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Polymer-Supported Sulfinimidoyl Chlorides: A Convenient Reagent for Oxidation of Alcohols

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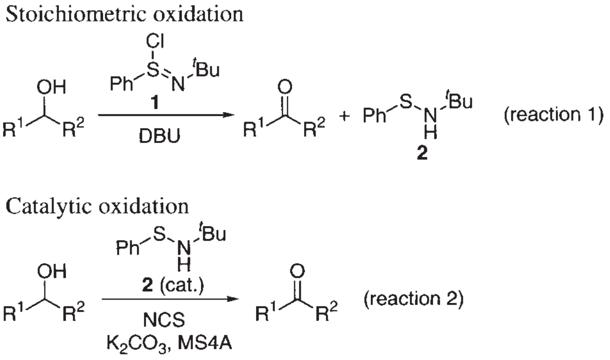
Two polymer-supported sulfinimidoyl chlorides, i.e., 4-(*N*-*tert*-butylchlorosulfinimidoyl)phenoxymethylpolystyrene (**3**) and 4-(*N*-*tert*-butylchlorosulfinimidoyl)polystyrene (**10**), were prepared from chloromethylpolystyrene and polystyrene, respectively. Stoichiometric or catalytic oxidation of various primary and secondary alcohols using these polymer-supported sulfinimidoyl chlorides proceeded smoothly, and the corresponding aldehydes and ketones were conveniently prepared in good-to-high yields by simple work-up procedures. The polymer-supported oxidant **10** was recycled repeatedly by chlorination of a used polymer **11** with *N*-chlorosuccinimide (NCS) after stoichiometric oxidation.

Two new methods were reported from our laboratory for efficient and mild oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones by utilizing sulfinimidoyl chloride as an oxidizing agent. The first one was stoichiometric oxidation using *N*-*tert*-butylbenzenesulfinimidoyl chloride (**1**) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). This oxidation smoothly oxidized various alcohols to give carbonyl compounds in good-to-high yields along with *N*-*tert*-butylbenzenesulfenamide (**2**) which was separated from carbonyl compounds by silica gel chromatography or distillation (Scheme 1, reaction 1).[1] The second method was the sulfenamide **2**-catalyzed oxidation of alcohols with a stoichiometric amount of *N*-chlorosuccinimide (NCS) in the coexistence of potassium carbonate and molecular sieves 4A (MS4A) (reaction 2).[2] This catalytic oxidation proceeded quite efficiently under mild conditions, and purification of the formed carbonyl compounds was much easier compared to the **1**-mediated stoichiometric oxidation.

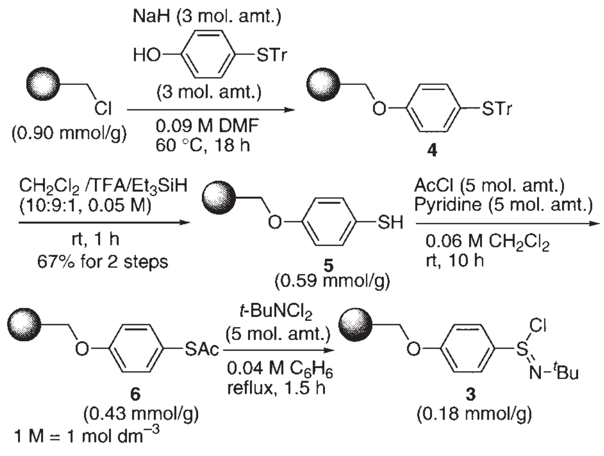
A polymer-supported sulfinimidoyl chloride was then considered to be useful for convenient and clean oxidation of alcohols because sulfenamide formed from sulfinimidoyl chloride after oxidation was easily and completely separated just by filtration of the polymer reagent.[3,4] In this article, we would like to report more detailed results on preparation of polymer-supported sulfinimidoyl chlorides and oxidation of alcohols using them.[5]



Scheme 1.

Results and Discussion

Preparation of Polymer-Supported Sulfinimidoyl Chloride 3. Preparation of polymer-supported sulfinimidoyl chloride **3** which has a phenoxymethylene unit as a linker between sulfinimidoyl chloride moiety and polystyrene core was first planned considering its availability from chloromethylpolystyrene. The preparation of **3** is illustrated in Scheme 2: that is, 4-(tritylsulfanyl)phenoxymethylpolystyrene (**4**) was prepared in the first place by treating chloromethylpolystyrene with sodium 4-(tritylsulfanyl)phenolate in DMF. The trityl group of **4** was then deprotected with trifluoroacetic acid in the presence of triethylsilane[6] to afford 4-sulfanylphenoxymethylpolystyrene (**5**)[7] in 67% yield in two steps. The loading (0.59 mmol/g) of a benzenethiol unit in **5** was determined by



Scheme 2.

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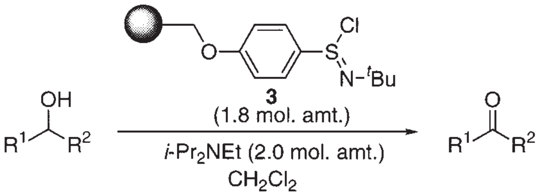
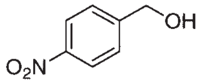
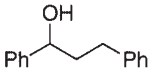
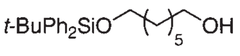
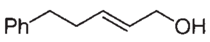
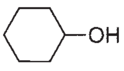
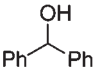
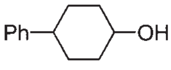
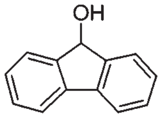
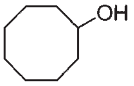
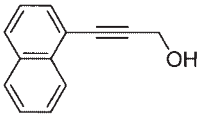
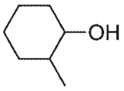
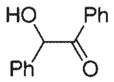
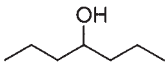
Table 1. Stoichiometric Oxidation of Various Alcohols to the Corresponding Carbonyl Compounds by Using Polymer-Supported Sulfinimidoyl Chloride **3**



Entry	Alcohol	Method[a)]	Yield/%[b)]	Entry	Alcohol	Method[a)]	Yield/%[b)]
1		A	98	8		B	89
2		A	58	9		B	85
3		A	84[c)]	10		A	50[d)]
				11		B	92[d)]
4		A	72	12		B	81
5		A	89	13		B	81[d)]
6		A	80	14		B	76[d)]
7		A	90	15		B	97[d)]

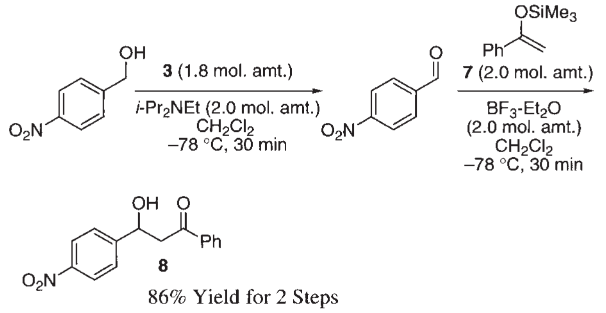
a) Method A: a mixture of alcohol and i-Pr_2NEt was added to the swelled polymer **3** in CH_2Cl_2 at −78 °C, and then the reaction mixture was stirred at −78 °C for 30 min. Method B: alcohol was added to the swelled polymer **3** in CH_2Cl_2 at 0 °C, followed by the addition of i-Pr_2NEt at −78 °C. The reaction mixture was stirred at −78 °C–rt for 30 min. b) Isolated yield unless otherwise noted. c) The stereoisomeric ratio ($E/Z = 96/4$) did not change by the present oxidation. d) Determined by GC-analysis using an internal standard.

isolating triphenylmethane which was formed in the above-mentioned deprotection of the trityl group. The thiol group was acetylated with acetyl chloride and pyridine to give 4-(acetylsulfanyl)phenoxymethylpolystyrene (**6**) which contained 0.43 mmol/g of an acetylsulfanyl group. The loading of the acetylsulfanyl group was determined by isolating *N*-benzylacetamide after heating **6** and benzylamine at 90 °C for 6 h. Finally, the desired polymer-supported sulfinimidoyl chloride resin **3** was prepared by the reaction of **6** and *N*,*N*-dichloro-*tert*-butylamine in refluxing benzene. The content of sulfinimidoyl group (0.18 mmol/g) of **3** was determined by detecting 4-methoxybenzyl chloride by GC-analysis after treating **3** with 4-methoxybenzyl alcohol in CH_2Cl_2 at room temperature for 2 h.[8]

Thus-prepared polymer-supported sulfinimidoyl chloride **3** showed no decline in activity when kept at room temperature under an argon atmosphere for eight days while hydrolysis took place rapidly when exposed to air. The hydrolysis of **3** was judged easily from the change in its color: from bright yellow to white when hydrolyzed.[9]

Stoichiometric Oxidation of Alcohols Using Poylmer-Supported Sulfinimidoyl Chloride 3. First, when effects of bases were examined in the oxidation of benzyl alcohol by using 1.8 molar amounts of the polymer oxidant **3**, i-Pr_2NEt was effective while DBU and K_2CO_3 were not. The use of DBU or K_2CO_3 gave a substantial amount of benzyl chloride together with the desired oxidation product, benzaldehyde.

In the oxidation of benzylic and allylic alcohols, a mixture of an alcohol and i-Pr_2NEt was added to the polymer **3** at −78 °C, and an alcohol was smoothly oxidized in less than 30 min at −78 °C (Table 1, Method A, Entries 1–7). However, this method gave the corresponding carbonyl compounds in low yields in the oxidation of simple primary and secondary alcohols: for example, the oxidation of cyclohexanol gave cyclohexanone in 50% yield (Entry 10). This result may be explained by the slow formation of alkyl sulfinimidate, an important oxidation intermediate,[1c] from **3** and cyclohexanol. Then, primary and secondary alcohols were mixed first with **3** at 0 °C, and then i-Pr_2NEt was added successively at −78 °C. The corresponding carbonyl compounds were obtained in good yields when the reaction temperature was raised up to room temperature (Method B, Entries 8–9, 11–15).

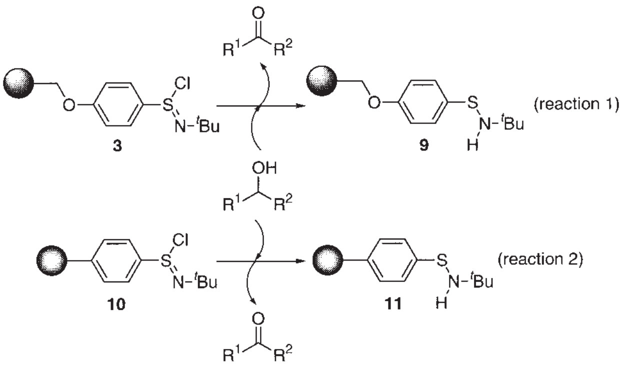


Scheme 3.

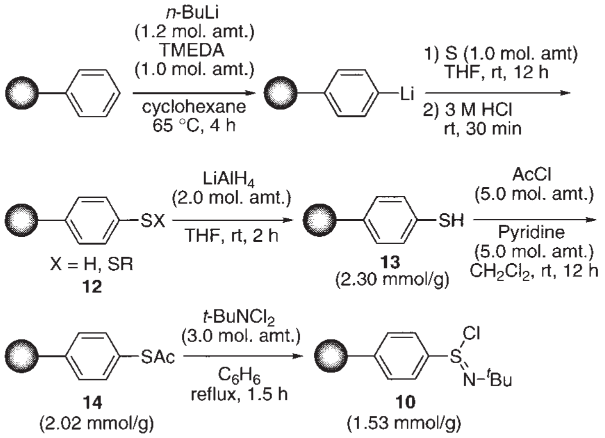
Double bond isomerization was not observed in the present oxidation using **3** and the protecting groups such as trityl and *tert*-butyldiphenylsilyl groups were not damaged. However, some alcohols such as 1,3-diphenylpropan-1-ol, diphenylmethanol, and 2-methylcyclohexan-1-ol were oxidized in moderate yields (Entries 2, 4, and 14).

Oxidation of primary alcohols to the corresponding aldehydes, and the successive carbon–carbon bond formation with carbon nucleophiles are often employed in the construction of a carbon skeleton. In order to exemplify the usefulness of the polymer reagent **3**, two-step reactions which consisted of the **3**-mediated oxidation of a primary alcohol and a Lewis acid-catalyzed aldol reaction of thus-formed aldehyde with silyl enol ether[10] were tried (Scheme 3). The oxidation of 4-nitrobenzyl alcohol with **3** rapidly gave 4-nitrobenzaldehyde after silica gel filtration which removed the used resin and i-Pr_2NEt. The obtained aldehyde was then treated with trimethylsilyl enol ether **7** and $BF_3 \cdot Et_2O$ at −78 °C to afford the corresponding aldol adduct **8** in 86% yield (for two steps). Thus, a convenient organic synthesis was rapidly carried out by using the polymer oxidant **3**.

Preparation of Polymer-Supported Sulfinimidoyl Chloride 10. As described above, the stoichiometric oxidation of alcohols with the polymer-supported sulfinimidoyl chloride resin **3** was performed conveniently. However, recyclization of **3** by chlorination of a used resin with NCS was not successful in spite of many trials. It was then assumed that the sulfenamide **9** which formed from **3** via the oxidation process decomposed during its isolation (Scheme 4, reaction 1). Therefore, preparation of the polymer-supported sulfinimidoyl chloride **10** whose sulfinimidoyl chloride group was directly attached on a polystyrene core was next planned on the consideration that sulfenamide **11**, a reduced product of **10**, would be more stable than **9** (Scheme 4, reaction 2).



Scheme 4.



Scheme 5.

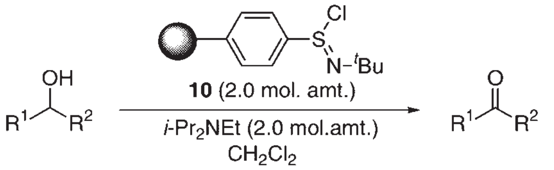
Preparation of a new polymer-supported sulfinimidoyl chloride resin **10** is shown in Scheme 5. 4-Sulfanylpolystyrene (**13**) was prepared according to Fréchet's method:[11] that is, cross-linked polystyrene was directly lithiated by using n-BuLi and *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA), and the lithiated polystyrene was then treated with sulfur. The S–S bonds in sulfurized polystyrene **12** were cleaved by reduction with two molar amounts of $LiAlH_4$ to afford 4-sulfanylpolystyrene (**13**). The desired sulfinimidoyl chloride resin **10** was prepared by acetylation of **13** to 4-acetylsulfanylpolystyrene (**14**), followed by a treatment with *N*,*N*-dichloro-*tert*-butylamine in refluxing benzene. The loadings of each functional groups on polystyrene were determined either by elemental analysis or by the chemical transformations described in the preparation of **3**.

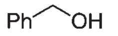
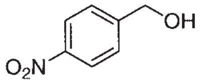
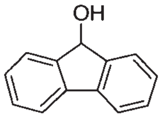
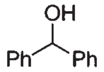
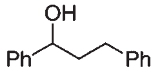
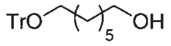
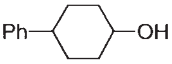
Stoichiometric Oxidation of Alcohols Using Poylmer-Supported Sulfinimidoyl Chloride 10. Similar to resin **3**, the new polymer-supported reagent **10** oxidized various primary and secondary alcohols to the corresponding carbonyl compounds in good to high yields in the coexistence of i-Pr_2NEt (Table 2). It was noted that the polymer **10** oxidized diphenylmethanol and 1,3-diphenylpropan-1-ol more effectively than **3** (Entry 4 and 5).

Moreover, oxidation of benzyl alcohol and 4-phenylcyclohexanol was repeatedly carried out for three times by recycling **10** from a used polymer **11** (Table 3). Since two molar amounts of **10** were employed in this oxidation, the reaction was quenched by adding excess amounts of ethanol and two molar amounts of i-Pr_2NEt in order to convert the remaining equimolar amount of **10** to sulfenamide **11** completely. The isolated sulfenamide **11** was chlorinated with two molar amouts of NCS to regenerate sulfinimidoyl chloride **10**.

Catalytic Oxidation of Alcohols Using Poylmer-Supported Sulfinimidoyl Chloride 3 and 10. The sulfenamide **2**-catalyzed oxidation of alcohols was developed by in situ chlorination (oxidation) of **2** with a stoichiometric amount of NCS to form a real oxidant, sulfinimidoyl chloride **1**.[2] Based on this concept, oxidation of alcohols using a catalytic amount (0.2 molar amount) of polymer-supported sulfinimidoyl chlo-

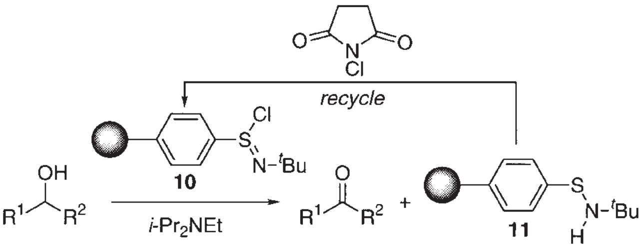
Table 2. Stoichiometric Oxidation of Alcohols by Using Polymer-Supported Sulfinimidoyl Chloride **10**

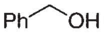


Entry	Alcohol	Method[a)]	Yield/%[b)]
1		A	98[c)]
2		A	94
3		A	97
4		A	89
5		A	84
6		B	86
7		B	86

a) Method A: a mixture of alcohol and *i*-Pr$_2$NEt was added to the swelled polymer **10** in CH$_2$Cl$_2$ at −78 °C, and then the reaction mixture was stirred at −78 °C for 30 min. Method B: alcohol was added to the swelled polymer **10** in CH$_2$Cl$_2$ at 0 °C then *i*-Pr$_2$NEt was added at −78 °C. The reaction mixture was stirred at 0 °C for 30 min. b) Isolated yield unless otherwise noted. c) Determined by GC-analysis.

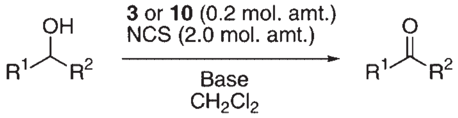
Table 3. Oxidation of Alcohols by Recycling Polymer-Supported Sulfinimidoyl Chloride **10**

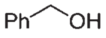
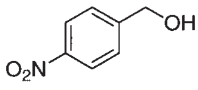
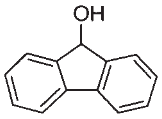
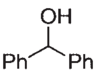
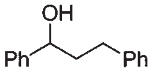
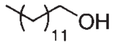
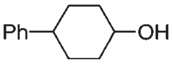


Alcohol	Yield/%[a)]			
	Recycle:	1st	2nd	3rd
		97	quant.	98
		95	98	87

a) Yield of the corresponding carbonyl compound.

Table 4. Catalytic Oxidation of Alcohols by Using Polymer-Supported Sulfinimidoyl Chlorides (**3** and **10**)



Entry	Alcohol	Conditions[a)]	Cat.	Yield/%[b)]
1[c)]		^{i}Pr$_2$NEt	**3**	94 (91)[d)]
2[c)]		−78 °C–0 °C, 1 h	**10**	94
3		^{i}Pr$_2$NEt	**3**	92
4		−78 °C–rt, 1 h	**10**	92
5		^{i}Pr$_2$NEt −78 °C–rt, 2 h	**10**	94
6		^{i}Pr$_2$NEt	**3**	92
7		−78 °C–rt, 1 h	**10**	93
8		K$_2$CO$_3$, MS4A −78 °C–rt, 14 h	**10**	83 (44)[e)]
9		K$_2$CO$_3$, MS4A 0 °C–rt, 5 h	**3**	85
10		K$_2$CO$_3$, MS4A 0 °C–rt, 2 h	**10**	82
11		K$_2$CO$_3$, MS4A	**3**	83
12		0 °C–rt, 16 h	**10**	91

a) *i*-Pr$_2$NEt (2.0 mol. amt.), K$_2$CO$_3$ (10 mol. amt.), and MS4A (1 g/mmol) were employed. b) Isolated yield unless otherwise noted. c) The yield was determined by GC-analysis. d) 0.1 mol. amt. of the catalyst **3** was used and the reaction time was 2 h. e) *i*-Pr$_2$NEt (2.0 mol. amt.) was used as a base (−78 °C–rt, 1 h).

ride **3** or **10** was tried by employing NCS as a stoichiometric oxidant (Table 4). In the **3** or **10**-catalyzed oxidation of benzylic alcohols, *i*-Pr$_2$NEt was found to be a suitable base and the carbonyl compounds were obtained in high yields (Entries 1–7). The catalytic oxidation of benzyl alcohol to benzaldehyde proceeded smoothly in 91% yield when the amount of the polymer catalyst **3** was reduced to 0.1 molar amount (Entry 1).

On the other hand, **3** or **10**-catalyzed oxidation of simple primary and secondary alcohols also proceeded smoothly to give the corresponding carbonyl compounds in good yields by using K$_2$CO$_3$ as a base (Entries 9–12). However, it was found that catalytic oxidation with polymer-supported sulfinimidoyl chlorides generally required a longer reaction time in comparison to the case with monomeric sulfenamide **2**.

Conclusion

Various primary and secondary alcohols were oxidized to the corresponding aldehydes and ketones in good-to-high yields by using a stoichiometric amount of polymer-supported sulfinimidoyl chlorides, **3** and **10**, while a catalytic amount of these polymer oxidants worked as a catalyst for the oxidation of alcohols with NCS. Concerning the effect of bases, *i*-Pr$_2$NEt was found effective in the **3** or **10**-mediated stoichiometric oxidation of various alcohols and the catalytic oxidation of benzylic alcohols with NCS. In the catalytic oxidation of normal primary and secondary alcohols, on the other hand, K_2CO_3 was effective.

The applicability of the polymer oxidant **10** in organic synthesis is wider compared to **3** for the following reasons: i) polymer **10** was prepared by the four-step procedure directly from polystyrene, ii) it oxidized a variety of alcohols more effectively than **3**, iii) it was employed repeatedly by recycling the used polymer **11** by chlorination with NCS.

The polymer-supported sulfinimidoyl chlorides, **3** and **10**, are applicable to other oxidation reactions which were carried out by using monomeric sulfinimidoyl chloride **1**. For example, **1** was used as an effective oxidant in oxidation (dehydrogenation) reactions such as oxidation of amines to imines,[12] hydroxylamines to nitrones,[13] and dehydrogenation of saturated carbonyl compounds to α,β-unsaturated carbonyl compounds.[14]

Experimental

General. 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 JEOL JMN-LA300 (300 MHz) spectrometer; chemical shifts (δ) 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 ($CDCl_3$; δ 77.0 ppm). High resolution mass spectra (HRMS) were recorded on a HITACHI M-80B or a JEOL JMS-AX505HA mass spectrometer. Elemental analyses were conducted by Elemental Analyzer 2400CHN (Perkin Elmer) and Ion Chromatograph DX-500 (Dionex) at the Lead Generation Laboratory of Taisho Pharmaceutical Co., Ltd. Analytical gas-liquid chromatography (GLC) was performed on a Shimadzu GC-9A or GC-17A instrument equipped with a flame ionizing detector and a capillary column of OV-101 (0.25 mm × 50 m) or CBP10 (0.25 mm × 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 nakalai tesque) were dried in vacuo at 250 °C for 8 h before use. Dry solvents were prepared by distillation under appropriate drying agents. Chloromethylpolystyrene resin (cross-linked with 1% DVB, 200–400 mesh, 0.8–1.0 mmol Cl/g) and polystyrene resin (cross-linked with 1% DVB, 200–400 mesh) were purchased from Tokyo Kasei Kogyo. Unless otherwise noted, commercially available reagents were used without purification. All of the reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. 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.

4-(Tritylsulfanyl)phenoxymethylpolystyrene (4). To a stirred suspension of NaH (55%, 2.65 g, 60.8 mmol) in DMF (40 mL) was added a solution of 4-(tritylsulfanyl)phenol (22.4 g, 60.8 mmol) in DMF (60 mL) at room temperature, and the mixture was stirred at 60 °C for 1 h. Chloromethylpolystyrene resin (0.9 mmol/g, 22.5 g, 20.3 mmol) and DMF (120 mL) were then added to the above-mentioned mixture at room temperature, and the reaction mixture was stirred at 60 °C for 18 h. After the reaction was quenched with H_2O, the mixture was stirred for 30 min and filtered. The resin was washed with DMF/H_2O (1:1) (100 mL × 5), CH_2Cl_2 (100 mL × 5), and Et_2O (100 mL × 3), and dried at 70 °C for 2 h to give **4** (27.3 g) as pale brown beads: IR (KBr, cm^{-1}) 1227, 687.

4-Sulfanylphenoxymethylpolystyrene (5). To a stirred suspension of **4** (27.3 g) in CH_2Cl_2 (200 mL) were added TFA (180 mL) and Et_3SiH (20 mL) at room temperature, and the mixture was stirred for 1 h. After the above mixture was filtered, the resin was washed with CH_2Cl_2 (100 mL × 5) and Et_2O (100 mL × 3), and dried at 70 °C for 2 h to give **5** (23.2 g) as pale yellow beads: IR (KBr, cm^{-1}) 2561, 1200, 687.

The filtrate was concentrated, and saturated $NaHCO_3$ solution was added to the residue. This mixture was then extracted with CH_2Cl_2 and the combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexanes) to give triphenylmethane (3.32 g, 13.6 mmol, 67% for 2 steps).

4-(Acetylsulfanyl)phenoxymethylpolystyrene (6). To a stirred suspension of **5** (23.2 g, 20.3 mmol) and pyridine (8.01 g, 101 mmol) in CH_2Cl_2 (230 mL) was added acetyl chloride (7.95 g, 101 mmol) at 0 °C, and the mixture was stirred at room temperature for 11 h. After the mixture was filtered, the resin was washed with CH_2Cl_2 (100 mL × 3) and Et_2O (100 mL × 2), and dried at 70 °C for 2 h to give **6** (23.0 g) as pale orange beads: IR (KBr, cm^{-1}) 1759, 1705, 1195, 687.

The loading of acetylsulfanyl group was determined as follows: a mixture of thus-obtained **6** (1.00 g), benzylamine (193 mg, 1.80 mmol) in 1,2-dichloroethane (10 mL) was stirred at 90 °C for 6 h. The mixture was filtered, and the filtrate was washed with 1 M (1 M = 1 mol dm^{-3}) hydrochloric acid, H_2O, saturated $NaHCO_3$, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by thin-layer chromatography to give *N*-benzylacetamide (63.6 mg, 0.43 mmol) as a colorless solid. Thus, the loading of acetylsulfanyl group of resin **6** was determined to be 0.43 mmol/g.

4-(*N-tert*-Butylchlorosulfinimidoyl)phenoxymethylpolystyrene (3). To a stirred suspension of **6** (5.0 g) in benzene (40 mL) was added a solution of *N*,*N*-dichloro-*tert*-butylamine (1.42 g, 10 mmol) at room temperature, and the mixture was refluxed for 1.5 h. After the mixture was filtered under an argon atmosphere, the obtained resin was dried in vacuo at 60 °C for 1 h to give **3** as bright-yellow beads: IR (KBr, cm^{-1}) 1203, 1108, 687.

The loading of *N-tert*-butylchlorosulfinimidoyl group was determined as follows: to a stirred suspension of resin **3** (1.0 g) in CH_2Cl_2 (10 mL) was added a solution of 4-methoxybenzyl alcohol (78.3 mg, 0.5 mmol) in CH_2Cl_2 (2.0 mL) at room temperature. The mixture was stirred at room temperature for 2 h. The formation of 4-methoxybenzyl chloride (0.18 mmol) was detected by GC-analysis using naphthalene as an internal standard. Thus, the loading of *N-tert*-butylchlorosulfinimidoyl group of the resin **3** was determined to be 0.18 mmol/g.

Typical Experimental Procedure for the Stoichiometric Oxidation of Benzylic Alcohol with 3 (Table 1, Entry 1, Method A). To a slurry of **3** (0.18 mmol/g, 1.0 g, 0.18 mmol) in CH_2Cl_2 (10 mL) was added a mixture of 4-nitrobenzyl alcohol (15.3 mg, 0.10 mmol) and *i*-Pr_2NEt (25.8 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min, and the reaction was quenched by adding H_2O

(2 mL). The mixture was filtered through a Celite pad, and filtrate was extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by preparative TLC to afford 4-nitrobenzaldehyde (14.8 mg, 98%).

Typical Experimental Procedure for the Stoichiometric Oxidation of Non-benzylic Alcohol with 3 (Table 1, Entry 11, Method B). To a stirred slurry of **3** (0.8 g, 0.15 mmol) in CH_2Cl_2 (8 mL) was added a solution of cyclohexanol (10.0 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at 0 °C. After the mixture was stirred for 5 min at 0 °C, *i*-Pr_2NEt (25.8 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) was added at -78 °C. The reaction mixture was stirred at room temperature for 30 min, and the reaction was quenched by adding 1% HCl solution (5 mL). The mixture was extracted with CH_2Cl_2 (20 mL × 3), and the yield of cyclohexanone (0.092 mg, 92%) was determined by GC-analysis of the organic extracts using naphthalene as an internal standard.

Oxidation of 4-Nitrobenzyl Alcohol with 3 and Aldol Reaction with 7 (Scheme 3). After 4-nitrobenzyl alcohol (15.3 mg, 0.10 mmol) was oxidized according to the above procedure, the reaction mixture was filtered through a silica gel pad instead of quenching the reaction with H_2O. Evaporation of the solvent gave a crude 4-nitrobenzaldehyde (13.8 mg). A solution of trimethylsilyl enol ether **7** (38.5 mg, 0.20 mmol) in CH_2Cl_2 (1.5 mL) was added to a solution of thus-obtained 4-nitrobenzaldehyde in CH_2Cl_2 (2 mL). Then, a solution of $BF_3 \cdot Et_2O$ (28.4 mg, 0.20 mmol) in CH_2Cl_2 (1.5 mL) was added to the above-mentioned mixture at -78 °C. After the mixture was stirred for 30 min at the same temperature, the reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was extracted with CH_2Cl_2. After the combined organic extracts were evaporated, THF (10 mL) and 1 M hydrochloric acid (10 mL) were added to the residue, and the mixture was stirred at room temperature for 3 h. After THF was evaporated, the mixture was extracted with Et_2O, and combined organic extracts were washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by preparative TLC (silica gel, hexane/ethyl acetate = 2/1) to give aldol adduct 3-hydroxy-3-(4-nitrophenyl)-1-phenylpropan-1-one (**8**) (23.2 mg, 86%) as a colorless oil: ^1H NMR (270 MHz, $CDCl_3$) δ 3.29–3.46 (2H, m), 3.89 (1H, brs), 5.44–5.48 (1H, m), 7.46–7.53 (2H, m), 7.59–7.64 (3H, m), 7.91–7.96 (2H, m), 8.22–8.26 (2H, m); ^{13}C NMR (68 Hz, $CDCl_3$) δ 46.9, 69.2, 123.8, 126.5, 128.1, 128.8, 134.0, 136.1, 147.3, 150.2, 199.5.

4-Sulfanylpolystyrene (13). To a stirred solution of polystyrene resin (14.9 g), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (21.6 mL, 143 mmol) in cyclohexane (120 mL) was added dropwise butyllithium (1.57 M in hexane, 110 mL, 172 mmol) at room temperature. After the reaction mixture was stirred at 65 °C for 2 h, solvents were removed. THF (220 mL) was added to the residue, and sulfur (4.60 g, 143 mmol) was then added to the suspension at 0 °C. After the reaction mixture was stirred at room temperature for 15 h, the reaction was quenched with 3 M hydrochloric acid (150 mL). The mixture was filtered, and the resin was washed with H_2O, THF, CH_2Cl_2, and Et_2O, and dried in vacuo at 60 °C for 2 h to give **12** (17.7 g). To the stirred suspension of the obtained resin **12** (17.7 g) in THF (250 mL) was added $LiAlH_4$ (2.02 g, 53.1 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 3 h. The reaction was quenched by adding H_2O (2 mL), followed by the addition of 15% aqueous NaOH solution (2 mL) and H_2O (6 mL). The mixture was filtered, and the resin was washed with H_2O, THF, CH_2Cl_2, and Et_2O, and dried in vacuo at 60 °C for 2 h to give **13** (15.8 g): IR (KBr, cm^{-1}) 2576, 687. Anal. Found: C, 83.83; H, 7.34; S, 7.37% (2.30 mmol/g).

4-Acetylsulfanylpolystyrene (14). To the stirred suspension of **13** (2.30 mmol/g, 15.8 g, 36.3 mmol) and pyridine (9.3 mL, 182 mmol) in CH_2Cl_2 (220 mL) was added acetyl chloride (8.2 mL, 182 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. The mixture was filtered, and the resin was washed with CH_2Cl_2 and Et_2O, and dried in vacuo at 60 °C for 2 h to give **14** (16.0 g); IR (KBr, cm^{-1}) 1751, 1705, 694. Anal. Found: C, 82.41; H, 7.11; S, 6.50% (2.03 mmol/g).

The loading of acetylsulfanyl group was determined by another method as follows: the mixture of **14** (296 mg), benzylamine (285 mg, 2.66 mmol), and THF (3 mL) was refluxed for 1 h. *N*-Benzylacetamide (0.60 mmol) was detected by GC-analysis of the reaction mixture using biphenyl as an internal standard. Thus, the loading was determined to be 2.02 mmol/g.

4-(*N-tert*-Butylchlorosulfinimidoyl)polystyrene (10). To a stirred suspension of **14** (2.02 mmol/g, 2.00 g) in dry benzene (20 mL) was added a solution of *N*,*N*-dichloro-*tert*-butylamine (1.73 g, 12.2 mmol) in dry benzene (3.0 mL) at room temperature, and the reaction mixture was refluxed for 1.5 h. After evaporation of the solvent in vacuo, the residue was suspended in CH_2Cl_2 (30 mL) for 30 min, and this suspension was filtered by a glass filter under an argon atmosphere. The resin was washed in this manner with CH_2Cl_2 (15 mL × 3), and then the resin was dried in vacuo at room temperature for 2 h to give a bright yellow resin **10**: IR (KBr, cm^{-1}) 1211, 1141, 694. Anal. Found: C, 71.63; H, 7.39; N, 2.53; S, 4.90 (1.53 mmol/g); Cl, 9.08%.

The loading of *N-tert*-butylchlorosulfinimidoyl group was determined by another method as follows: to a stirred suspension of **10** (300 mg) in CH_2Cl_2 (3 mL) was added a solution of 4-methoxybenzyl alcohol (117 mg, 0.85 mmol) in CH_2Cl_2 (2 mL) at room temperature, and the mixture was stirred for 20 h. 4-Methoxybenzyl chloride (0.46 mmol) was detected by GC-analysis of the reaction mixture using naphthalene as an internal standard. Then, the loading of *N-tert*-butylchlorosulfinimidoyl group was determined to be 1.53 mmol/g.

Typical Experimental Procedure for the Oxidation of Alcohols by Recycling 10 (Table 3). To a stirred suspension of **10** (0.72 mmol/g, 0.54 g, 0.39 mmol) in CH_2Cl_2 (3.0 mL) was added a solution of benzyl alcohol (21 mg, 0.19 mmol) and *i*-Pr_2NEt (50 mg, 0.39 mmol) at -78 °C. After the mixture was stirred at -78 °C for 30 min, the reaction was quenched by adding a solution of *i*-Pr_2NEt (50 mg, 0.39 mmol) in ethanol (2 mL). The mixture was filtered and the resin was washed with CH_2Cl_2 (15 mL × 3). The yield of benzaldehyde (0.18 mmol, 95%) was determined by GC-analysis of the filtrate using naphthalene as an internal standard. After the resin was further washed with Et_2O (10 mL × 3), it was dried in vacuo at room temperature for 2 h. Thus-obtained resin **11** was suspended in CH_2Cl_2 (2.5 mL), and a solution of NCS (60 mg, 0.45 mmol) in CH_2Cl_2 (2.5 mL) was added at room temperature. After the mixture was stirred for 1 h at room temperature, a solution of benzyl alcohol (16 mg, 0.15 mmol) and *i*-Pr_2NEt (40 mg, 0.31 mmol) in CH_2Cl_2 (2.0 mL) was added at -78 °C. After the mixture was stirred at the same temperature for 30 min, the reaction was quenched by adding a solution of *i*-Pr_2NEt (40 mg, 0.31 mmol) in ethanol (2.0 mL), and the mixture was stirred up to room temperature. The mixture was filtered by glass-filter, and the yield of benzaldehyde (0.15 mmol, quant.) was determined by GC-analysis.

Typical Experimental Procedure for the Catalytic Oxidation of Benzylic Alcohols by Using 10, NCS, and *i*-Pr_2NEt

(Table 4, Entry 4). To a stirred suspension of **10** (1.25 mmol/g, 0.13 g) in CH_2Cl_2 (3.0 mL) was added a solution of 4-nitrobenzyl alcohol (124 mg, 0.81 mmol) and *i*-Pr_2NEt (209 mg, 1.62 mmol) in CH_2Cl_2 (2.0 mL) at -78 °C. Then, NCS (216 mg, 1.62 mmol) was added and the mixture was stirred at room temperature for 1 h. After the reaction was quenched with H_2O (1 mL), the mixture was filtered through a Celite pad, and the filtrate was extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 3/1) to afford 4-nitrobenzaldehyde (112 mg, 92%).

Typical Experimental Procedure for the Catalytic Oxidation of Non-Benzylic Alcohols by Using 10, NCS, K_2CO_3, and MS4A (Table 4, Entry 12). To a stirred suspension of K_2CO_3 (950 mg, 6.87 mmol), MS4A (687 mg), NCS (184 mg, 1.38 mmol), and **10** (1.25 mmol/g, 0.11 g) in CH_2Cl_2 (5.0 mL) was added a solution of 4-phenylcyclohexan-1-ol (121 mg, 0.69 mmol) in CH_2Cl_2 (2.0 mL) at 0 °C. After the mixture was stirred at room temperature for 16 h, it was filtered through a Celite pad, and the filtrate was extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 4/1) to afford 4-phenylcyclohexan-1-one (108 mg, 91%).

1,3-Diphenylpropan-1-ol.[15] R_f 0.40 (hexane/ethyl acetate = 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94–2.17 (3H, m), 2.59–2.78 (2H, m), 4.65–4.73 (1H, m), 7.16–7.36 (10H, m); ^{13}C NMR (75.5 Hz, $CDCl_3$) δ 32.0, 40.4, 73.8, 125.8, 125.9, 127.6, 128.3, 128.4, 128.5, 141.7, 144.5.

1,3-Diphenylpropan-1-one.[16] R_f 0.60 (hexane/ethyl acetate = 4/1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.07 (2H, t, $J = 7.50$ Hz), 3.31 (2H, t, $J = 7.50$ Hz), 7.15–7.33 (5H, m), 7.40–7.56 (3H, m), 7.93–8.00 (2H, m); ^{13}C NMR (68 Hz, $CDCl_3$) δ 30.2, 40.5, 126.0, 127.9, 128.3, 128.4, 128.5, 132.9, 136.7, 141.1, 199.0.

(2*E*)-5-Phenylpent-2-en-1-ol.[17] R_f 0.20 (hexane/ethyl acetate = 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33–2.41 (2H, m), 2.68–2.73 (2H, m), 4.06 (2H, d, $J = 4.80$ Hz), 5.61–5.78 (2H, m), 7.16–7.30 (5H, m); ^{13}C NMR (75.5 Hz, $CDCl_3$) δ 33.9, 35.5, 63.6, 125.8, 128.3, 128.4, 129.5, 132.2, 141.6.

(2*E*)-5-Phenylpent-2-enal. R_f 0.50 (hexane/ethyl acetate = 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.68 (2H, dt, $J = 6.60$, 7.50 Hz), 2.84 (2H, t, $J = 7.50$ Hz), 6.14 (1H, dd, $J = 7.80$, 15.6 Hz), 6.86 (1H, td, $J = 6.60$, 15.6 Hz), 7.18–7.33 (5H, m), 9.50 (1H, d, $J = 7.80$ Hz).

3-(1-Naphthyl)prop-2-yn-1-ol.[18] R_f 0.30 (hexane/ethyl acetate = 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (1H, brs), 4.65 (2H, d, $J = 4.80$ Hz), 7.38–7.68 (4H, m), 7.81–7.85 (2H, m), 8.32 (1H, d, $J = 7.20$ Hz); ^{13}C NMR (75.5 Hz, $CDCl_3$) δ 51.8, 83.8, 92.0, 120.1, 125.1, 126.0, 126.4, 126.8, 128.2, 129.0, 130.6, 133.1, 133.2.

3-(1-Naphthyl)prop-2-ynal.[19] R_f 0.70 (hexane/ethyl acetate = 4/1); IR (KBr, cm^{-1}) 2183, 1651; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.67 (3H, m), 7.86–8.00 (3H, m), 8.33 (1H, d, $J = 7.20$ Hz), 9.56 (1H, s); ^{13}C NMR (75.5 Hz, $CDCl_3$) δ 93.1, 93.4, 116.9, 125.1, 125.6, 127.0, 127.9, 128.6, 132.1, 133.0, 133.6, 133.7, 176.6. HRMS (EI) Found: m/z 180.0572. Calcd for $C_{13}H_{18}O$ [M$^+$]: 180.0575.

3-Trityloxypropan-1-ol.[20] R_f 0.40 (hexane/ethyl acetate = 3/1); IR (KBr, cm^{-1}) 3595, 3525, 1597, 1489, 1450; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.23–1.42 (7H, m), 1.49–1.65 (4H, m), 3.04 (2H, t, $J = 6.60$ Hz), 3.61 (2H, t, $J = 6.60$ Hz), 7.12–7.32 (9H, m), 7.42–7.46 (6H, m); ^{13}C NMR (68 Hz, $CDCl_3$) δ 25.6, 26.2, 29.2, 29.9, 32.7, 63.0, 63.5, 86.2, 126.8, 127.7, 128.7, 144.5. HRMS (ESI) Found: m/z 375.2324. Calcd for $C_{26}H_{31}O_2$ [M + H]: 375.2317.

3-Trityloxypropanal.[20] R_f 0.70 (hexane/ethyl acetate = 3/1); IR (KBr, cm^{-1}) 1728, 1597, 1489, 1450; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.23–1.42 (4H, m), 1.56–1.66 (4H, m), 2.38 (2H, dt, $J = 1.90$, 7.20 Hz), 3.05 (2H, t, $J = 6.60$ Hz), 7.18–7.32 (9H, m), 7.41–7.45 (6H, m), 7.93 (1H, t, $J = 1.90$ Hz); ^{13}C NMR (68 Hz, $CDCl_3$) δ 22.0, 26.0, 29.0, 29.8, 43.8, 63.4, 86.3, 126.8, 127.7, 128.7, 144.4, 202.8. HRMS (ESI) Found: m/z 373.2168. Calcd for $C_{26}H_{29}O_2$ [M + H]: 373.2152.

7-*tert*-Butyldiphenylsiloxyheptan-1-ol.[21] R_f 0.20 (hexane/ethyl acetate = 4/1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.04 (9H, s), 1.31 (6H, m), 1.54 (4H, m), 1.78 (1H, brs), 3.63 (2H, t, $J =$ 6.60 Hz), 3.70 (2H, t, $J = 6.60$ Hz), 7.34-7.41 (6H, m), 7.64–7.67 (4H, m); ^{13}C NMR (68 Hz, $CDCl_3$) δ 19.3, 25.7, 25.8, 26.9, 29.2, 32.5, 32.8, 63.0, 63.9, 127.4, 129.4, 134.0, 135.4.

7-*tert*-Butyldiphenylsiloxyheptanal.[21] R_f 0.60 (hexane/ethyl acetate = 4/1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.05 (9H, s), 1.28–1.41 (4H, m), 1.51–1.66 (4H, m), 2.39 (2H, dt, $J = 1.90$, 7.50 Hz), 3.65(2H, t, $J = 6.60$ Hz), 7.34–7.42 (6H, m), 7.64–7.68 (4H, m), 9.74 (1H, t, $J = 1.90$ Hz); ^{13}C NMR (68 Hz, $CDCl_3$) δ 19.3, 22.1, 25.6, 26.9, 28.9, 32.3, 43.9, 63.7, 127.5, 129.4, 133.9, 135.4, 202.6.

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