## *Headline Articles*

# A New Method for Oxidation of Various Alcohols to the Corresponding Carbonyl Compounds by Using *N*-*t*-Butylbenzenesulfinimidoyl Chloride

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Various primary and secondary alcohols were smoothly oxidized to the corresponding aldehydes and ketones by using a new oxidizing agent, *N*-*t*-butylbenzenesulfinimidoyl chloride (**4a**), in the coexistence of DBU or zinc oxide. The present oxidation proceeded under mild conditions via five-membered intramolecular proton-transfer of an alkyl arenesulfinimidate intermediate.

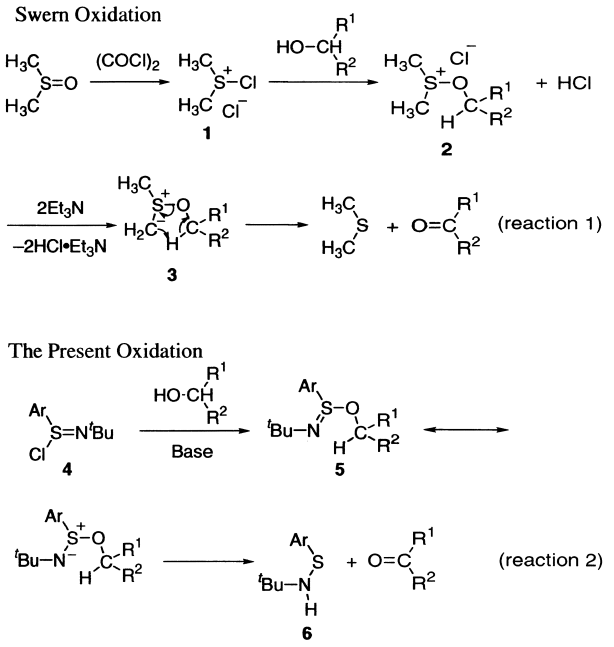
Oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is one of the most fundamental and important transformations in organic synthesis because thus formed aldehydes and ketones are valuable synthetic intermediates especially in carbon–carbon bond forming reactions for constructing a targeted carbon skeleton. Many oxidation methods have been reported to date[1] and simple alcohols that form stable carbonyl products are oxidized by a number of oxidants. In recent years, the structures of target molecules in organic synthesis are becoming more complicated, so better functional compatibility and higher selectivity are required for the efficient oxidation. In this regard, conventional oxidants do not always satisfy such requirements; therefore, exploration of new oxidizing agents is worth challenging.

Oxidation of alcohols by using heavy metal oxidants such as chromium or manganese is a classical method. As a matter of fact, chromium(VI)-based oxidizing reagents known as Jones reagent,[2] Collins reagent,[3] pyridinium chlorochromate (PCC),[4] pyridinium dichromate (PDC),[5] etc. have been used quite commonly in organic synthesis. However, toxic chromium residues formed after the oxidation were the causes of some problems during work-up and also at their disposal. To solve those problems, oxidation by using a catalytic amount of transition metals has been developed in the past two decades, and tetrapropylammonium perruthenate (TPAP)-catalyzed oxidation of alcohols has spread because of its wide applicability as well as its easy work-up procedures.[6]

Of various non-metal oxidants, Dess–Martin periodinate (1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one, DMP) is known to be one of the mildest reagents for the oxidation of alcohols.[7] It is more often employed in the oxidation of complex or labile molecules because of the following advantages: mildness, wider functional group tolerance, high yielding without over-oxidation, and easy work-up. However, DMP and its synthetic precursor, 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (IBX), are reported to be explosive on impact or heating to $> 200$ °C.[7d] Therefore, these reagents must be kept in a refrigerator and should not be used in large scales.

In 1963, Pfitzner and Moffatt discovered a new dimethyl sulfoxide-based oxidation method in which primary and secondary alcohols were efficiently oxidized to the corresponding aldehydes and ketones, respectively, by using dimethyl sulfoxide, dicyclohexylcarbodiimide, and certain kinds of acids.[8a] Many similar oxidation reactions using activated dimethyl sulfoxides have been developed since then:[8e] for example, activation of dimethyl sulfoxide by using acetic anhydride,[8b] $SO_{2-}$ pyridine,[8c] and trifluoroacetic anhydride.[8d] Among them, Swern's method is known to be one of the most useful oxidation methods.[9] In Swern oxidation, dimethyl sulfoxide is activated with oxalyl chloride to form chlorodimethylsulfonium chloride (**1**) at $-60$ °C, and then an alcohol reacts with **1** to give alkoxysulfonium chloride (**2**). The formed **2** is deprotonated with triethylamine to form alkoxysulfonium ylide (**3**), in which an intramolecular proton transfer affords a carbonyl product along with dimethyl sulfide (Scheme 1, reaction 1). A wide variety of alcohols have effectively been oxidized and carbonyl products are easily purified after the Swern oxidation. However, the oxidation reaction must be carried out at strictly controlled low reaction temperatures since **1** is not stable above $-20$ °C.[9a] Also, an unpleasant odor of dimethyl sulfide formed by the oxidation is another disadvantage of Swern oxidation.

During our study on the asymmetric total synthesis of Taxol™,[10] it was noticed that there were many alcohol-oxidation steps in constructing the basic skeleton of Taxol. Therefore, our interest was focused on the exploration of a conve-

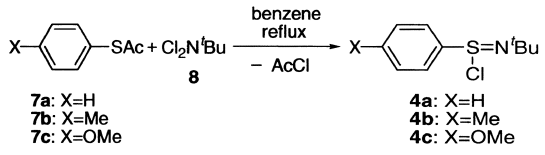



Scheme 1.

nient and useful new oxidation method. It was then thought that alkyl sulfinimidate **5** would work as the intermediate for oxidation of alcohols by considering its intramolecular proton transfer as in **3** (Scheme 1, reaction 2). Further, it was expected that **5** would be readily formed from sulfinimidoyl chloride **4** and alcohols. The results of new oxidation of alcohols under basic or almost neutral conditions by using **4** as a new oxidizing agent were preliminary reported.[11] Here, we would like to report on a novel and efficient oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones by using *N*-*t*-butylbenzenesulfinimidoyl chlorides (**4a**) and DBU or zinc oxide in further detail.

## Results & Discussion

**Synthesis of *N*-*t*-Butylarenesulfinimidoyl Chlorides 4a–c.** Since electron-donating alkyl groups were considered to increase the nitrogen's basicity[12] of alkyl sulfinimidate **5**, *t*-butyl group was chosen for *N*-substituent of sulfinimidoyl chloride, expecting that the proposed proton-transfer in **5** would proceed more favorably. The preparation of sulfinimidoyl chlorides was already reported by Markovskii et al.,[13] and *N*-*t*-butylarenesulfinimidoyl chlorides **4a–c** were prepared easily from the corresponding *S*-aryl thioacetates **7a–c** and *N*,*N*-dichloro-*t*-butylamine (**8**)[14] (Scheme 2). That is, the two reagents were refluxed in benzene and then the solvent and the formed acetyl chloride were removed from the reaction mixture. The residues contained the desired *N*-*t*-butylarenesulfinimidoyl chlorides **4a–c** in high purities, which could be used without further purification. They could be further purified by distillation under reduced pressures, if necessary.




Scheme 2.

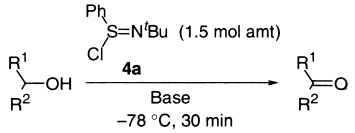
These oxidizing agents **4a–c** were synthesized in large quantities and thus prepared **4a–c** were handled without using inert-atmosphere techniques when a slightly larger amount of the reagents was employed. Also, they could be stored for a long time in a sealed bottle at room temperature. Compared with **1**, the thermal stability of **4** increased a great deal just by changing sulfur-carbon bond to sulfur-nitrogen bond. On the other hand, the preparation of sulfinimidoyl chlorides took place sluggishly according to the similar procedures when electron-withdrawing groups such as $NO_2$ or Cl were introduced on the aromatic rings of *S*-aryl thioacetates **7**. Also, *S*-alkyl substituted sulfinimidoyl chlorides such as *N*-*t*-butylmethanesulfinimidoyl chlorides or *N*-*t*-butyl-1,1-dimethylethanesulfinimidoyl chlorides were not successfully prepared by the reaction of **8** with *S*-methyl thiobutyrate or *S*-*t*-butyl thioacetate.

**Oxidation of Benzyl Alcohol (9a) and Cyclopentanol (10a) by Using *N*-*t*-Butylbenzenesulfinimidoyl Chloride (4a).** In the first place, oxidation of benzyl alcohol (**9a**) to benzaldehyde (**9b**) was examined by using **4a** as an oxidizing agent (Table 1). When **4a** and **9a** were mixed in dichloromethane at −78 °C in the absence of bases, benzyl chloride was formed as a main product while the expected oxidation reaction hardly took place (Table 1, entry 1). It was assumed that this chloride substitution took place via in situ formed benzyloxy(*N*-*t*-butylamino)(phenyl)sulfonium chloride (**11**) as shown in Scheme 3. Similar substitution of chloride ion for hydroxy groups was reported in the reaction of sulfonimidoyl chlorides and alcohol.[15] When an equimolar amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used for trapping hydrogen chloride, the desired oxidation took place in 65% yield along with 26% of benzyl chloride (Table 1, entry 2). In the case of using two molar amounts of DBU, the above-mentioned substitution reaction by chloride ion was completely suppressed and the desired oxidation smoothly took place at −78 °C to afford **9b** in almost quantitative yield (Table 1, entry 3).

The oxidation of **9a** proceeded also in high yields by using amine bases such as ethyldiisopropylamine or 1,4-diazabicyclo[2.2.2]octane (DABCO) (Table 1, entries 4 and 5), whereas other organic bases such as triethylamine and any types of pyridines were not effective (Table 1, entries 6–9). These results suggest that the present oxidation proceeded more efficiently when sterically hindered and sufficiently basic amines were used. As described by Gilchrist et al., basicities of *N*-non-substituted sulfinimidates are compatible to those of primary amines.[12] Therefore, bases stronger than primary amines are essential for the effective generation of the important intermediate, alkyl sulfinimidate **5.**

In the above experiments, the oxidizing agent **4a** was added to the mixture of alcohol **9a** and an amine base since the undesired by-product, benzyl chloride, was formed if **4a** and **9a** were mixed in advance. Further, it was found that the oxidizing agent **4a** reacted also with amine bases because the mixture of **4a** and DBU prepared in advance did not afford the oxidation product. Therefore, it was thought that a part of **4a** de-

Table 1. Oxidation of Benzyl Alcohol (**9a**) and Cyclopentanol (**10a**) by Using **4a**

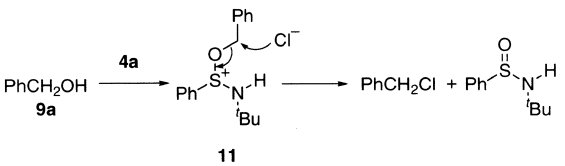



**9a**: $R^1$=Ph, $R^2$=H
**10a**: $R^1$, $R^2$=$(CH_2)_4$

**9b**: $R^1$=Ph, $R^2$=H
**10b**: $R^1$, $R^2$=$(CH_2)_4$

| Entry | Alcohol | Base (mol amt)[a)] | Solvent | Temp/°C | Yield[b)]/% |
|---|---|---|---|---|---|
| 1 | **9a** | none | $CH_2Cl_2$ | −78 | 2 (28) |
| 2 | **9a** | DBU (1.0) | $CH_2Cl_2$ | −78 | 65 (26) |
| 3 | **9a** | DBU (2.0) | $CH_2Cl_2$ | −78 | 98 (0) |
| 4 | **9a** | $^i$Pr$_2$NEt(2.0) | $CH_2Cl_2$ | −78 | 91 (1) |
| 5 | **9a** | DABCO (2.0) | $CH_2Cl_2$ | −78 | 85 (7) |
| 6 | **9a** | $Et_3N$ (2.0) | $CH_2Cl_2$ | −78 | 57 (3) |
| 7 | **9a** | $Et_3N$ (5.0) | $CH_2Cl_2$ | −78 | 24 (1) |
| 8 | **9a** | 2,6-di$^t$Bu-Py (2.0) | $CH_2Cl_2$ | −78 | 10 (17) |
| 9 | **9a** | pyridine (2.0) | $CH_2Cl_2$ | −78 | 6 (25) |
| 10 | **9a** | NaH (1.0) | THF | −78 | 85 (trace) |
| 11 | **9a** | MS4A (1 g/mmol) | $CH_2Cl_2$ | −78 | 67 (14) |
| 12 | **9a** | MS4A (3 g/mmol) | $CH_2Cl_2$ | −78 | 71 (14) |
| 13 | **9a** | DBU (2.0) | $CH_2Cl_2$ | −45 | 94 (1) |
| 14 | **9a** | DBU (2.0) | $CH_2Cl_2$ | −20 | 87 (5) |
| 15 | **9a** | DBU (2.0) | $CH_2Cl_2$ | 0 | 81 (5) |
| 16 | **9a** | DBU (2.0) | $CH_2Cl_2$ | rt | 80 (5) |
| 17 | **9a** | DBU (2.0) | toluene | 0 | 76 (trace) |
| 18 | **9a** | DBU (2.0) | THF | 0 | 69 (trace) |
| 19 | **9a** | DBU (2.0) | $CH_3CN$ | 0 | 88 (5) |
| 20 | **9a** | DBU (2.0) | DMF | 0 | 72 (0) |
| 21 | **10a** | DBU (1.0) | $CH_2Cl_2$ | rt | 90 (10) |
| 22 | **10a** | DBU (2.0) | $CH_2Cl_2$ | rt | >99 (0) |

a) DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene. DABCO: 1,4-diazabicyclo[2.2.2]octane. 2,6-di$^t$Bu-Py: 2,6-Di-*t*-butylpyridine. MS4A: Powdered molecular sieves. b) Yields were determined by GC-analysis using an internal standard. Numbers in parentheses were yields of benzyl chloride (Entries 1–20) or cyclopentyl chloride (Entries 21–22).




Scheme 3.

composed by the interaction with amine bases before the key intermediate **5** was formed, and better oxidation results were obtained when sterically hindered amines which reacted slowly with **4a** were used.

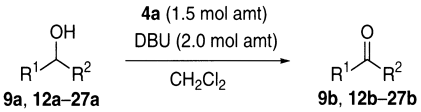
The oxidation using **4a** and sodium alkoxide, prepared from equimolar amount of sodium hydride and **9a**, gave **9b** in 85% and the undesirable substitution reaction by chloride ion was suppressed (Table 1, entry 10). Interestingly, the oxidation proceeded in a moderate yield when molecular sieves 4A was used as a solid base (Table 1, entries 11 and 12). Other examples about the oxidation of alcohols by using **4a** and solid bases will be described later.

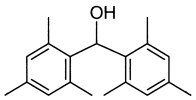
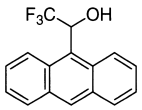
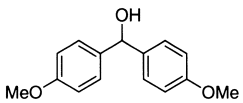
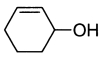
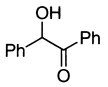
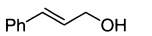
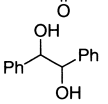
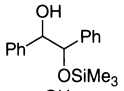
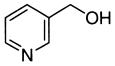
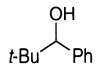
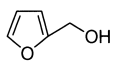
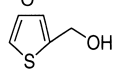
Our study of reaction temperatures found that the yields of **9b** decreased gradually at the temperatures above −45 °C (Table 1, entries 3 and 13–16). The present oxidation reaction could still be carried out at the temperatures higher than those required in Swern oxidation due to the higher stability of **4a**. After screening several other solvents such as toluene, THF, acetonitrile, and DMF, it was found that any of the solvents could be used and dichloromethane was the most preferable (Table 1, entries 17–20).

Since benzylic position was easily substituted by chloride ion, the effect of the amount of DBU was further examined in the oxidation of cyclopentanol (**10a**) to cyclopentanone (**10b**). It was then revealed that the use of an equimolar amount of DBU gave **10b** in high yield (90%), but cyclopentyl chloride was still accompanied in 10% yield (Table 1, entry 21). As in the case of oxidation of benzyl alcohol (**9a**), the use of two molar amounts of DBU completely prevented the formation of cyclopentyl chloride. In general, the oxidation experiments using **4a**, therefore, were carried out in the presence two molar amounts of DBU.

**Oxidation of Benzylic and Allylic Alcohols.** Oxidation of various primary and secondary alcohols was tried by using 1.5 molar amounts of **4a** and 2.0 molar amounts of DBU in dichloromethane (Tables 2 and 3). Most of benzylic and allyl-

Table 2. Oxidation of Benzylic and Allylic Alcohols **9a** and **12–27a** to the Corresponding Aldehydes and Ketones **9b** and **12–27b** by using **4a** and DBU




| Entry | Alcohol | | Conditions | Yield/%[a] | Entry | Alcohol | | Conditions | Yield/%[a] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $PhCH_2OH$ | **9a** | −78 °C, 30 min | 98 | 10 |  | **20a** | −78–0 °C, 1 h | 92[b] |
| 2 | $p$-$MeOC_6H_4CH_2OH$ | **12a** | −78 °C, 30 min | 90 | | | | | |
| 3 |  | **13a** | −78 °C, 30 min | 93 | 11 |  | **21a** | −78 °C–rt, 2 h | 81[b] |
| 4 |  | **14a** | −78 °C, 30 min | 99[b] | | | | | |
| 5 |  | **15a** | −78 °C, 30 min | 99[b] (99)[b),c)] | 12 |  | **22a** | −78 °C, 30 min | 94 |
| 6 |  | **16a** | −78 °C, 30 min | 92[b] | 13 |  | **23a** | −78 °C, 30 min | 82 |
| 7[d] |  | **17a** | −78 °C, 30 min | 86[b] | 14 | $C_2H_5-C\equiv C-CH_2OH$ | **24a** | −78 °C, 30 min | 87[e] |
| 8[c] |  | **18a** | −78 °C, 30 min | 91[b] | 15[c] |  | **25a** | −78 °C, 30 min | 90 |
| 9 |  | **19a** | 0 °C, 30 min | 87 | 16[c] |  | **26a** | −78 °C, 30 min | 80 |
| | | | | | 17[c] |  | **27a** | −78 °C, 30 min | 92 |

a) Yields were determined by GC-analysis unless otherwise mentioned. b) Isolated yield. c) Reactions were quenched by addition of saturated aqueous sodium hydrogencarbonate. d) **4a** (3.7 mol amt) and DBU (4.9 mol amt) were used. e) Isolated yield of the corresponding 2,4-dinitrophenylhydrazone.

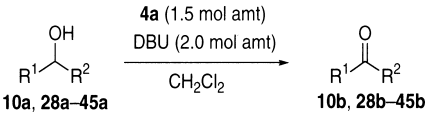
ic alcohols were oxidized smoothly at −78 °C (Table 2); however, hydroxy groups at sterically hindered positions (Table 2, entries 9 and 10) or those adjacent to an electron-withdrawing trifluoromethyl group (Table 2, entry 11) were oxidized at elevated temperatures (up to room temperature). $\alpha$-Ketol (**16a**) and 1,2-diol (**17a**) were oxidized efficiently to the corresponding dicarbonyl compounds without accompanying glycol carbon–carbon bond cleavage (Table 2, entries 6 and 7). It was noted that the secondary hydroxy group of **18a** was successfully oxidized in the presence of trimethylsiloxy group by the present oxidation method (Table 2, entry 8). Further, the attempted direct oxidation of trimethylsilyl ether of cyclohexanol did not afford cylohexanone, and almost all the starting material was recovered. Different from Swern oxidation which affords the corresponding carbonyl compounds directly on treating trimethysilyl ethers of primary and secondary alcohols,[16] selective oxidation successfully proceeded by the present procedure. An acetylenic alcohol (**24a**) was also oxidized at −78 °C in a high yield (Table 2, entry 14), and those having heterocyclic rings were again readily oxidized regardless of the kind of hetero atoms included in the heterocyclic rings (Table 2, entries 15–17). Pyridine, furan, and thiophene rings were not damaged during the oxidation with **4a**. Thus, an effective oxidation method for a wide variety of alcohols having various highly functional groups was established.

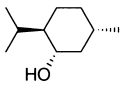
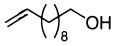
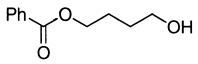
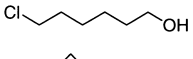
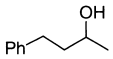
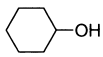
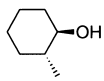
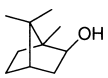
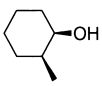
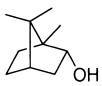
**Oxidation of Primary and Secondary Alcohols.** Primary and secondary alcohols were also smoothly oxidized by the combined use of **4a** and DBU at the temperatures between 0 °C and room temperature (Table 3). The temperatures for the oxidation of primary alcohols were obviously lower than that of secondary ones, which indicated the influence of steric factors on the present oxidation. In fact, oxidation of a sterically hindered alcohol, (+)-menthol (**39a**), was slow and gave menthone in only 49% yield (entry 13), while secondary alcohols giving methyl ketones such as 2-pentanol and 4-phenyl-2-butanol were oxidized in about 80% yields (Table 3, entries 15–17). Interestingly, the oxidation of isoborneol (**44a**) was somewhat different from that of borneol (**45a**) (Table 3, entries 18 and 19), and **44a** was oxidized more effectively than **45a**.

In addition to **4a**, several *N*-*t*-butylarenesulfinimidoyl chlorides were prepared and oxidations were examined by taking 4-phenyl-2-butanol (**42a**) as a model substrate. Substituents at *para* position of the aryl group such as methyl (**4b**) or methoxy (**4c**) group did not exhibit any advantageous effects (Table 3, entry 16).

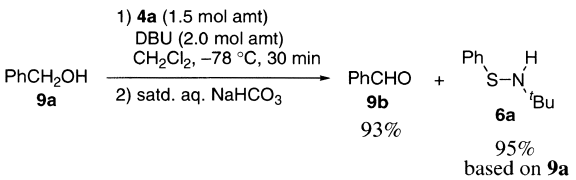
According to the assumed mechanism of the present oxidation (Scheme 1, reaction 2), the oxidizing reagent **4a** was converted to *N*-*t*-butylbenzenesulfenamide (**6a**).[17] In fact, 95% of **6a** was detected by $^1$H NMR after the oxidation of benzyl alcohol (**9**) by using **4a** and DBU (Scheme 4).

Table 3. Oxidation of Various Alcohols **10a** and **28–45a** to the Corresponding Carbonyl Compounds **10b** and **28–45b** by using **4a** and DBU




| Entry | Alcohol | | Conditions | Yield/%[a] | Entry | Alcohol | | Conditions | Yield/%[a] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $Ph(CH_2)_3OH$ | **28a** | 0 °C, 30 min | 94[b] | | | | | |
| 2 | $CH_3(CH_2)_7OH$ | **29a** | 0 °C, 30 min | 97(98)[b),e)] | 13 |  | **39a** | rt, 30 min | 49 |
| 3 | $BnO(CH_2)_8OH$ | **30a** | 0 °C, 30 min | 87[c)] | | | | | |
| 4 | $BnO(CH_2)_{10}OH$ | **31a** | 0 °C, 1 h | 92[c)] | 14 |  | **40a** | rt, 30 min | 98 |
| 5 |  | **32a** | 0 °C–rt, 1 h | 75 (77)[d)] | | | | | |
| 6 |  | **33a** | 0 °C, 30 min | 76[c)] | 15 |  | **41a** | rt, 30 min | 82 |
| 7 |  | **34a** | 0 °C–rt, 1 h | 99 | 16 |  | **42a** | rt, 30 min | 78 74[f)] 83[g)] |
| 8 |  | **35a** | rt, 30 min | 82 | | | | | |
| 9 |  | **10a** | rt, 30 min | > 99 | 17 |  | **43a** | rt, 1 h | 78 |
| 10 |  | **36a** | rt, 30 min | 91 | | | | | |
| 11 |  | **37a** | rt, 30 min | 87 | 18 |  | **44a** | rt, 30 min | 97 |
| 12 |  | **38a** | rt, 30 min | 82 | 19 |  | **45a** | rt, 30 min | 74 |

a) Determined by GC-analysis unless otherwise mentioned. b) Isolated yields of the corresponding 2,4-dinitrophenylhydrazones. c) Isolated yield. d) Reactions were quenched by addition of saturated aqueous sodium hydrogencarbonate. e) Reaction conditions: rt, 30 min. f) **4b** was used instead of **4a**. g) **4c** was used instead of **4a**.



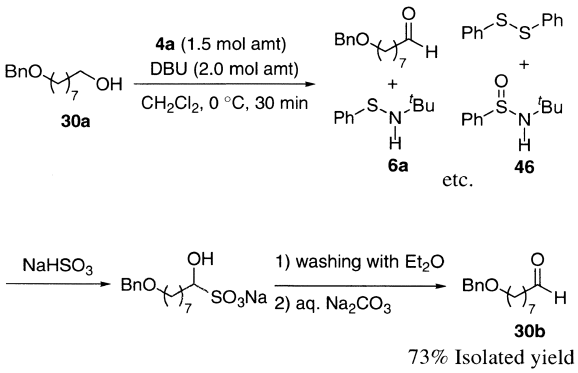

Scheme 4.

The detected **6a** was formed by the reduction of **4a** during the oxidation process. The sulfenamide **6a** whose basicity was much weaker than that of *t*-butylamine[18] could not be removed from the reaction mixture by washing with 1% aqueous HCl solution. On the other hand, diphenyl disulfide which was formed by the direct hydrolysis of **4a** and by the decomposition of **6a**[18] was isolated by the purification with silica gel column chromatography. It was also shown that **6a** was partially decomposed during the purification with silica gel column chromatography.

Most of the present oxidation reactions shown in Tables 1, 2, and 3 were quenched with dilute hydrochloric acid. When carbonyl products had acid-sensitive functional groups, saturated aqueous $NaHCO_3$ solution was used for quenching the present reaction. The same results were obtained when carbonyl products were kept stable under these two work-up procedures: for example, **15b** was isolated in 99% yield by quenching with both 1% aqueous HCl solution and saturated aqueous $NaHCO_3$ (Table 2, entry 5).

To purify the formed carbonyl compounds was often troublesome because co-products of the present oxidation, such as **6a**, diphenyl disulfide, and *N*-*t*-butylbenzenesulfinamide (**46**), had to be removed by silica gel- or alumina-column chromatography after the oxidation using **4b**. However, aldehydes could be isolated without purification with column chromatography by transforming them into the corresponding hydrogensulfite addition compounds[19]: that is, i) converting them first to water-soluble hydrogensulfite addition compounds with aqueous sodium hydrogensulfite solution; ii) washing out the oxidation co-products by extraction with organic solvents; iii) desired aldehydes were regenerated from the aqueous solution by the decomposition of hydrogensulfite addition compounds. The above-mentioned procedure afforded the desired aldehyde **30b** in 73% yield without purification by column chromatography (Scheme 5).

**Oxidation of Alcohols Giving Labile Carbonyl Compounds.** The oxidization of relatively simple alcohols giving stable carbonyl compounds smoothly proceeded by using **4a** and DBU whereas the oxidation of several alcohols such as $\beta$-aryl, and $\beta$-carbonyl alcohols proceeded to give the corresponding carbonyl compounds in low yields. For example, the




Scheme 5.

oxidation of 2-phenylethanol (**47a**) by using **4a** and DBU gave phenylacetaldehyde (**47b**) in only 24% yield. Swern et al. reported also that the oxidation of **47a** by using dimethyl sulfoxide, oxalyl chloride, and triethylamine afforded **47b** in a low yield (23%).[9b] It was assumed that a labile aldehyde **47b** decomposed under those basic oxidation conditions since 3-phenylpropanol was oxidized to 3-phenylpropanal in 94% yield by using **4a** and DBU (Table 3, entry 1). In fact, decomposition of **47b** was observed in the presence of two molar amounts of DBU, giving a complex mixture. Therefore, it was necessary to perform this oxidation reaction under nearly neutral conditions, and thus it was planned to use a suitable solid base as a scavenger of hydrogen chloride.

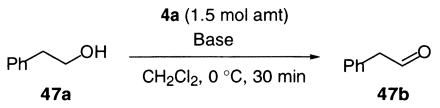
Solid bases were screened by model oxidation of **47a** into a labile aldehyde **47b** by using 1.5 molar amounts of **4a** (Table 4). In the first place, molecular sieves 4A (MS4A) was tested as a solid base since the oxidation of benzyl alcohol (**9a**) by the combined use of **4a** and MS4A had given good results (Table 1, entries 11 and 12). Similar behavior of MS4A to work as a neutral scavenger of hydrogen chloride was reported.[20] Expectedly, the yield of **47b** was improved from 24% up to 73% when 1 g/mmol of MS4A was used instead of DBU. Other types of zeolites such as MS3A and 5A were not as effective as MS4A. Also, cesium fluoride,[21] which is another type of dehydrohalogenating agent, was ineffective in this oxidation.

Next, the oxidation was further examined by using several metal oxides as acid scavengers since solid bases such as magnesium oxide[22] and zinc oxide[23] were reported to be effective in Friedel–Crafts type reactions. Of several metal oxides screened, zinc oxide, which did not work as an oxidant by itself, was found to be the most effective acid-scavenger in the oxidation of **47a**. Interestingly, a considerable amount (55%) of (2-chloroethyl)benzene was detected only in the case of using NiO (Table 4, entry 10). Because the yield of **47b** lowered considerably when the amount of zinc oxide decreased from five to two molar amounts, five molar amounts of zinc oxide were used in all the experiments thereafter.

It was found that the oxidation of **47a** by the combined use of **4a** and zinc oxide was more effective than others, including Swern,[9] a modified Swern,[24] PDC,[5] and TPAP[6] oxidations (Table 5, entries 1–5). The oxidation of **47a** to **47b** with Dess–Martin periodinate[7] proceeded in high yield under wet conditions.[7c]

Other primary and secondary alcohols involving $\beta$-aryl, $\beta$-alkoxy, and $\beta$-phenoxy ones were oxidized smoothly by the present oxidation method of using **4a** and zinc oxide (Table 5, entries 6–15). However, oxidation of secondary alcohols was slower than that of primary ones, and yields of ketones remained moderate to good.

Table 4. Effect of Solid Bases on the Oxidation of 2-Phenylethanol (**47a**) to Phenylacetaldehyde (**47b**) by Using **4a**




| Entry | Base | Yield/%[a] |
|---|---|---|
| 1 | DBU (2 mol amt) | 24 |
| 2 | MS3A (1 g/mmol) | 21 |
| 3 | MS4A (1 g/mmol) | 73(56)[b] |
| 4 | MS5A (1 g/mmol) | 35 |
| 5 | CsF (5 mol amt) | 6 |
| 6 | MgO (10 mol amt) | 58 |
| 7 | CaO (5 mol amt) | 56 |
| 8 | BaO (5 mol amt) | 70 |
| 9 | $TiO_2$ (5 mol amt) | 0 |
| 10 | NiO (5 mol amt) | trace |
| 11 | CuO (5 mol amt) | 37 |
| 12 | ZnO (5 mol amt) | 91(35)[c] (0)[d] |
| 13 | $Al_2O_3$ (5 mol amt) | trace |

a) Determined by GC-analysis using an internal standard. b) MS4A (3 g/mmol) was used. c) Zinc oxide (2 mol amt) was used. d) **4a** was not used.

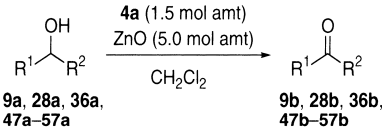
Since simple primary and secondary alcohols were quite smoothly oxidized to the corresponding carbonyl compounds according to the procedure using DBU as a base (Table 5, entries 17–19), oxidation conditions of using **4a** and zinc oxide had an advantage over the above-mentioned procedure of using DBU only in the oxidations of $\beta$-aryl, $\beta$-alkoxy, and $\beta$-phenoxy primary alcohols.

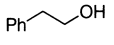
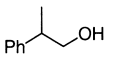
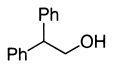
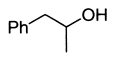
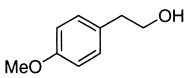
**Mechanism.** In order to investigate the present oxidation pathway whether intramolecular or intermolecular proton transfer took place in the key oxidation step, the oxidation reactions using two alkoxysulfonium salts (**59** and **61**) were tried (Scheme 6). These two alkoxysulfonium salts[25] were prepared in high yields by selective *O*-alkylation of the corresponding sulfinamides (**58** and **60**) as shown in Scheme 6. It is noted that the alkoxysulfonium salts having low-nucleophilic counter anions such as tetrafluoroborate or triflate anion were isolated as stable salts. On the other hand, it was hard to isolate the alkoxysulfonium salts when the counter anion was chloride ion because the nucleophilic substitution by chloride ion took place as previously described in the oxidation of benzyl alcohol (Cf. Scheme 3).

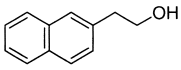
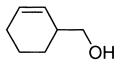
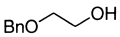
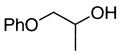
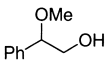
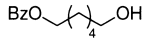
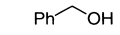
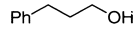
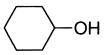
When thus prepared *N*-monoalkylated sulfonium salt **59** was treated with DBU, octanal (**29b**) was detected in 88% yield, as expected (Scheme 6, reaction 2).[26] On the other hand, a similar experiment using *N*,*N*-diethylsulfonium salt **61** with DBU did not afford octanal at all and *N*-octylated DBU (**62**) was obtained in 34% yield along with 41% of sulfinamide **60** and 37% of **61** was recovered (Scheme 6, reaction 3).

Thus, it is noted that alkyl sulfinimidate **5** was the important intermediate of the oxidation reaction because **5** was easily

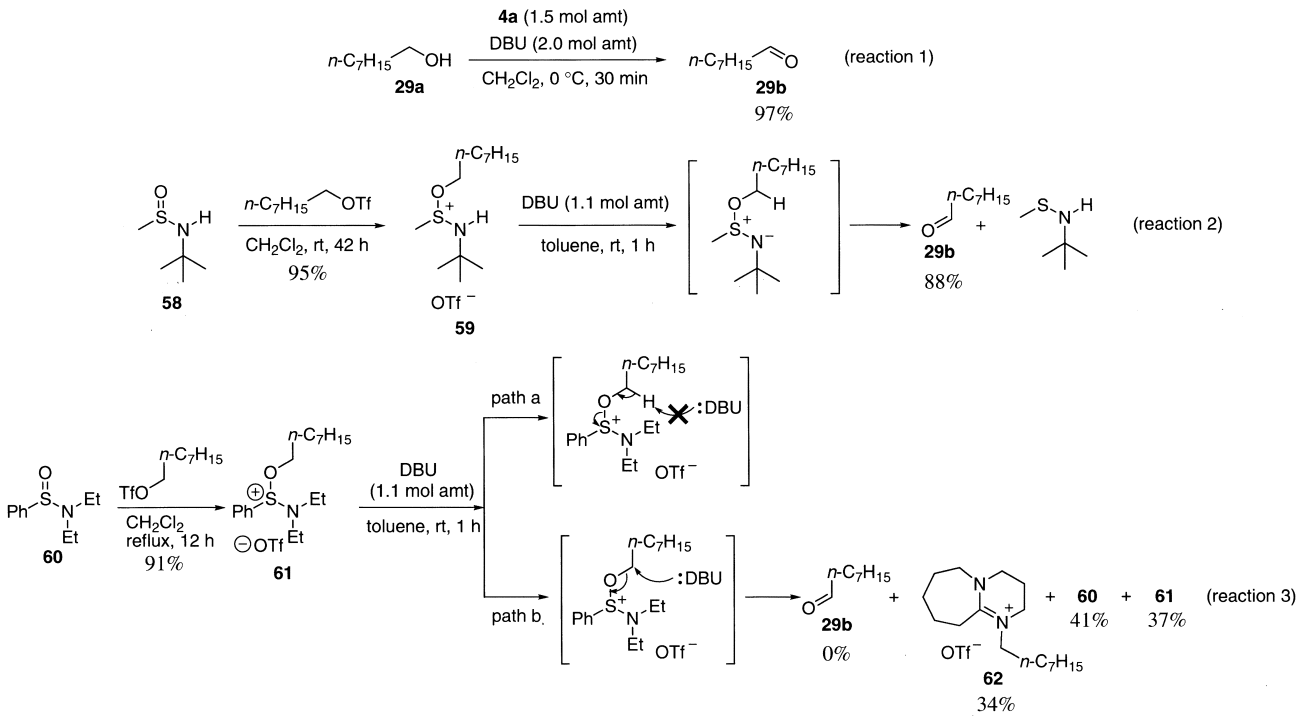
Table 5. Oxidation of Alcohols by Using **4a** and Zinc Oxide




| Entry | Alcohol | | Conditions | Yield/%[a] |
|---|---|---|---|---|
| 1 |  | **47a** | 0°C, 30 min | 91 (24) |
| 2 | | | Swern Oxidation | 23[b],73[c] |
| 3 | | | PDC | 31 |
| 4 | **47a** | | TPAP/NMO | trace |
| 5 | | | Dess–Martin Oxidation | 96 |
| 6 |  | **48a** | 0 °C, 30 min | 94 (0) |
| 7 | **48a** | | Swern Oxidation | 38[b] |
| 8 |  | **49a** | 0 °C, 30 min | 91 |
| 9 |  | **50a** | rt, 30 min | 66 (62) |
| 10 |  | **51a** | 0 °C, 30 min | 84[d] |

| Entry | Alcohol | | Conditions | Yield/%[a] |
|---|---|---|---|---|
| 11 |  | **52a** | −78 °C, 2 h | 52[e] |
| 12 |  | **53a** | 0 °C, 30 min | 84 |
| 13 |  | **54a** | 0 °C, 1 h | 78 |
| 14 |  | **55a** | rt, 30 min | 60 |
| 15 |  | **56a** | 0 °C, 30 min | 78 |
| 16 |  | **57a** | 0 °C, 4 h | 78[e] |
| 17 |  | **9a** | −78 °C, 30 min | 90 (98) |
| 18 |  | **28a** | 0 °C, 30 min | 92 (94) |
| 19 |  | **36a** | 0 °C, 30 min | 77 (91) |

a) Determined by GC-analysis using an internal standard unless otherwise noted. Numbers in parentheses were yields of carbonyl products obtained by the original method of using DBU (2 mol amt) as a base instead of using zinc oxide. b) Ref. 9b. c) By Walba's procedure. See Ref. 24. d) Isolated yield of its 2,4-dinitrophenylhydrazone. e) Isolated yield.




Scheme 6.

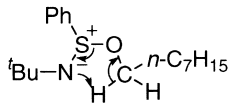



Fig. 1.

formed from *N*-monoalkylated sulfonium salt **59** by treating with bases. On the other hand, *N*,*N*-diethylsulfonium salt **61** could not form a similar oxidation intermediate. Further, it was suggested that the oxidation proceeded by five-membered intramolecular proton-transfer of alkyl sulfinimidate because *N*,*N*-diethylsulfonium salt **61** could not be oxidized when it was treated with DBU; that is, intermolecular deprotonation of the octyloxy $\alpha$-proton had never occurred (Scheme 6, reaction 3, path a). In the case of the oxidation of *N*-monoalkylated sulfonium salt **59**, DBU worked only to neutralize **59**, and the nitrogen of the formed alkyl sulfinimidate **5** directly participated in the oxidation step via the intramolecular five membered cyclic transition state as shown in Fig. 1.

## Conclusion.

A new oxidizing agent, *N*-*t*-butylbenzenesulfinimidoyl chloride (**4a**), efficiently oxidizes a variety of primary and secondary alcohols to the corresponding aldehydes and ketones in the presence of DBU or zinc oxide by simple oxidation procedures. Mechanistic investigations suggested that the oxidation proceeded via an intermediate, alkyl sulfinimidate **5** which afforded the corresponding carbonyl compound by the intramolecular proton transfer via the five-membered cyclic transition state.

The oxidation using **4a** and DBU proceeded under basic conditions without affecting double bonds, triple bonds, and an acid labile protecting group such as trimethylsilyl group. By changing the base from DBU to zinc oxide, the oxidation proceeded under nearly neutral conditions. Therefore, it was useful for the oxidation giving labile aldehydes and ketones which readily decompose under basic conditions. Each oxidization procedure with **4a** and DBU or with **4a** and zinc oxide has its own advantages; therefore, an appropriate choice of suitable oxidation conditions would provide very useful methodologies in organic synthesis.

## Experimental

**General.** All melting points were determined on a Yanagimoto micro melting point apparatus (Yanaco MP-S3) and are uncorrected. Infrared (IR) spectra were recorded on a Horiba FT300 FT-IR spectrometer. $^1$H NMR spectra were recorded on a JEOL EX270 (270 MHz) or a JEOL JNM-LA300 (300 MHz) spectrometer; chemical shifts ($\delta$) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. $^{13}$C NMR spectra were recorded on a JEOL EX270 (68 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$; $\delta$ 77.0 ppm). High resolution mass spectra (HRMS) were recorded on a HiTACHI M-80B or a JEOL JMS-AX505HA mass spectrometer. Analytical gas-liquid chromatography (GLC) was performed on a Shimadzu GC–9A instrument equipped with a flame ionizing detector and a capillary column of OV–101 (0.25 mm $\times$ 50 m) or CBP10 (0.25 mm $\times$ 25 m) using helium as carrier gas. Analytical TLC was performed on Merk precoated TLC plates (silica gel 60 GF254, 0.25 mm). Silica-gel column chromatography was carried out on Merk silica gel 60 (0.063–0.200 mm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. Powdered molecular sieves 4A (purchased from nakarai tesque) was dried in vacuo at 250 °C for 8 h before use. Unless otherwise noted, commercially available reagents were used without purification. Dry solvents were prepared by distillation under appropriate drying agents. Organic bases such as DBU, diisopropylamine, DABCO, triethylamine, and pyridine were purified by distillation. 4-Methylphenyl thioacetate (**7b**),[27] 4-methoxyphenyl thioacetate (**7c**),[28] 8-benzyloxy-1-octanol (**30a**),[29] 10-benzyloxy-1-decanol (**31a**),[30] 4-hydroxybutyl benzoate (**33a**),[31] and 6-hydroxyhexyl benzoate (**56a**)[32] were prepared according to the literature procedures. The oxidation products were identified by comparing those authentic samples with their GC retention times, spectroscopic data such as $^1$H NMR, $^{13}$C NMR, and on analytical TLC. Their derivatization to 2,4-dinitrophenylhydrazones was conducted according to Swern's procedure.[33]

All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring.

***N*,*N*-Dichloro-*t*-butylamine (8).**[14] To a stirred suspension of *t*-butylamine (10.0 g, 0.14 mol) and calcium hypochlorite (60%, 68.4 g, 0.29 mol) in dichloromethane (360 mL), 3 M hydrochloric acid (1 M = 1 mol dm$^{-3}$) (360 mL) was added dropwise during 1 h at 0 °C. Both liquid phases became yellow and the reaction mixture was stirred for 2 h at the same temperature. The layers were separated, and an aqueous layer was extracted with dichloromethane (100 mL $\times$ 2). The combined organic phases were washed with $H_2O$ and brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated on a rotary evaporator ($>$ 20 kPa) to afford a pale yellow oil (16.9 g, 0.12 mol, 87%). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.39 (9H, s). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 25.80, 72.52.

***N*-*t*-Butylbenzenesulfinimidoyl Chloride (4a).**[13a] A yellow solution of *S*-phenyl thioacetate (**7a**) (12.2 g, 80.0 mmol) and *N*,*N*-dichloro-*t*-butylamine (**8**) (11.9 g, 84.0 mmol) in benzene (80 mL) was refluxed for 1 h. Volatiles were removed under reduced pressure and by azeotropic distillation with benzene to give **4a** as a red-orange oil (17.2 g, 79.6 mmol, quantitative yield determined by $^1$H NMR). This product partially solidified to yellow solid by keeping it still or by cooling it at 0 °C. The crude product was used for the present oxidation without further purification. If necessary, it could be purified by careful distillation (112–116 °C/67 Pa). The sulfinimidoyl chloride **4a** decomposed at ca. above 160 °C. $^1$H NMR (270 MHz, dry $CDCl_3$) $\delta$ 1.58 (9H, s), 7.5–7.7 (3H, m), 8.1–8.2 (2H, m). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 29.53, 64.15, 125.91, 129.19, 133.17, 142.63.

***N*-*t*-Butyl-4-methylbenzenesulfinimidoyl Chloride (4b).**[13a] $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.57 (9H, s), 2.44 (3H, s), 7.38 (2H, d, $J$ = 8.1 Hz), 8.01 (2H, dd, $J$ = 1.5, 8.1 Hz). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 21.61, 29.57, 64.36, 126.04, 129.93, 139.86, 144.48.

***N*-*t*-Butyl-4-methoxybenzenesulfinimidoyl Chloride (4c).** $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.57 (9H, s), 3.86 (3H, s), 7.05 (2H, d, $J$ = 9.2 Hz), 8.08 (2H, d, $J$ = 8.9 Hz). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 29.35, 55.58, 64.46, 114.53, 128.18, 133.86, 163.68.

**Typical Experimental Procedure for Oxidation of Alcohols. A. Determination of Yields of Carbonyl Products by GC-Analysis (Table 1, entry 3).** A solution of **4a** (266 mg, 1.23

mmol) in $CH_2Cl_2$ (1.5 mL) was added to a solution of benzyl alcohol (103 mg, 0.82 mmol) and DBU (251 mg, 1.65 mmol) in $CH_2Cl_2$ (1.5 mL) at −78 °C. The reaction mixture was stirred for 30 min at the same temperature and the reaction was quenched by adding 1% hydrochloric acid (5 mL). The mixture was extracted with $CH_2Cl_2$ (20 mL × 3) and the yield of benzaldehyde was determined by GC-analysis using naphthalene as an internal standard (0.80 mmol, 98%).

**B. Isolation of Carbonyl Products by an Acidic Work-Up Procedure (Table 2, entry 5).** To a solution of **15a** (117 mg, 0.48 mmol) and DBU (146 mg, 0.96 mmol) in $CH_2Cl_2$ (1.5 mL) was added a solution of **4a** (155 mg, 0.72 mmol) in $CH_2Cl_2$ (1.5 mL) at −78 °C. After the reaction mixture was stirred at −78 °C for 30 min, 1% hydrochloric acid (5 mL) was added and the mixture was extracted with $CH_2Cl_2$ (20 mL × 3). The combined organic extracts were washed with $H_2O$ and brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo to afford a crude product (216 mg), which was purified by column chromatography on silica gel (hexanes–ethyl acetate, 12/1–5/1) to give **15b** (115 mg, 99%) as a colorless solid: mp 138–140 °C (lit.[34] 144.5 °C).

**C. Isolation of Carbonyl Products by a Basic Work-Up Procedure (Table 2, entry 5).** The oxidation of **15a** to **15b** using **4a** was quenched by adding saturated aqueous $NaHCO_3$ solution (5 mL) and the mixture was extracted with $CH_2Cl_2$ (20 mL × 3). The combined organic extracts were washed with $H_2O$ and brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo to afford a crude product, which was purified by column chromatography on silica gel (hexanes–ethyl acetate, 12/1–5/1) to obtain **15b** (99%) as a colorless solid: mp 139–140 °C (lit.[34] 144.5 °C).

**1,2-Diphenyl-2-trimethylsiloxyethanol (18a).** To a solution of (±)-1,2-diphenyl-1,2-ethanediol (510 mg, 2.38 mmol) and triethylamine (242 mg, 2.39 mmol) in dichloromethane (15 mL), a solution of chlorotrimethylsilane (256 mg, 2.36 mmol) was added at 0 °C. After the reaction mixture was stirred at room temperature for 24 h, the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with dichloromethane (10 mL × 3), and combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, hexanes–ether) to afford **18a** as a colorless solid (540 mg, 79%): mp 38 °C. IR (KBr, $cm^{-1}$) 3371, 2900, 1088. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ −0.02 (9H, s), 3.32 (1H, brs), 4.56 (1H, d, $J$ = 7.0 Hz), 4.62 (1H, d, $J$ = 7.0 Hz), 7.0–7.1 (4H, m), 7.1–7.2 (6H, m); $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ −0.04, 79.14, 80.56, 127.02, 127.53, 127.61, 127.81, 127.87, 139.89, 140.63. MS (EI) $m/z$ 179 (M − PhC=OH$^+$), 107 (PhC=OH$^+$). HRMS Found: $m/z$ 271.1140. Calcd for $C_{17}H_{22}O_2Si$ − $CH_3$: 271.1154.

**1,2-Diphenyl-2-(trimethylsilyloxy)ethanone (18b).** Isolated as a colorless solid: mp 75–77 °C (lit.[35] 79–80 °C). $R_f$ 0.67 (hexane–ethyl acetate = 5/1). IR (KBr, $cm^{-1}$) 1681(C=O). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.00 (9H, s), 5.70 (1H, s), 7.14–7.37 (8H, m), 7.86–7.88 (2H, m); $^{13}$C NMR (76 MHz, $CDCl_3$) $\delta$ 0.00, 79.38, 126.38, 127.94, 128.22, 128.66, 129.64, 132.92, 134.64, 138.80, 198.54.

**Dimesityl Ketone (20b).** Isolated as a colorless solid: mp 135–137 °C (lit.[36] mp 136–137 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.12 (12H, s), 2.27 (6H, s), 6.83 (4H, s).

**Trifluoromethyl 9-Anthryl Ketone (21b).** A colorless solid: mp 82–85 °C (lit.[37] mp 81–84 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.4–7.6 (4H, m), 7.72 (2H, d, $J$ = 8.4 Hz), 7.97–8.00 (2H, m), 8.52 (1H, s).

**(2,4-Dinitrophenyl)hydrazone Derivative of 2-Pentynal (24b).** Isolated as a yellow solid: mp 91.5–92.5 °C (lit.[38] mp 91 °C). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.36 (3H, t, $J$ = 7.4 Hz), 2.63 (2H, qd, $J$ = 7.4, 1.7 Hz), 6.81 (1H, t, $J$ = 1.7 Hz), 7.94 (1H, d, $J$ = 9.4 Hz), 8.34 (1H, ddd, $J$ = 9.4, 2.5, 0.7 Hz), 9.13 (1H, d, $J$ = 2.5 Hz), 12.0 (1H, brs). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 13.1, 13.4, 70.8, 109.6, 116.9, 123.2, 126.8, 129.7, 129.9, 138.6, 144.1.

**2,4-Dinitrophenylhydrazone Derivative of 3-Phenylpropanal (28b).** Isolated as a yellow solid: mp 148–149 °C (lit.[39] 149 °C). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 2.7–2.8 (2H, m), 2.98 (2H, t, $J$ = 7.3 Hz), 7.00 (0.14H, t, $J$ = 5.1 Hz), 7.2–7.4 (5H, m), 7.56 (0.86H, t, $J$ = 5.1 Hz), 7.90, 7.92 (1H, d, $J$ = 9.5 Hz), 8.2–8.3 (1H, m), 9.12 (1H, dd, $J$ = 0.9, 2.6 Hz), 11.01 (0.86H, brs), 11.14 (0.14H, brs).

**2,4-Dinitrophenylhydrazone Derivative of 1-Octanal (29b).** A yellow solid: mp 105–106 °C (lit.[40] 106 °C). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.90 (3H, t, $J$ = 6.8 Hz), 1.3–1.6 (8H, m), 1.6–1.7 (2H, m), 2.2–2.4 (2H, m), 6.96 (0.2H, t, $J$ = 5.4 Hz), 7.54 (0.8H, t, $J$ = 5.4 Hz), 7.93 (0.8H, d, $J$ = 9.5 Hz), 7.96 (0.2H, d, $J$ = 9.5 Hz), 8.30 (0.8H, dd, $J$ = 2.4, 9.5 Hz), 8.33 (0.2H, dd, $J$ = 2.4, 9.5 Hz), 9.12 (0.8H, d, $J$ = 2.4 Hz), 9.14 (0.2H, d, $J$ = 2.4 Hz), 11.01 (0.8H, brs), 11.19 (0.2H, brs).

**8-Benzyloxy-1-octanal (30b).**[41] $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.3–1.4 (5H, m), 1.5–1.7 (5H, m), 2.39 (2H, td, $J$ = 7.4, 1.7 Hz), 3.45 (2H, t, $J$ = 6.4 Hz), 4.48 (2H, s), 7.2–7.3 (5H, m), 9.71 (1H, t, $J$ = 1.7 Hz).

**10-Benzyloxy-1-decanal (31b).**[42] $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.2–1.5 (10H, m), 1.5–1.7 (4H, m), 2.39 (2H, t, $J$ = 6.5 Hz), 3.45 (2H, t, $J$ = 6.6 Hz), 4.49 (2H, s), 7.2–7.3 (5H, m), 9.73 (1H, s).

**3-Formylpropyl Benzoate (33b).**[31] $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 2.11 (2H, tt, $J$ = 6.2, 7.0 Hz), 2.64 (2H, td, $J$ = 7.0, 1.1 Hz), 4.36 (2H, t, $J$ = 6.2 Hz), 7.39–7.59 (3H, m), 7.99–8.05 (2H, m), 9.83 (1H, t, $J$ = 1.1 Hz); $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 21.3, 40.4, 63.8, 128.3, 129.4, 129.9, 132.9, 166.3, 201.1.

**Oxidation of Cyclohexyloxytrimethylsilane.** To a stirred solution of cyclohexyloxytrimethylsilane (81.2 mg, 0.47 mmol) and DBU (143 mg, 0.94 mmol) in dichloromethane (1.5 mL), a solution of **4a** (152 mg, 0.71 mmol) in dichloromethane (1.0 mL) was added at −78 °C. After the mixture was stirred at −78 °C for 1 h, a cooling bath was removed and the reaction temperature was gradually raised to room temperature during 30 min. The reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was extracted with dichloromethane. Yields of cyclohexanone (36b) (0%) and recovered cyclohexyloxytrimethylsilane (> 99%) were determined by GC-analysis using naphthalene as an internal standard.

**Detection of 6a after the Oxidation Reaction of 9a by Using 4a and DBU (Scheme 4).** To a stirred solution of **9a** (52.6 mg, 0.49 mmol) and DBU (148 mg, 0.97 mmol) in $CH_2Cl_2$ (2 mL), a solution of **4a** (157 mg, 0.73 mmol) in $CH_2Cl_2$ (1 mL) was added at −78 °C. After the reaction mixture was stirred at −78 °C for 30 min, the reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL), and the mixture was extracted with $CH_2Cl_2$ (10 mL × 3). The yield of **9b** (93%) was determined by GC-analysis after adding naphthalene (62.8 mg) as an internal standard. After the GC-analysis, the organic extracts were dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo to give a crude product. Triphenylmethane (100 mg, 0.41 mmol) was added to the crude product, and the yield of **6a** (95%) was determined by $^1$H NMR. The authentic sample of **6a** was prepared according to the procedure described below.

***N*-*t*-Butylbenzenesulfenamide (6a).**[17] To a stirred solution of *t*-butylamine (13.6 g, 185 mmol) in dry ether (150 mL), a solution of benzenesulfenyl chloride[43] (12.2 g, 84.2 mmol) in dry ether (30 mL) was added dropwise during 30 min at 0 °C. After the reaction mixture was stirred for 2 h at room temperature, the resulting white suspension was filtered and the filtrate was concentrated. The crude product was distilled (94–95 °C/933 Pa) to give **6a** as a colorless oil (9.53 g, 62%). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.18 (9H, s), 2.79 (1H, brs), 7.0–7.1 (1H, m), 7.2–7.3 (2H, m), 7.3–7.4 (2H, m). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 29.14, 54.71, 122.35, 124.40, 128.34, 144.35.

***N*-*t*-Butylbenzenesulfinamide (46).** To a mixture of *S*-phenyl thioacetate (1.22 g, 8.01 mmol) and acetic anhydride (0.82 g, 8.03 mmol), sulfuryl chloride (2.20 g, 16.3 mmol) was added dropwise at 0 °C. After stirring at 0 °C for 8 h, volatiles were removed under reduced pressure to afford a crude benzenesulfinyl chloride.[44] Then, to a solution of the crude benzenesulfinyl chloride in dichloromethane (10 mL), *t*-butylamine (1.76 g, 24.1 mol) was added dropwise at 0 °C. After the reaction mixture was stirred at room temperature for 1 h, $H_2O$ (10 mL) was added and the mixture was extracted with dichloromethane (20 mL × 3). Combined organic extracts were washed with saturated aqueous $NaHCO_3$ (10 mL) and brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated to give a colorless solid (1.48 g). The crude product was purified by column chromatography (silica gel, hexanes–AcOEt) to give **12** as a colorless solid (1.20 g, 6.08 mmol, 76%). Recrystallization from hexanes gave **12** as colorless leaflets: mp 189–191 °C. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.41 (9H, s), 3.96 (1H, brs), 7.4–7.5 (3H, m), 7.6–7.8 (2H, m). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 30.96, 54.12, 125.49, 128.56, 130.42, 146.39. IR (KBr, cm$^{-1}$) 3564, 1412 1088 1041; MS(EI) *m*/*z* 197 ($M^+$). HRMS Found: *m*/*z* 198.0947. Calcd for $C_{10}H_{16}NOS$: 198.0953.

**Purification of Formed Aldehyde 30b via a Hydrogensulfite Addition Compound (Scheme 5).** To a stirred mixture of **30a** (131 mg, 0.55 mmol) and DBU (168 mg, 1.11 mmol) in $CH_2Cl_2$ (2 mL) was added a solution of **4a** (179 mg, 0.83 mmol) in $CH_2Cl_2$ (1.5 mL) at 0 °C. After the reaction mixture was stirred for 30 min at the same temperature, the oxidation reaction was quenched by adding saturated $NaHCO_3$ (5 mL). The resulting mixture was extracted with $Et_2O$, and combined organic extracts were then washed with water.

Saturated $NaHSO_3$ solution (2 mL) and THF (8 mL) were added to the above etheral solution containing **30b**, and the mixture was stirred for 17 h at room tempetature. After evaporation of organic solvents, the resulting aqueous solution was washed with $Et_2O$. Then $Na_2CO_3$ was added to the washed aqueous phase and the mixture was stirred for 4 h at room temperature. The mixture was extracted with $Et_2O$, and the extracts were washed with $H_2O$ and brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated to give **30b** as a colorless oil (95 mg, 73%). Spectrum data of thus obtained **30b** were identical with those of the authentic sample.

**Typical Experimental Procedure for the Oxidation of 47a to 47b by Using 4a and Zinc Oxide (Table 5, entry 1).** To a stirred white suspension of **47a** (70 mg, 0.57 mmol) and zinc oxide[45] (233 mg, 2.86 mmol) in dry $CH_2Cl_2$ (1.5 mL) was added a solution of **4a** (185 mg, 0.86 mmol) in $CH_2Cl_2$ (2 mL) at 0 °C. The reaction mixture was stirred for 30 min at the same temperature and then quenched with water (5 mL). The mixture was filtered through Celite and the Celite pad was washed with $CH_2Cl_2$ and water. The layers were separated and the aqueous phase was extracted with $CH_2Cl_2$. The yield of **47b** (0.52 mmol, 91%) was determined by GC-analysis of the combined organic phase using an internal standard.

**(2,4-Dinitrophenyl)hydrazone Derivative of 2-(4-Methoxyphenyl)acetaldehyde (51b).** Isolated as orange needles: mp 135–136 °C. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 3.69 (2H, d, $J$ = 5.7 Hz), 3.81 (3H, s), 6.88–6.93 (2H, m), 7.56 (1H, t, $J$ = 5.9 Hz), 7.97 (1H, d, $J$ = 9.7 Hz), 8.32 (1H, dd, $J$ = 9.5, 2.2 Hz), 9.12 (1H, d, $J$ = 2.4 Hz), 11.04 (1H, brs); $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 38.15, 55.31, 114.37, 114.60, 116.53, 123.45, 127.22, 129.69, 129.98, 145.10, 149.08, 150.64, 158.83. IR (KBr, cm$^{-1}$) 1612, 1512, 1335. MS (EI) *m*/*z* 330 ($M^+$). HRMS (ESI) Found: *m*/*z* 330.0970. Calcd for $C_{15}H_{14}N_4O_5$: 330.0964.

**2-(2-Naphthyl)ethanal (52b).**[46] Isolated as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.10 (2H, d, $J$ = 2.4 Hz), 7.39–7.57 (4H, m), 7.82–7.91 (3H, m), 9.77 (1H, t, $J$ = 2.4 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 48.33, 123.51, 125.62, 126.05, 126.69, 128.37, 128.39, 128.46, 128.88, 128.89, 133.91, 199.61.

**5-Formylpentyl Benzoate (57b).**[32] Isolated as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.49–1.54 (2H, m), 1.66–1.84 (4H, m), 2.47 (2H, dt, $J$ = 1.8, 7.5 Hz), 4.32 (2H, t, $J$ = 6.6 Hz), 7.41–7.46 (2H, m), 7.52–7.58 (1H, m), 8.02–8.05 (2H, m), 9.77 (1H, t, $J$ = 1.8 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 21.53, 25.49, 28.38, 43.56, 64.51, 128.21, 129.37, 130.18, 132.76, 166.46, 202.28.

***N*-*t*-Butylmethanesulfinamide (58).** To a stirred solution of *t*-butylamine (6.12 g, 83.7 mmol) in $CH_2Cl_2$ (40 mL) was added dropwise a solution of methanesulfinyl chloride[47] (3.3 g, 33.5 mmol) in $CH_2Cl_2$ (5 mL) at 0 °C. After the white suspension was stirred for 30 min at room temperature, $H_2O$ and NaCl were added and the mixture was extracted with $CH_2Cl_2$. The combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The obtained crude oil was distilled (85–90 °C/2 KPa) to afford **58** (2.87 g, 63%) as a colorless solid. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.31 (9H, s), 2.59 (3H, s), 3.72 (1H, brs); $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 30.85, 43.95, 53.86. IR (neat, cm$^{-1}$) 3487, 1049. MS (EI) *m*/*z* 135 ($M^+$). HRMS Found: *m*/*z* 135.0723. Calcd for $C_5H_{13}NOS$: 135.0718.

***N*-*t*-Butylamino(methyl)(octyloxy)sulfonium Triflate (59).** To a stirred solution of **58** (2.99 g, 11.4 mmol) in $CH_2Cl_2$ (10 mL) was added a solution of octyl triflate[48] (1.54 g, 11.4 mmol) in $CH_2Cl_2$ (15 mL) at room temperature. A slight exothermic reaction was observed. After the reaction mixture was stirred for 42 h at room temperature, the solvent was removed and the residue was washed with petroleum ether (5 mL × 5) and dried in vacuo to afford **59** as a colorless oil (4.31 g). Purity of the obtained **59** (99.8 wt% purity) was checked by $^1$H NMR analysis using triphenylmethane as an internal standard and its yield was estimated to be 95%. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.88 (3H, t, $J$ = 7.1 Hz), 1.27–1.48 (10H, m), 1.42 (9H, s), 1.66–1.76 (2H, m), 3.39 (3H, s), 4.09 (1H, td. $J$ = 6.4, 9.2 Hz), 4.27 (1H, td, $J$ = 6.4, 9.2 Hz), 8.34 (1H, bs). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 13.78, 22.33, 25.12, 28.76, 28.90, 29.59, 31.42, 34.06, 34.11, 57.40, 69.08, 120.20 ($J$ = 319 Hz). MS ($FAB^+$) *m*/*z* 248 ([*n*-BuOSMeNH′Bu]$^+$). MS ($FAB^-$) *m*/*z* 149 ($OTf^-$). IR (neat, cm$^{-1}$) 1242, 1296. HRMS (ESI positive) Found: *m*/*z* 248.2050. Calcd for $C_{13}H_{30}NOS$: 248.2048.

**Oxidation Reaction via 59 (Scheme 6, reaction 2).** To a stirred suspension of **59** (99.8% purity, 205 mg, 0.51 mmol) in toluene (1.5 mL) was added a solution of DBU (86 mg, 0.57 mmol) in toluene (2 mL) at room temperature, then the reaction mixture was stirred for 1 h at the same temperature. The reaction was next quenched with 1% hydrochloric acid and the resulting mixture

was extracted with $CH_2Cl_2$. The yield of octanal (**29b**, 0.45 mmol, 88%) was determined by GC-analysis using an internal standard.

***N*,*N*-Diethylbenzenesulfinamide (60).**[49] It was prepared according to the procedure for the preparation of **46**, and isolated as a colorless oil (82% yield). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.41 (6H, t, $J$ = 7.3 Hz), 3.14 (4H, q, $J$ = 7.3 Hz), 7.4–7.5 (3H, m), 7.6–7.7 (2H, m). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 14.30, 41.94, 126.18, 128.61, 130.45, 144.19.

***N*,*N*-Diethylamino(octyloxy)(phenyl)sulfonium Triflate (61).** To the stirred solution of **60** (334 mg, 2.47 mmol) in $CH_2Cl_2$ (2 mL) was added a solution of octyl triflate (712 mg, 2.72 mg) at room temperature. After the mixture was stirred at the same temperature for 43 h, the solvent was evaporated and the residue was washed with petroleum ether (5 mL × 5) and dried in vacuo to afford *N*,*N*-diethylamino(octyloxy)(phenyl)sulfonium triflate (**61**) as a colorless oil (91% yield, 94% purity which was determined by $^1$H NMR using an internal standard). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.88 (3H, t, $J$ = 6.5 Hz), 1.27–1.44 (16H, m), 1.86–1.96 (2H, m), 3.54 (4H, m), 4.52 (1H, td, $J$ = 6.5, 9.7 Hz), 4.62 (1H, td, $J$ = 6.5, 9.7 Hz). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 11.0, 13.9, 22.5, 25.3, 28.9, 29.7, 31.6, 43.2, 45.5, 76.2, 120.7 (q, $J$ = 318 Hz), 127.9, 129.5, 130.8, 134.8. IR (neat, cm$^{-1}$) 1242, 1273. HRMS (ESI positive) Found: *m*/*z* 310.2207. Calcd for $C_{18}H_{32}NOS$: 310.2205.

**8-Octyl-1,8-diazabicyclo[5.4.0]undec-7-ene Trifluoromethanesulfonate (62).** To the stirred solution of **61** (216 mg, 0.44 mmol) in toluene (1.5 mL) was added a solution of DBU (84 mg, 0.55 mmol) in toluene (2.0 mL) at room temperature. After the reaction mixture was stirred at the same temperature for 1 h, 1% hydrochloric acid was added to the reaction mixture, and the resulting mixture was extracted with $CH_2Cl_2$. Octanal (**29b**) was not detected in the combined $CH_2Cl_2$ extracts by GC-analysis. The combined $CH_2Cl_2$ solution was dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The residue was purified by thin layer chromatography (silica gel, elution with $CHCl_3$–MeOH, 5:1) to give recovered **61** (74 mg, 0.16 mmol, 37%), **60** (36 mg, 0.18 mmol, 41%), and 8-octyl-1,8-diazabicyclo[5.4.0]-7-undec-7-ene trifluoromethanesulfonate (**62**) (62 mg, 0.15 mmol, 34%) as colorless oils. **62**: $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.88 (3H, t, $J$ = 6.4 Hz), 1.29–1.30 (10H, m), 1.62–1.79 (8H, m), 2.09–2.17 (2H, m), 2.84 (2H, d, $J$ = 9.2 Hz), 3.45–3.69 (8H, m). $^{13}$C NMR (68 MHz, $CDCl_3$) $\delta$ 14.0, 20.0, 22.5, 23.0, 25.9, 26.4, 28.3, 28.5, 28.6, 29.0, 29.0, 31.6, 47.0, 49.0, 54.1, 55.2, 120.8 (q, $J$ = 318 Hz), 166.5. HRMS (ESI positive) Found: *m*/*z* 265.2637. Calcd for $C_{17}H_{33}N_2$: 265.2644.

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