warmed to −40°C over 200 min. The mixture was then warmed to room temperature by removing the cooling bath and stirred for 1 h. The mixture was quenched with water (10 ml), neutralized with an 1N HCl (0.5 ml) solution then extracted with chloroform (40 ml×3). The combined organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated in vacuo. Purification of the residue by silica gel column chromatography (hexane/ethyl acetate=40/1) gave an aldehyde or a ketone and dodecyl methyl sulfide (**1**). The resulting products were analyzed by comparing their NMR spectra and TLC with those of authentic samples.

3.4.1. Benzophenone (Table 5, entry1). According to the general procedure, the reaction was performed using benzhydrol (50 mg, 0.27 mmol), dodecyl methyl sulfoxide (95 mg, 0.41 mmol), oxalyl chloride (36 μl, 0.52 mmol), triethylamine (0.19 ml, 1.36 mmol), and dichloromethane (5 ml), to give benzophenone (47 mg, 95%).

The 10-times scale-up experiment under the above conditions using benzhydrol (500 mg, 2.7 mmol) gave benzophenone (460 mg, 93%), along with dodecyl methyl sulfide (**1**) (540 mg, 92%).

3.4.2. Benzil (Table 5, entry 2). According to the general procedure, the reaction was performed using benzoin (50 mg, 0.24 mmol), dodecyl methyl sulfoxide (82 mg, 0.35 mmol), oxalyl chloride (45 μl, 0.70 mmol), triethylamine (0.16 ml, 1.18 mmol) and dichloromethane (6 ml) to give benzil (46 mg, 99%).

3.4.3. *o*-Bromobenzaldehyde (Table 5, entry 3). According to the general procedure, the reaction was performed using *o*-bromobenzyl alcohol (50 mg, 0.27 mmol), dodecyl methyl sulfoxide (93 mg, 0.40 mmol), oxalyl chloride (35 μl, 0.40 mmol), triethylamine (0.19 ml, 1.34 mmol), and dichloromethane (5 ml) to give *o*-bromobenzaldehyde (47 mg, 95%).

3.4.4. Cinnamaldehyde (Table 5, entry 4). According to the general procedure, the reaction was performed using cinnamyl alcohol (50 mg, 0.37 mmol), dodecyl methyl sulfoxide (129 mg, 0.56 mmol), oxalyl chloride (39 μl, 0.56 mmol), triethylamine (0.26 ml, 1.86 mmol), and dichloromethane (6 ml), to give cinnamaldehyde (46 mg, 93%).

3.4.5. Geranial (Table 5, entry 5). According to the general procedure, the reaction was performed using geraniol

(50 mg, 0.32 mmol), dodecyl methyl sulfoxide (113 mg, 0.49 mmol), oxalyl chloride (43 μl, 0.49 mmol), triethylamine (0.23 ml, 1.62 mmol), and dichloromethane (14 ml), to give geranial (46 mg, 93%).

3.4.6. 1-Adamantanecarboxaldehyde (Table 5, entry 6). According to the general procedure, the reaction was performed using 1-adamantanemethanol (50 mg, 0.30 mmol), dodecyl methyl sulfoxide (104 mg, 0.45 mmol), oxalyl chloride (40 μl, 0.45 mmol), triethylamine (0.21 ml, 1.50 mmol), and dichloromethane (6 ml), to give 1-adamantanecarboxaldehyde (46 mg, 93%).

3.4.7. Camphor (Table 5, entry 7). According to the general procedure, the reaction was performed using borneol (50 mg, 0.32 mmol), dodecyl methyl sulfoxide (113 mg, 0.49 mmol), oxalyl chloride (43 μl, 0.49 mmol), triethylamine (0.23 ml, 1.62 mmol) and, dichloromethane (14 ml), to give camphor (45 mg, 91%).

3.4.8. 2-Octanone (Table 5, entry 8). According to the general procedure, the reaction was performed using 2-octanol (50 mg, 0.38 mmol), dodecyl methyl sulfoxide (134 mg, 0.58 mmol), oxalyl chloride (40 μl, 0.58 mmol), triethylamine (0.27 ml, 1.92 mmol) and dichloromethane (6 ml) to give 2-octanone (40 mg, 81%).

3.5. Manipulation of odorless Swern oxidation of acidic alcohol (mandelic acid) using dodecyl methyl sulfoxide (2)

To a CH_2Cl_2/THF (3/1, 90 ml) solution of dodecyl methyl sulfoxide (1680 mg, 7.23 mmol) was added dropwise a CH_2Cl_2/THF (3/1, 5 ml) solution of oxalyl chloride (0.63 ml, 7.23 mmol) at −60°C, and the resulting mixture was stirred for 15 min. Then, a CH_2Cl_2/THF (3/1, 5 ml) solution of mandelic acid (500 mg, 3.23 mmol) was added dropwise at −60°C. The mixture was stirred for 2 h, triethylamine (2.29 ml, 16.4 mmol) was added dropwise, and the resulting mixture was gradually warmed to −40°C over 2 h. The mixture was then warmed to room temperature by removing the cooling bath and stirred for 40 min. The mixture was quenched with 10% NaOH solution, and concentrated in vacuo. The residue was washed with ether, a 1N HCl solution was added, then the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated in vacuo. Without further purification, the pure phenylglyoxylic acid (466 mg, 96%) was obtained. The product was analyzed by comparing the NMR spectrum and TLC with those of the authentic sample.

Acknowledgements

We are grateful for a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan, for partial financial support of this research.

References

1. Barrett, G. C. *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Jones, N., Eds.; Pergamon: Oxford, 1979; Vol. 3, p 3 Part 11, Organic Sulphur Compounds.
2. (a) Hoard, D. W.; Luke, W. D. Eur. Pat. Appl. EP 875511, 1998. (b) Dahl, B. H.; Bjergaarde, K.; Henriksen, L.; Dahl, O. *Acta Chem. Scand.* **1990**, *44*, 639–641.
3. (a) Nishide, K.; Shigeta, Y.; Obata, K.; Node, M. *J. Am. Chem. Soc.* **1996**, *118*, 13103–13104. (b) Node, M.; Nishide, K.; Shigeta, Y.; Shiraki, H.; Obata, K. *J. Am. Chem. Soc.* **2000**, *122*, 1927–1936. (c) Shiraki, H.; Nishide, K.; Node, M. *Tetrahedron Lett.* **2000**, *41*, 3437–3441. (d) Node, M. *Yakugaku Zasshi* **2002**, *122*, 71–88. (e) Nishide, K.; Node, M. *Chirality* **2002**, *14*, 759–767.
4. Node, M.; Kumar, K.; Nishide, K.; Ohsugi, S.; Miyamoto, T. *Tetrahedron Lett.* **2001**, *42*, 9207–9210.
5. Nishide, K.; Miyamoto, T.; Kumar, K.; Ohsugi, S.; Node, M. *Tetrahedron Lett.* **2002**, *43*, 8569–8573.
6. Nishide, K.; Ohsugi, S.; Shiraki, H.; Tamakita, H.; Node, M. *Org. Lett.* **2001**, *3*, 3121–3124.
7. (a) Node, M.; Nishide, K.; Sai, M.; Ichikawa, K.; Fuji, K.; Fujita, E. *J. Org. Chem.* **1981**, *46*, 1991–1993. (b) Fuji, K.; Node, M. *Synth. Org. Chem. Jpn* **1984**, *42*, 193–205. (c) Node, M. *Yakugaku Zasshi* **1986**, 1–16. Also see the references cited therein.
8. Corey, E. J.; Kim, C.; U, . *J. Am. Chem. Soc.* **1972**, *94*, 7586–7587.
9. Crich, D.; Neelamkavil, S. *Tetrahedron* **2002**, *58*, 3865–3870.
10. Crich, D.; Neelamkavil, S. *J. Am. Chem. Soc.* **2001**, *123*, 7449–7450.
11. (a) Harris, J. M.; Liu, Y.; Chai, S.; Andrews, M. D.; Vederas, J.-C. *J. Org. Chem.* **1998**, *63*, 2407–2409. (b) Liu, Y.; Vederas, J.-C. *J. Org. Chem.* **1996**, *61*, 7856–7859.
12. Scott, D. W.; Mccullough, J. P. *US Bur. Mines, Bull.* **1962**, 68.
13. The preliminary communication: Nishide, K.; Ohsugi, S.; Fudesaka, M.; Kodama, S.; Node, M. *Tetrahedron Lett.* **2002**, *43*, 5177–5179.
14. (a) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651–1660. (b) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480–2482.
15. Ireland, R. E.; Norbeck, D. W. *J. Org. Chem.* **1985**, *50*, 2198–2200.
16. Depending on the physical property and the amounts of the products, extraction, crystallization, or distillation could be used for isolation of the products.
17. The same extraction in the case of Corey–Kim oxidation gave a mixture of phenylglyoxylic acid and succinimide.
18. Both Dod-S-Me (**1**) and dodecyl methyl sulfoxide (**2**) are now available from Wako Pure Chemical Industries, Ltd.