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Baeyer−Villiger Oxidation in Supercritical CO_2 with Potassium Peroxomonosulfate Supported on Acidic Silica Gel

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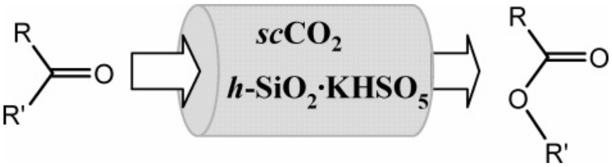
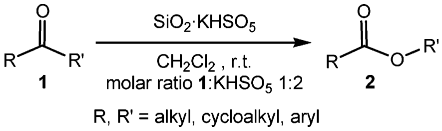


Supercritical carbon dioxide ($scCO_2$) is an efficient reaction medium to perform the Baeyer−Villiger oxidation with hydrated silica-supported potassium peroxomonosulfate (h-SiO_2·$KHSO_5$) under flow-through conditions. Hydration modulates the reactivity of the active surface by softening the acidity of the $KHSO_4$ present in the supported reagent. The reaction in $scCO_2$ is much more efficient than in *n*-hexane under similar conditions, which is attributed to better transport and solvating properties of the supercritical medium with regard to *n*-hexane.

Introduction

The Baeyer−Villiger oxidation of ketones **1** into esters **2** is one of the most widely applied transformations in organic synthesis.[1] However, the standard protocol for this selective oxidation still suffers several disadvantages. The most common reagents for performing these transformations are organic peracids,[1] resulting in the formation of 1 equiv of the corresponding carboxylic acid, which has to be separated from the reaction products. Moreover, organic peracids are expensive and/or hazardous (because of shock sensitivity), which limits their commercial application. Also, Baeyer−Villiger oxidation generally requires the use of organic solvents, typically dichloromethane or aromatics, which further enhances the environmental impact of the process.

SCHEME 1. Baeyer−Villiger Reaction with SiO_2·$KHSO_5$



We have recently reported[2] that potassium peroxomonosulfate deposited onto silica, SiO_2·$KHSO_5$, efficiently reacts with ketones in dichloromethane to provide the corresponding esters or lactones in quantitative yields. Potassium peroxomonosulfate is a good alternative to organic peracids in the Baeyer−Villiger reaction (Scheme 1) since it is inexpensive and safe. In addition, silica-supported potassium peroxomonosulfate avoids the hydrolysis of reaction products, an extensive side process associated with the use of aqueous solutions of Oxone, and offers advantages in relation to the use of supported reagents in organic synthesis, such as facilitating the separation of the products from the reduced reagent. Further improvement of the Baeyer−Villiger reaction with supported potassium peroxomonosulfate could be achieved by avoiding the use of chlorinated organic solvents.

Supercritical carbon dioxide ($scCO_2$), which has readily accessible critical conditions ($T_c = 31.0$ °C, $P_c = 73.8$ bar), a truly benign character, and low cost, is a frequently discussed alternative reaction medium for chemical synthesis.[3] Furthermore, there is an existing technology platform for the use of $scCO_2$ in large-scale applications in both the food and nutrition industries. These properties have prompted intense research to further develop the potential of $scCO_2$ as an alternative solvent for green chemistry. Transport properties of $scCO_2$ (adjustable

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solvating power, low surface tension, low viscosity, and high diffusivity)[3c] confer interesting opportunities on this medium to perform reactions with supported reagents and catalysts. For instance, efficient nucleophilic substitution reactions have been described with supported phase-transfer reagents,[4] dehydration of alcohols,[5] and Friedel−Crafts alkylation[6] over solid acid catalysts, as has the oxidation of alcohols with silica-supported chromium trioxide.[7]

We herein report that hydrated potassium peroxomonosulfate deposited onto silica, h-SiO_2•$KHSO_5$, is an efficient reagent to perform the Baeyer−Villiger oxidation of ketones into esters or lactones in scCO_2 under continuous-flow conditions. Hydration not only modifies the surface reactivity of the supported reagent, but also suppresses acid-catalyzed side reactions which are important competing pathways when the anhydrous reagent is being used. The reactions were performed by flowing a solution of the ketone in scCO_2 through a column containing the supported reagent and by recovering the product by depressurization. Handling the peroxide under the reaction conditions herein described simply involves placing a suitable polypropylene container charged with the supported reagent into the column and removing it once the reaction is complete. The method significantly improves conventional Baeyer−Villiger reaction procedures since it avoids the use of organic solvents and reduces the physical operations required to isolate the products to a simple depressurization. The reaction in scCO_2 is more efficient than in solution, and the results evidence the solvating properties of scCO_2.

Results and Discussion

Potassium peroxomonosulfate supported on silica was prepared[2] by mixing a ca. 2 M aqueous solution of the peroxide with chromatographic-grade silica gel (particle size 0.040−0.060 mm) and by evaporating the solvent at room temperature under vacuum. The resulting free-flowing white solid was either lyophilized or dried under vacuum until a constant weight was achieved. A peroxidic content of 0.5−2.2 mmol of peracid g^{-1} was determined in SiO_2•$KHSO_5$ by iodometric titration. Deposition was quantitative in all cases. Acid−base titration of the reagent gave a total acid content ($KHSO_4$ + $KHSO_5$) of 0.6−2.3 mmol g^{-1}, indicating a potassium hydrogen sulfate content of 0.1−0.05 mmol g^{-1}. The reagent can be stored at 2 °C in a desiccator for weeks with no significant loss of peroxidic content.

Prior to the reactions in scCO_2, the supported reagent was hydrated with 1.5 equiv of water in relation to the amount of total acid ($KHSO_4$ + $KHSO_5$) on the silica. Hydration was performed by placing two open vials containing the supported reagent and the required amount of water respectively in a closed chamber and by allowing the system to stand overnight at 4 °C. The reagent was used without further treatment. h-SiO_2•$KHSO_5$ can be stored at 4 °C for 2−3 weeks without significant loss of peroxidic titer.

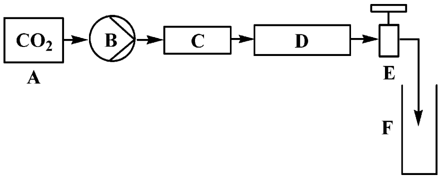

FIGURE 1. Schematic view of the apparatus used in the oxidation reactions: (A) CO_2 cylinder; (B) diaphragm pump; (C) substrate reservoir; (D) column charged with h-SiO_2•$KHSO_5$; (E) micrometric valve; (F) trap.

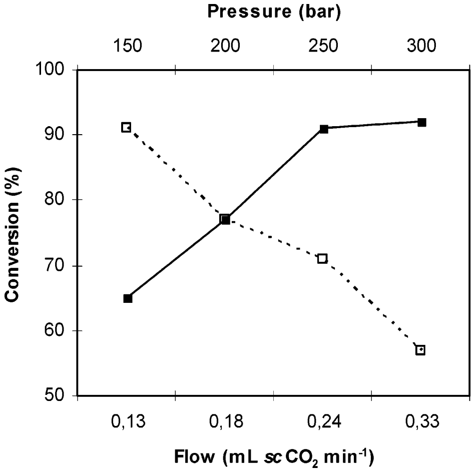

FIGURE 2. Effect of scCO_2 pressure (■) and flow (□) on the conversion of ketone **1c** at 40 °C.

Oxidation of ketones with h-SiO_2•$KHSO_5$ in scCO_2 was carried out by flowing scCO_2 (0.12 mL of scCO_2 min^{-1}) at 250 bar and 40 °C for 3.5 h through a reservoir containing the substrate (0.8 mmol) and then through a column packed with the supported reagent (molar ratio $KHSO_5$:ketone = 2:1) (Figure 1). The system was depressurized through a micrometric valve, and the reaction products were collected in a trap cooled with liquid nitrogen (Figure 1). Once the reaction was complete, the consumed reagent recovered from the column had a white color and loose appearance. GC analysis of the solution obtained by a thorough washing of the recovered reagent with dichloromethane allowed us to verify that organic material was not retained on the solid. The results are shown in Table 1.

The results showed that cyclic ketones **1a**−**g** efficiently react with hydrated h-SiO_2•$KHSO_5$ in scCO_2 to exclusively provide the corresponding lactones **2a**−**g** with no hydrolysis of the reaction products. Once the reaction was complete, iodometric titration of the recovered supported reagent showed a nearly stoichiometric conversion of the peroxide in relation to the reacted ketone in most cases. The yields of the reactions reveal the relative reactivities of the different ketones **1**, which depend on the ring size and the migratory ability of the substituents. Increasing amounts of $KHSO_5$ led to improved yields for the less reactive ketones **1g** and **1i**. Thus, oxidation of acetophenone (**1i**) with molar ratios $KHSO_5$:ketone = 2:1 and 4:1 enable phenyl acetate (**2i**) to be obtained with 33% and 86% yields, respectively, while decalone (**1g**) required 3 equiv of peroxide to achieve a quantitative conversion of the substrate (entries 9 and 7, Table 1). For cycloheptanone (**1d**) and 2-octanone (**1h**), however, an increase of the molar ratio $KHSO_5$:**1** did not significantly improve the reaction yield (entries 4 and 8, Table 1).

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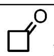
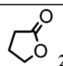
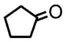
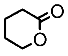
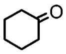
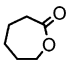
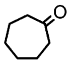
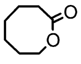
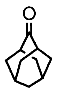
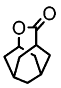
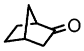
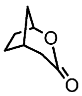
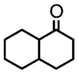
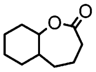
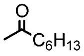
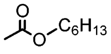
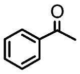
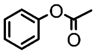
TABLE 1. Oxidation of Ketones 1 with h-SiO_2·$KHSO_5$ in $scCO_2$[a]

Run	Substrate	Product[b]	Conv.[c](%)
1	 **1a**	 **2a**	96
2	 **1b**	 **2b**	98
3	 **1c**	 **2c**	91
4	 **1d**	 **2d**	15
5	 **1e**	 **2e**	99
6[d]	 **1f**	 **2f**	90
7[e]	 **1g**	 **2g**	99
8[f]	 **1h**	 **2h**	22
9[e]	 **1i**	 **2i**	86

[a] Reactions in $scCO_2$ at 250 bar, 40 °C, and flow rate 0.11−0.15 mL of $scCO_2$ min^{-1}, h-SiO_2·$KHSO_5$ hydrated with 1.5 equiv of water with a load of peroxide of 0.60−0.70 mmol of $KHSO_5$ g^{-1}, molar ratio ketone:$KHSO_5$ = 1:2. [b] Esters or lactones were the only products (yield >99%). [c] Determined by GC analysis of the reaction mixtures, mass balance >98% in all the cases. [d] Flow rate 0.41 mL of $scCO_2$ min^{-1}. [e] Molar ratio ketone:$KHSO_5$ = 1:3. [f] Molar ratio ketone:$KHSO_5$ = 1:5.

Recirculation of the $scCO_2$ flow containing the mixture of partially converted ketone and ester product over the supported reagent allows for improving the conversion of the substrate. A control experiment carried out by flowing a mixture of **1h** and the corresponding ester **2h** (molar ratio **1h**:**2h** = 4:1) over h-SiO_2·$KHSO_5$ hydrated with 1.5 equiv of water and 0.65 mmol of $KHSO_5$ g^{-1} under our standard reaction conditions allowed a further 20% conversion of the ketone **1h** without significant loss of the ester product **2h**.

Reactions under flow-through conditions are generally less effective than reactions in batch since the contact between the substrate and immobilized reagent is limited to the residence time of the flowing substrate solution over the solid reagent. Accordingly, the use of a molar ratio $KHSO_5$:cyclopentanone (**1b**) = 1:1 led to an incomplete conversion of the substrate. On the other hand, the use of excess ketone **1b** (molar ratio $KHSO_5$:**1b** = 1:5) allowed a nearly complete conversion of the supported peroxide and 20% conversion of ketone **1b** into the corresponding lactone **2b**. In fact, this result indicates that all the hydroperoxide groups at the active surface are available for reacting with the substrate.

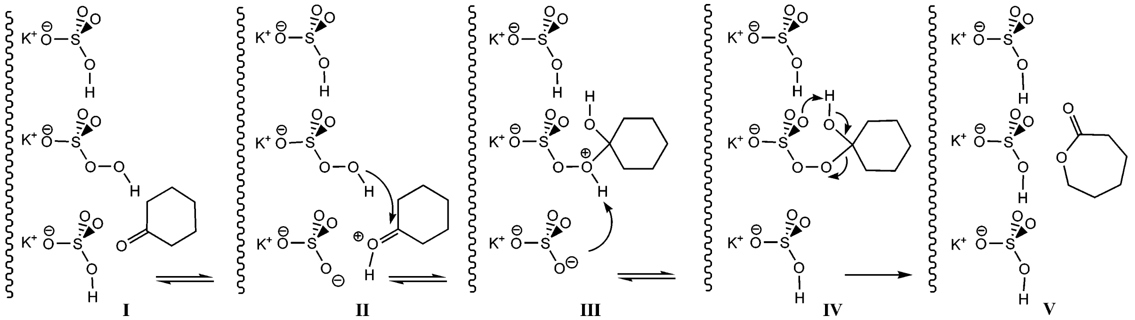
Pressure and flow effects on substrate conversion are shown in Figure 2. When the pressure was increased from 100 to 250 bar at a constant flow (0.12 mL of $scCO_2$ min^{-1}), temperature (40 °C), and load of peracid (0.7 mmol of $KHSO_5$ g^{-1}), the substrate conversion increased from 65% to 91%. However, a further increase of up to 300 bar did not improve the reaction efficiency (92%). Alternatively, when the flow of $scCO_2$ was increased from 0.13 to 0.33 mL of $scCO_2$ min^{-1} at a constant pressure (250 bar), temperature (40 °C), and load of peracid (0.7 mmol of $KHSO_5$ g^{-1}), substrate conversion fell from 91% to 57%. These results are apparently related to the substrate residence time over the supported reagent, which diminishes by either lowering the pressure at constant flow or increasing the flow at a constant pressure.

The load of peracid on h-SiO_2·$KHSO_5$ also has a significant effect on the reaction efficiency, although it depends on the ketone used. Thus, at 250 bar and 40 °C with a flow of 0.12 mL of $scCO_2$ min^{-1}, the maximum conversion of **1b** and cyclohexanone (**1c**) was achieved with a load of 0.6−0.8 mmol of peroxide g^{-1}, yet the optimum load was 0.2−0.3 mmol of $KHSO_5$ g^{-1} in the case of the most reactive cyclobutanone (**1a**). Evidently, the lower the load of the reagent, the lower the formal concentration of the peroxide becomes at the surface of the solid for a given molar ratio $KHSO_5$:ketone. Alternatively, the higher the amount of solid reagent required, the longer the path and residence time of the substrate dissolved in $scCO_2$ over the reagent. An optimized load of peroxide in h-SiO_2·$KHSO_5$ for a given substrate would then be a compromise between the opposite effects of the hydroperoxide concentration at the surface and the residence time on the reaction rate. Also, the fact that increasing the load of the reagent could lead the hydroperoxide to occupy less accessible regions on the silica surface should not be disregarded since this reduces its availability to react with the flowing substrate.

Hydration of SiO_2·$KHSO_5$ is a critical parameter for a successful reaction. We found that the oxidation of **1c** with anhydrous SiO_2·$KHSO_5$ in $scCO_2$ at 250 bar, 0.20 mL of $scCO_2$ min^{-1}, and 40 °C failed to produce any significant amount of ϵ-caprolactone (**2c**) in the trap. A thorough washing of the supported reagent recovered from the column with dichloromethane allowed isolation of (mass balance 75%) ϵ-caprolactone (**2c**) (22%) and 2-cyclohexylidenecyclohexanone (78%). A similar result was found[2] for the reaction of cyclohexanone (**1c**) with anhydrous SiO_2·$KHSO_5$ in *n*-hexane. On the other hand, hydration of SiO_2·$KHSO_5$ with more than 2 equiv of water in relation to the amount of total acid ($KHSO_4$ + $KHSO_5$) on the silica led to a partial hydrolysis of the reaction products. Hydroxyacids are not eluted by the flow of $scCO_2$ since their increased H-bonding ability with regard to esters provokes their strong adsorption onto the acidic reagent surface. Thus, the reaction of **1c** with SiO_2·$KHSO_5$ hydrated with 3 equiv of water (molar ratio $KHSO_5$:ketone = 2:1) in $scCO_2$ at 250 bar, 0.20 mL of $scCO_2$ min^{-1}, and 40 °C enabled us to recover only 46% of the organic material and obtain only 88% of **2c** and 5% of unreacted ketone in the trap. Thoroughly washing the solid reagent with dichloromethane allowed a recovery of 6-hydroxyhexanoic acid (7%).

We have previously reported[2] that surface-adsorbed potassium hydrogen sulfate helps to catalyze the oxidation of ketones with anhydrous SiO_2·$KHSO_5$ in dichloromethane. The reaction pathway can then be envisaged (Scheme 2) as an initial adsorption equilibrium (**I**, **II**) of the substrate onto the acidic surface. This is followed by a nucleophilic attack of a proximate hydroperoxide group to the carbonyl group of an acid−base

SCHEME 2. Reaction Mechanism at the Active Surface



complex (**II**, **III**) to provide the tetrahedral intermediate, which then undergoes transposition of the alkyl chain (**IV**, **V**).

The relative position of the adsorption equilibrium is determined by the polarity and solvating ability of the solvent. Apolar solvents favor strong adsorption of the ketone onto the acidic centers of the active surface[8] and reduce the possibility of the substrate reaching a reactive hydroperoxide group. The acid–base complex ketone–$KHSO_4$ becomes a new reactive species immobilized onto the active surface which then has the opportunity to condense with further ketone molecules carried by the flowing $scCO_2$ solution. It is worth noting that the oxidation reaction produces $KHSO_4$ as the reduced species of the peracid.

The dramatic effect of hydration of $SiO_2{\cdot}KHSO_5$ on the efficiency and selectivity of the reaction in $scCO_2$ can then be attributed to a lowering of the acidic strength of surface-bonded $KHSO_4$ by coordination with water. In this way, substrate adsorption at the acidic sites of the solid surface becomes weaker and the ketone molecules have more opportunities to find reactive hydroperoxide groups at different regions of the solid surface. In addition, the fact that hydration forms a polar and protic layer over the reagent surface should not be disregarded, which extends the availability of acidic protons farther from the anchoring center of potassium hydrogen sulfate and increases the efficiency of acid catalysis at the reagent surface.

Comparison of $scCO_2$ and *n*-Hexane under Flow-Through Reaction Conditions. To compare the solvating properties of $scCO_2$ and *n*-hexane in the Baeyer–Villiger reaction with hydrated h-$SiO_2{\cdot}KHSO_5$, we performed the reaction of **1c** in *n*-hexane under flow-through conditions. We previously established the average concentration of **1c** in $scCO_2$ under our standard reaction conditions by placing a weighed amount of the ketone in the substrate reservoir, flowing $scCO_2$ at 250 bar, 40 °C, and 0.12 mL min^{-1} for 90 min, and determining the amount of ketone which remained in the reservoir after depressurization. The experiment was repeated four times with different amounts of **1c**, and a 0.027 ± 0.002 M average concentration of **1c** in *sc*CO_2 was yielded under our standard reaction conditions.

The reaction of **1c** with hydrated h-$SiO_2{\cdot}KHSO_5$ in *n*-hexane under flow-through conditions was carried out by flowing a 0.03 M solution of the ketone in *n*-hexane at 0.106 mL min^{-1} through a column containing the supported reagent (molar ratio ketone: $KHSO_5$ = 1:2), which was heated at 40 °C. The solution was collected in an ice-cooled flask placed at the end of the column. We could recover only 70% of the organic material, 70% of which was recovered in the collector and 30% from the washings of the solid support with dichloromethane. GC analysis of the mixture showed unreacted ketone (45%), ϵ-caprolactone (33%), and 2-cyclohexylidenecyclohexanone (22%).

These results show that the reaction in $scCO_2$ is much more efficient than in *n*-hexane. This can be attributed to the transport properties of $scCO_2$,[3] whose high diffusivity, low viscosity, and low surface tension allow for the substrate solution to penetrate the porous matrix better and to reach a more extensive active surface of the solid reagent than *n*-hexane. However, the results also evidence a better solvating ability of $scCO_2$ compared to *n*-hexane since the former completely removes the reaction products from the acidic solid support and avoids the formation of aldol condensation side products. The association of either the ketone or ester with the acidic sites at the supported-reagent surface is less favorable in $scCO_2$ than in *n*-hexane, which should be attributed to a better solvation of polar oxygenated molecules in the supercritical medium. These results indicate that $scCO_2$ has peculiar solvating properties which cannot be compared so easily to those of hydrocarbons.

In short, we have shown that hydrated h-$SiO_2{\cdot}KHSO_5$ is an efficient reagent to perform the Baeyer–Villiger reaction of a variety of ketones in $scCO_2$ under flow-through conditions. The reactions were performed by flowing a solution of the ketone in $scCO_2$ through a column containing the supported reagent and recovering the product by depressurization. Handling the peroxide under the reaction conditions herein described simply involves placing a suitable polypropylene container charged with the supported reagent into the column and removing it once the reaction is complete. This method, which requires high-pressure equipment, avoids the use of organic solvents as well as the contamination of products with the reduced form of the oxidant and simplifies the physical operations required to isolate reaction products. The efficiency of the method depends on the reactivity of the substrate and its solubility in $scCO_2$, which determine the consumption of CO_2 and duration of the experiment. We have shown that the surface reactivity of the supported reagent can be modulated by hydration, which diminishes the strength of the acidic sites of the active surface. The results also show that the transport and solvating properties of $scCO_2$ are significantly better than those of *n*-hexane in these reactions.

Experimental Section

General Procedures. Aqueous solutions of peroxomonosulfate and $SiO_2{\cdot}KHSO_5$ were prepared following reported procedures.[2] Peroxidic and total acid contents of the supported reagent were determined by iodometric and acid–base titrations. The amount of $KHSO_4$ in the supported reagent was determined by the difference found between the total acid and peroxidic contents. Hydration of $SiO_2{\cdot}KHSO_5$ was performed by placing in a 50 mL

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[8] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Germany, 1988.

closed chamber two vials containing, respectively, a weighed sample of SiO_2•$KHSO_5$ and 1.5 equiv of H_2O with regard to the total acid content in the supported reagent, and the system was left to stand overnight at 4 °C.

The high-pressure equipment consisted of a 250 mL AISI 316 stainless steel jacketed reactor, a high-pressure micrometric valve placed at the outlet of the reactor, a diaphragm pump (Orlita MHS 30/8) with a maximum theoretical flow of 8.44 L/h of liquid CO_2, and a set of HIP high-pressure valves, pressure and temperature probes, and security rupture disks suitably placed to control the flow of CO_2 along the system.

Oxidation of Ketones 1 to Esters 2 with h-SiO_2·$KHSO_5$ in scCO_2. General Procedure. Cyclohexanone (**1c**) (0.85 mmol) was placed in a Teflon cylinder covered at the top with a screw cap with two 1/4-28 UNF threaded ports. The reservoir was kept open in one of the ports, while the second was connected to a 5 mL Rezorian Luer-lock syringe-tip cartridge (Supelco) charged with 2.5 g of h-SiO_2•$KHSO_5$ (1.7 mmol) by 1/8 in. Teflon tubing and suitable fittings. Two filters placed at the bottom and the top of the cartridge prevented any displacement of the solid reagent. The assembly was placed within the 250 mL autoclave thermostated at 40 °C, and the column outlet was connected to the reactor outlet by Teflon tubing and a septum. The high-pressure micrometric valve outlet was connected to a trap cooled with a liquid nitrogen bath by 1/8 in. Teflon tubing. The pressure in the trap was equilibrated with a flow of nitrogen.

The reactor was closed, charged with CO_2, and then pressurized to 250 bar. This operation usually required ca. 15 min. The stroke volume of the pump and the aperture of the high-pressure micrometric valve at the reactor outlet were regulated to achieve steady continuous-flow conditions at 250 bar. The CO_2 flow at the system outlet was monitored with a bubble flow meter.

The system was left to operate for 3.5 h and then completely depressurized through the micrometric valve. The trap was allowed to warm to room temperature. The colorless residue was dissolved in deuterated chloroform and analyzed by GC, GC−MS, and ^{1}H and ^{13}C NMR. The solid reagent recovered from the column was washed four times with 15 mL of dichloromethane in a round-bottomed flask under magnetic stirring. The filtered solution was analyzed by GC and then evaporated under vacumm at 0 °C.

Oxidation of 1c with h-SiO_2·$KHSO_5$ in *n*-Hexane under Flow-Through Conditions. A 5 mL Rezorian Luer-lock syringe-tip cartridge (Supelco) was charged with 2.5 g of h-SiO_2•$KHSO_5$ (1.75 mmol) and placed within a vertical jacketed cylinder heated at 40 °C by a circulating bath. The cartridge outlet was connected to a 100 mL flask cooled at 0 °C by 1/8 in. Teflon tubing. A 50 mL polypropylene syringe was charged with 30 mL of a 0.03 M solution of **1c** in *n*-hexane, placed in a syringe pump set at 0.106 mL min^{-1}, and connected to the cartridge inlet by 1/8 in. Teflon tubing and suitable fittings. The assembly was operated until the syringe was emptied. Then the cartridge was washed with an additional 30 mL of *n*-hexane. The solution in the collector was analyzed by GC, and the solvent was removed under vacuum at 0 °C. The solid reagent recovered from the column was washed four times with 15 mL of dichloromethane in a round-bottomed flask under magnetic stirring. The filtered solution was analyzed by GC and then evaporated under vacuum at 0 °C.

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Supporting Information Available: Gas chromatograms and NMR spectra of the reaction crudes. This material is available free of charge via the Internet at http://pubs.acs.org.

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