JOC The Journal of Organic Chemistry

Article

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Reactions at Interfaces: Oxygenation of *n*-Butyl Ligands Anchored on Silica Surfaces with Methyl(trifluoromethyl)dioxirane

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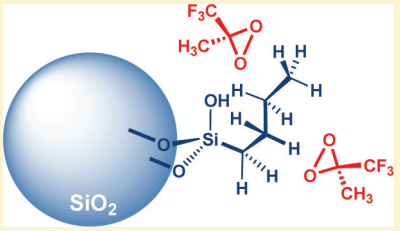
Supporting Information

ABSTRACT: The oxygenation of *n*-butyl and *n*-butoxy chains bonded to silica with methyl(trifluoromethyl)dioxirane (**1**) revealed the ability of the silica matrix to release electron density toward the reacting C_2−H σ-bond through the Si−C_1 and Si−O_1 σ-bonds connecting the alkyl chain to the surface (silicon β-effect). The silica surface impedes neither the alkyl chain adopting the conformation required for the silicon β-effect nor dioxirane **1** approaching the reactive C_2 methylene group. Reaction regioselectivity is insensitive to changes in the solvation of the reacting system, the location of organic ligands on the silica surface, and the H-bonding character of the silica surface. Reaction rates are faster for those organic ligands either within the silica pores or bonded to hydrophilic silica surfaces, which evidence the enhanced molecular dynamics of confined dioxirane **1** and the impact of surface phenomena on the reaction kinetics. The oxygenation of *n*-butyl and *n*-butoxy chains carrying trimethylsilyl, trimethoxysilyl, and *tert*-butyl groups with dioxirane **1** under homogeneous conditions confirms the electronic effects of the silyl substituents and the consequences of steric hindrance on the reaction rate and regioselectivity. Orthosilicic acid esters react preferentially at the methylene group adjacent to the oxygen atom in clear contrast with the reactivity of the carboxylic or sulfonic acid alkyl esters, which efficiently protect this position toward oxidation with **1**.

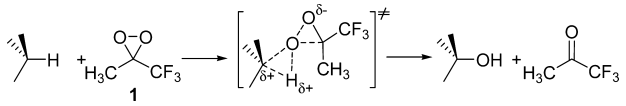


INTRODUCTION

Hybrid silica materials with large specific surface areas and tunable morphology[1] are of considerable importance in relation to potential applications in areas such as adsorption, chromatography, heterogeneous catalysis, sensor technology, and gas storage.[1,2] Preparation of organically modified silica materials requires suitable substituted alkyltrialkoxysilanes as monomers, which are incorporated onto the silica surface by either sol−gel or grafting procedures.[3] Anchoring of complex organic functionalities onto silica or some applications of the hybrid materials themselves frequently involve having to perform chemical transformations on organic moieties bonded to the silica surface. On these occasions, the silica matrix plays the role of a singular substituent that can alter the reaction course due to electronic and steric effects, restrictions of the translational and conformational freedom of ligands, the silica surface's hydrophilic nature, topological effects derived from the location and bonding of ligands, the interfacial dynamics, and kinetic changes associated with the heterogeneous character of the reactions, among others.

Research addressing the understanding of the interactions of solid surfaces with reagents, catalyst, and products or transition states is of great importance in the fields of heterogeneous catalysis, surfaces engineering, and life sciences.[4] Studies on organically modified solid nanoparticles[5] addressing these issues generally face the challenge of determining reaction products, which remain anchored to the solid surface once the reaction has been performed. A few years ago, we devised[6] suitable procedures for determining the amount and structure of organic ligands bonded to silica surfaces by means of conventional GC−MS and NMR techniques. This precedent prompted us to examine the reactivity of simple alkyl and alkoxy ligands bonded to silica nanoparticles toward methyl(trifluoromethyl)dioxirane **1**[7] as a tool for exploring the electronic and steric effects exerted by the silica matrix.

Scheme 1. Concerted O-Atom Insertion Mechanism for the Oxygenation of the C−H σ-Bond with Methyl(trifluoromethyl)dioxirane (1)



Electrophilic O-atom insertion into C−H σ-bonds with dioxirane **1** proceeds through a concerted transition state with a spiranic structure in which the reacting carbon and hydrogen atoms develop significant electron deficiencies (Scheme 1).[8] Dioxirane **1** reacts efficiently under very mild conditions to give the corresponding alcohols or ketones with good yields, while the reaction rate and stereoselectivity depend strongly on the electronic and steric effects of the substituents.[9] Moreover,

Received: September 28, 2011
Published: November 8, 2011

dioxirane **1** is inert to silica, and reaction products are compatible with the analysis protocols for hybrid silicas.[6] Therefore, this reaction is a suitable probe for determining the effects of the silica matrix on the reactivity of surface organic ligands.

Herein we report the oxygenation of *n*-butyl- and *n*-butoxy-functionalized silica with methyl(trifluoromethyl)dioxirane (**1**). The results evidence the ability of the surface Si−C_1 and Si−O_1 σ-bonds to activate the adjacent C_2−H σ-bonds toward the electrophilic oxidant. The silica surface neither prevents the *n*-butyl and *n*-butoxy chains from adopting the conformation required for this activation nor significantly hinders the approach of dioxirane **1** to this position. Reaction regioselectivity is insensitive to changes in the solvation of the reacting system, the location of the organic ligands on the silica surface, and the silica surface's hydrophilic character. Nevertheless, reaction rates are faster for those organic ligands either confined within the silica pores or bonded to hydrophilic silica surfaces, which evidence the enhanced molecular dynamics induced by confinement and the impact of surface phenomena on the reaction kinetics.

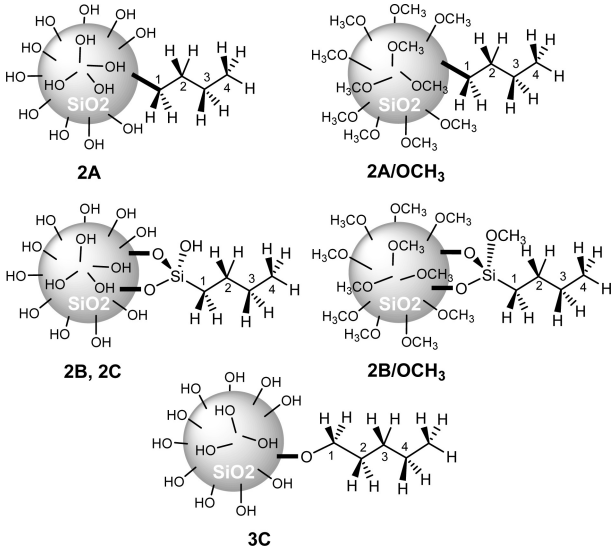
The interplay of conformational, steric, inductive, and hyperconjugative factors, which determine the reactivity of a linear C_4-alkyl chain toward dioxirane **1**, was also ascertained under homogeneous conditions using trimethylsilyl-, trimethoxysilyl-, and *tert*-butyl-substituted *n*-butyl and *n*-butoxy chains as models. The preferential oxidation of orthosilicic acid esters at the methylene group adjacent to the oxygen atom contrasts with the reactivity described for carboxylic or sulfonic acid esters,[9e] which efficiently protect this position toward oxidation with **1**.

RESULTS

Heterogeneous Reactions. The oxygenation of the *n*-butyl groups bonded to silica nanoparticles was performed on hybrid mesoporous silicas, prepared by co-condensation (**2A**) and grafting (**2B**), chromatographic silica derivatized by grafting (**2C**), and *n*-butoxy-functionalized chromatographic silica (**3C**) (Chart 1). Mesoporous *n*-butyl-functionalized silica (**2A**) was prepared through reaction of *n*-butyltrimethoxy silane with tetraethoxysilane (TEOS) in the presence of cetyltrimethylammonium bromide.[10] The solid material was thoroughly washed with acidic water until ^{1}H NMR[6] showed complete removal of the surfactant. Mesoporous silica was prepared following a reported procedure.[10,11] *n*-Butyl ligands were grafted by treating the corresponding silica material with *n*-butyltrimethoxysilane (**4c**) in toluene under reflux.[10] *n*-Butoxy-functionalized silica (**3C**) was prepared by treating commercial chromatographic silica with *n*-butanol in toluene under reflux in the presence of sulfuric acid.[12] The amount of ligands bonded to the silica surface was quantified by ^{1}H NMR analysis[6] and ranged between 0.4 and 0.6 mmol g^{-1}. Additional experiments were carried out on hydrated and methyl-capped hybrid silica materials, **2A/H_2O**, **2A/OCH_3**, and **2C/OCH_3** (Chart 1), which were prepared by adding the corresponding amount of water to anhydrous hybrid silica **2A** and by treating **2A** and **2C** with anhydrous methanol under reflux in the presence of sulfuric acid, respectively.[12] Electron micrographs and NMR spectra for materials **2** and **3** are collected in the Supporting Information.

Oxidation of the different *n*-butyl- and *n*-butoxy-functionalized silicas **2** and **3** in solution was performed at −15 °C by adding an aliquot of a dichloromethane solution of dioxirane **1** to a stirred suspension of the hybrid material in the same solvent. The GC analysis of the supernatant solution showed no detachment of organic ligands into the solution. Reactions without solvent were performed by placing an aliquot of a dichloromethane solution of dioxirane **1** and the hybrid silica material in separate containers inside a 100 mL closed chamber and by allowing the system to stand for 6 days at 3 °C in the dark. After removing the volatiles under vacuum, a portion of the solid material was treated with aqueous hydrofluoric acid at 0 °C and the solution was extracted with dichloromethane. The organic phase was treated with anhydrous magnesium sulfate and sodium hydrogenphosphate, and was then analyzed by GC and GC−MS.[6] MS spectra of the reaction products are collected in the Supporting Information.

Chart 1. *n*-Butyl- and *n*-Butoxy-Functionalized Silicas 2A−C, 2A,B/OCH_3, and 2C[a]



[a]The figures illustrate the distinct surface functionalization of the hybrid materials.

The reaction of the oxidized hybrid silicas with hydrofluoric acid gave mixtures of tetrafluorosilane, *n*-butyltrifluorosilane, 2-butanone, and 3-oxobutyltrifluorosilane, which were identified by their EI+ mass spectra in all cases. 2-Butanone formation was attributed to quantitative desilylation of 2-oxobutyltrifluorosilane by hydrofluoric acid. The thermal stability of 3-oxobutyltrifluorosilane was determined by the reaction of *n*-butyltrimethoxysilane (**4c**) with dioxirane **1** in dichloromethane for 6 h, followed by treatment of the resulting solution with hydrofluoric acid at 0 °C, and drying and neutralizing the organic phase with anhydrous sodium sulfate and sodium hydrogenphosphate. The GC and GC−MS analyses of both the reaction mixture and the organic phase obtained after the treatment with hydrofluoric acid showed consistent ratios between the C_2- and C_3-oxidized trialkoxysilanes and the corresponding 2-butanone and 3-oxobutyltrifluorosilane, respectively. 1,1,1-Trifluoroacetone hydrate, the reduced form of dioxirane **1**, was also detected in the dichloromethane solution. The results shown in Table 1 are the averages of at least five independent experiments.

Monitoring dioxirane **1** decay over time in the oxidations of *n*-butyl-functionalized mesoporous hybrid silica **2A**, *n*-butyl-grafted chromatographic silica **2C**, and their corresponding methyl-capped derivatives **2A/OCH_3** and **2C/OCH_3** was

dx.doi.org/10.1021/jo2019703 | J. Org. Chem. 2011, 76, 10129−10139

Table 1. Oxygenation of the *n*-Butyl- and *n*-Butoxy-Functionalized Silicas, 2 and 3, with Methyl(trifluoromethyl)dioxirane (1)[a]

functionalized silica	reaction conditions	C_2/C_3[b]
C_4-mesoporous (**2A**)	CH_2Cl_2	0.74 ± 0.07
	solventless	0.77 ± 0.05
C_4-mesoporous/grafting (**2B**)	CH_2Cl_2	0.78 ± 0.08
	solventless	0.80 ± 0.06
C_4-Merck/grafting (**2C**)	CH_2Cl_2	0.81 ± 0.05
	solventless	0.82 ± 0.06
C_4-mesoporous/OCH_3 (**2A/OCH$_3$**)	CH_2Cl_2	0.69 ± 0.10
C_4-Merck/grafting/OCH_3 (**2C/OCH$_3$**)	CH_2Cl_2	0.72 ± 0.08
C_4-mesoporous/H_2O (**2A/H$_2$O**)	CH_2Cl_2	0.73 ± 0.06
n-butoxy-functionalized silica (**3C**)	CH_2Cl_2	only C_2

[a]Reactions in dichloromethane were carried out at −15 °C for 12 h, with 3 equiv of dioxirane **1** and initial dioxirane **1** concentration of 0.2 M. Reactions in the gas phase were carried out at 3 °C. [b]C_2/C_3 values indicate the relative ratios of the oxygenation sites and are the average of at least five independent runs.

performed by adding an aliquot of a dichloromethane solution of dioxirane **1** to a suspension of the hybrid material in a dichloromethane solution involving methyl *p*-chlorobenzoate as a standard at −15 °C. Sucessive 0.1 mL aliquots were withdrawn from the reaction mixture and quenched with a cold dichloromethane solution of cyclopentanol. The resulting solutions were analyzed by gas chromatography, and the relations of the peak areas were corrected by the response factor of cyclopentanone versus methyl *p*-chlorobenzoate, which were previously obtained from calibration curves under

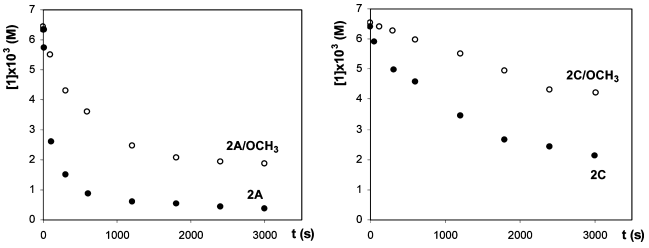
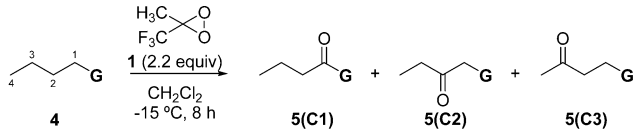


Figure 1. Decay of dioxirane **1** in the oxidation of (left) *n*-butyl-functionalized mesoporous hybrid silica **2A** (●) and its methyl-capped derivative **2A/OCH$_3$** (○); (right) *n*-butyl-grafted chromatographic silica **2C** (●) and its methyl-capped derivative **2C/OCH$_3$** (○).

the same analysis conditions. The results are shown in Figure 1. Second-order reaction plots of [**1**] versus time for the earlier reaction stages resulted in straight lines in all cases, which enabled the determination of the initial rate constants for dioxirane **1** consumption: 1.605 M^{-1} s^{-1} (**2A**), 0.1162 M^{-1} s^{-1} (**2C**), 0.258 M^{-1} s^{-1} (**2A/OCH$_3$**) and 0.024 M^{-1} s^{-1} (**2C/OCH$_3$**).

Homogeneous Reactions. The oxygenations of *n*-butyltrimethylsilane (**4a**), 2,2-dimethylhexane (**4b**), and *n*-butyltrimethoxysilane (**4c**) were carried out at −15 °C by adding an aliquot of a solution of methyl(trifluoromethyl)dioxirane (**1**) in dichloromethane to a solution of substrate **4** in the same solvent and by allowing the mixture to react for 8 h. The results are shown in Scheme 2. Reaction products **5a(C3)**, **5b(C1−3)**, and **5c(C3)** were identified by comparison with authentic samples prepared according to standard procedures. Silylated ketones **5a(C2)** and **5c(C2)** were identified from the NMR

Scheme 2. Relative Reaction Rates and Regioselectivity Found in the Oxygenation of Substrates 4a, 4b and 4c with Methyl(trifluoromethyl)dioxirane (1)[a]



	G	5(C1) (%)	5(C2) (%)	5(C3) (%)	C_2/C_3	k_{REL}
4a	$(CH_3)_3Si$	--	87	13	6.7	6
4b	$(CH_3)_3C$	14	9	77	0.12	1.7
4c	$(CH_3O)_3Si$	--	79	21	3.8	1

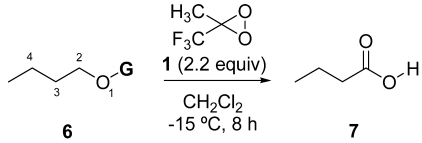
[a]The results are the averages of at least three independent experiments.

and mass spectra of the reaction mixtures. Oxidation at the C_4 positions was not detected under these reaction conditions.

The relative reaction rates for substrates **4** were determined by competition experiments carried out at −15 °C in dichloromethane with methyl *p*-chlorobenzoate as an internal standard. Reaction mixtures were quenched with 2,3-dimethyl-2-butene and analyzed by GC. The relative reaction rates were established by integrating the signals corresponding to the unreacted substrates. The results are shown in Scheme 2.

The oxidations of *n*-butoxytrimethylsilane (**6a**), *n*-butyl *tert*-butyl ether (**6b**), *n*-butoxytrimethoxysilane (**6c**), *n*-butanol (**6d**), and *n*-butyl methyl ether (**6e**) with dioxirane **1** and the measurement of their relative reaction rates were performed as described above. The reaction product was *n*-butanoic acid (**7**) in all cases. The results are shown in Scheme 3. MS and NMR spectra of starting materials and reaction products are provided in the Supporting Information.

Scheme 3. Relative Reaction Rates Found in the Oxygenation of Substrates 6a−e with Methyl(trifluoromethyl)dioxirane (1)[a]



	6d	6a	6e	6b	6c
G	H	$(CH_3)_3Si$	CH_3	$(CH_3)_3C$	$(CH_3O)_3Si$
k_{REL}	42.5	25.5	25	19.3	1

[a]The results are the averages of at least three independent experiments.

DISCUSSION

Heterogeneous Reactions: *n*-Butyl Chains. The oxygenation of C−H σ-bonds with dioxirane **1** is highly sensitive to steric effects,[7,9] and accordingly, reactions of hybrid silicas **2** with dioxirane **1** in solution were expected to take place preferentially at the methylene group farthest from the silica surface. However, the reactions showed only a slight preference for the C_3 methylene group, with C_2/C_3 ratios ranging from 0.69 (41:59) for **2A/OCH$_3$** to 0.81 (45:55) for **2C** (Table 1). These results evidence a competitive advantage of the C_2−H σ-

dx.doi.org/10.1021/jo2019703 | J. Org. Chem. 2011, 76, 10129−10139

bonds in relation to the C_3−H σ-bonds to react with dioxirane **1**, which counterbalances the larger steric hindrance posed by the silica surface to the C_2 methylene group.

The regioselectivity observed in these reactions might be attributed to the H-bonding interactions of the surface silanol groups with the O-atom of dioxirane **1**, which develops a negative charge density in the transition state (Scheme 1). This interaction would favor the oxygenation at the C_2 position, which is closer to the silica surface than C_3. This type of directing effect has been previously described[9h,13] for the hydroxyl and ammonium substituents in the oxygenation of C=C and C−H bonds with dioxiranes. However, the C_2/C_3 regioselectivities for both the 25% hydrated silica **2A/H$_2$O** (0.73; Table 1), in which a polar protic layer interconnecting the silanol groups improves the silica surface's H-bonding ability, and the hydrophobic methyl-capped hybrid silicas **2A/OCH$_3$** and **2C/OCH$_3$** (0.69 and 0.72, respectively; Table 1), which lack surface silanol groups, did not deviate significantly from anhydrous silicas **2A** and **2C** (0.74 and 0.81, respectively; Table 1). These results indicate that H-bonding between the surface silanol groups and dioxirane **1** is not a differential factor for the reactions at C_2 and C_3.

Reaction regioselectivity (Table 1) might also be attributed to differences in solvation for the transition states at C_2 and C_3 due to the solvent structure at the solid−liquid interface.[14] However, the reactions of the hybrid silicas **2A-C** with dioxirane **1** in the absence of a solvent revealed a slight, albeit consistent, increase in the oxygenation at C_2 (Table 1), suggesting that the solid−liquid interface in fact hinders the approach of dioxirane **1** to the C_2 methylene group. Therefore, the differential solvation at the interface is not a major factor to improve the reactivity of the C_2 methylene group.

Involvement of an activating silicon β-effect,[15] in which the highly polarized Si−C_1 σ-bond connecting the silica surface to the *n*-butyl chain delocalizes electron density into the electron deficiency generated at the C_2−H σ-bond by the electrophilic attack of dioxirane **1** (Figure 2), would account for the

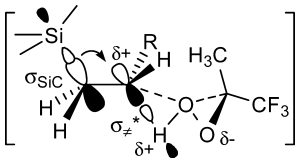


Figure 2. Hyperconjugative interaction of a Si−C_1 σ-bond with the electronic deficiency developed at the β position by the electrophilic attack of dioxirane **1**.[9a,15]

regioselectivity observed in these reactions. The silicon β-effect,[15] which can reach kinetic factors k_{TMS}/k_H up to 10^{12} for those reactions involving carbocations,[16] has proven useful for performing stereoselective transformations of interest in organic synthesis.[17] Trialkoxysilyl substituents are also able to activate the β-position of allylgroups,[18] which then undergo highly regioselective electrophilic additions despite the inductive deactivation exerted by three electronegative oxygen atoms.[19]

The silicon β-effect requires the *n*-butyl chains bonded to the silica surface to adopt a reactive conformation with *antiperiplanar* C_2−H and Si−C_1 σ-bonds (Figure 2).[15,16] MAS ^{29}Si NMR analysis of hybrid silicas **2A−C** indicates that most of the *n*-butyl ligands are connected to the silica surface through two siloxane bonds (T2 groups, *n*-Bu(OH)Si(O−Si)$_2$). Figure 3 depicts the most stable limit conformations for the T2 *n*-butyl groups. Rotation of the T2 moiety around the siloxane bridge gives rise to two different *anti* and *gauche* conformers, **I-IIA** and **I-IIB**; the latter is greater in energy due to the proximity of the alkyl chain to the silica surface. This conformational change is expected to be fast because the barrier to linearization for the Si−O−Si angles in siloxanes ranges between 0.3 and 1.4 kcal mol^{-1}.[20] The conformers arising from **IIA** by rotation around the Si−C_1 σ-bond maintain the orientation of the Si−C_1 and C_2−H σ-bonds, although they differ in energy due to the distinct substituents at the oxygen atoms (Figure 3). For **IIB,** the silica surface limits the rotation around the Si−C_1 σ-bond.

Conformation **IIA** and its rotamers permit both the hyperconjugative interaction of the Si−C_1 and C_2−H σ-bonds and the approach of dioxirane **1** to the activated C_2 methylene group.[21] Conversely, none of the *anti* conformers **IA,B** permit the silicon β-effect. The most stable *anti* conformation **IA** is the least reactive of the series as the silica surface prevents the approach of dioxirane **1** to the C_2−H σ-bonds (Figure 3).[21]

The results shown in Table 1 suggest that the reactive *gauche* conformations **IIA,B** (Figure 3) are accessible for the T2 *n*-butyl groups on hybrid silicas **2** despite the apparently large steric size of the silica surface. The large Si−O σ-bond lengths and the Si−O−Si angles in silica and silicates, which range[20] between 1.624 and 1.742 Å and 140°−180°, respectively, and the presence of Q4 silicon atoms forming part of the inner silica matrix[22] surrounding the T2 *n*-butyl groups all provide a relatively large free space for conformational mobility and the approach of reactants from the solution. Figure 4 illustrates the spatial separation between the surface silanol groups provided by the adjacent Q4 silicon atoms for an idealized silica surface. The modest bias toward C_3 observed in the reactions of methyl-capped hybrid silicas **2A/OCH$_3$** and **2C/OCH$_3$** with dioxirane **1** (Table 1) is also indicative of the large separation between the surface silanol groups on the silica surface.

Dioxirane **1** did not react with the C_1 methylene groups of the *n*-butyl chains bonded to the silica surface despite the inductive activation of this position by the electropositive silicon atom and the relatively free access of dioxirane **1** to the C_1−H σ-bonds in the most stable *anti* and *gauche* conformations **I,IIA** (Figure 3).[21] These results are in agreement with the destabilization exerted by the silicon atom on electron deficiencies at the α-position[23] (silicon α-effect).

The location of the organic ligands on the silica surface determines differences in their reactivity. The *n*-butyl ligands on mesoporous hybrid silica **2A**, prepared by co-condensing *n*-butyltriethoxysilane and TEOS, are located mainly within the silica pores, whereas those on **2C**, grafted onto the chromatographic silica with a low pore surface, are distributed mainly on the external silica surface.[24] Kinetic experiments (Figure 1) show that dioxirane **1** reacted 13.8-fold faster with mesoporous silica **2A** compared with silica **2C** and 10.8-fold faster with methyl-capped mesoporous silica **2A/OCH$_3$** compared with **2C/OCH$_3$**. These results are attributed to the confinement[25] of dioxirane **1** within the silica mesopores in **2A** and **2A/OCH$_3$**, which determines an increased number of effective collisions with the organic ligands anchored to the pore walls. The differences in the surface geometry inside and outside the mesopores have minor effects on C_2/C_3 regioselectivities (Table 1).

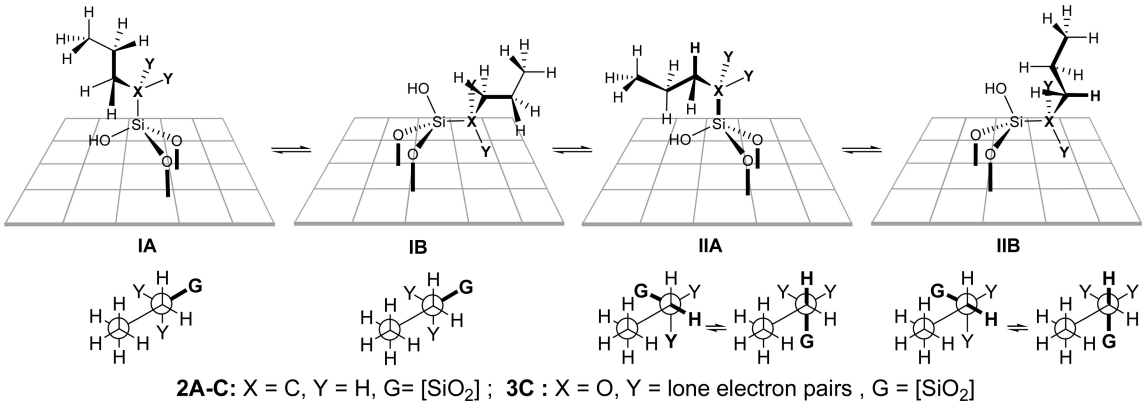


Figure 3. Most stable limit conformations *anti* (**I**) and *gauche* (**II**) for T2 *n*-butyl and *n*-butoxy groups bonded to silica surfaces. The silicon atom depicted in the figures belongs to the silica surface for **2A** and **3C** and is grafted onto the surface silanol groups for **2B** and **2C** (Chart 1).

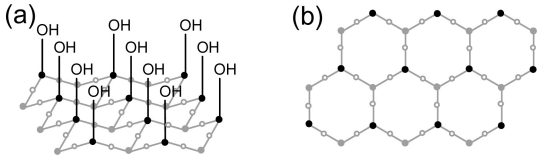


Figure 4. Idealized model of the silica surface depicted as the truncation of a network composed of siloxane rings containing six silicon atoms per ring placed at the vertices of the polygons with the oxygen atoms (○) midway on the sides.[22] The figures show the silanol groups (black dots) surrounded by Q4 silicon atoms (grey dots). (a) Side view (the figure ommits the Si−O σ-bonds connecting the Q4 silicon atoms to the inner silica matrix). (b) Top view.

Methylation of the surface silanol groups also had a significant impact on the reaction rate (Figure 1). Thus, hybrid silicas **2A** and **2C** react 6.2- and 4.8-fold faster than for **2A**/**OCH$_3$** and **2C**/**OCH$_3$**, respectively, while regioselectivity did not alter in correspondence with the drastic change on the silica surface. These results suggest a stronger adsorption and longer residence time of the highly polar dioxirane **1** on the hydrophilic silica surface, which contribute to facilitating the encounter with immobilized organic ligands.[26] Stabilization of the O-atom insertion-transition states by the surface silanol groups should not be disregarded as an additional factor that enhances the reaction rates.[9h,13]

Heterogeneous Reactions: *n*-Butoxy Chains. The chemical properties of silicon derivatives show that the SiX$_3$ (X = H, alkyl, NR$_2$, OR) groups efficiently delocalize the electron density from the O, N, and C atoms bonded to silicon into the highly polarized and low-lying antibonding orbitals of the Si-X σ-bonds (X = H, C, N, O).[27] For instance, silicon substituents strongly deactivate the positive charge densities at the α-position (silicon α-effect) despite the electropositive effect of silicon,[23] alkylsilanes, silanols, and silylamines are significantly more acidic than their corresponding carbon derivatives[28] and the oxygen and nitrogen atoms of silanols, siloxanes, silylethers, and silylamines are significantly less basic than alcohols, ethers, and amines.[29] Consequently, the O$_1$-atom lone electron pairs of the *n*-butoxy chains bonded to silica are not available for stabilizing the positive charge density developed at C$_2$ by the electrophilic attack of dioxirane **1**, and the *n*-butyl chain is inductively deactivated toward electrophiles. The same electronic effects accounted for the reactivity of the carboxylic acid esters of linear aliphatic alcohols toward dioxirane **1**, which react preferentially at the most distant methylene group from the substituent.[9e] Accordingly, the oxygenation reaction of the *n*-butoxy ligands bonded to silica was expected to follow the same trend.

Interestingly, the reactions of dioxirane **1** with hybrid silica **3C** took place exclusively in the C$_2$ methylene group, giving butanoic acid (**7**) as the only product (Table 1). These results evidence a strong activation of C$_2$−H σ-bonds, which cannot be attributed to the O$_1$-atom lone electron pairs. The most stable *anti* and *gauche* conformations for the *n*-butoxy chains bonded to Q2 and Q3 surface silicon atoms are **IA** and **IIA** in Figure 3. The former prevents the approach of dioxirane **1** to the C$_2$ methylene group, while the latter impedes the activation of the C$_2$−H σ-bonds by the O$_1$-atom lone electron pairs. It is worth noting that the steric hindrance exerted by the silica surface on the *n*-butyl chains is stronger for hybrid silica **3C** than it is for **2C** as the *n*-butyl ligands are connected to the surface silicon atoms through an oxygen bridge (Si−O−C$_1$) in the former and through a siloxane bridge (Si−O−Si−C$_1$) in the latter (Chart 1).

The results suggest that the Si−O$_1$ σ-bond connecting the silica matrix to the surface *n*-butyl groups is able to efficiently activate the C$_2$−H σ-bonds toward the electrophilic dioxirane **1**. Only conformation **IIA** (Figure 3) permits this interaction. The delocalizaton of the lone electron pairs of O-atoms within the silica matrix into the low-lying antibonding orbitals of Si−O$_1$ σ-bonds raises both the polarization and the energy of the bonding Si−O$_1$ σ-orbitals,[30] thus improving its ability to interact with adjacent empty orbitals. This electronic delocalization justifies also the highly ionic character of the Si−O σ-bonds of silica, the low basicity of its oxygen atoms, and the enhanced acidity of the surface silanol groups.[20]

Homogeneous Reactions: *n*-Butyl Chains. The steric and electronic effects operating in the oxygenation of *n*-butyl chains with dioxirane **1** were ascertained for model substrates **4a** (G = (CH$_3$)$_3$Si), **4b** (G = (CH$_3$)$_3$C) and **4c** (G = (CH$_3$O)$_3$Si) under homogeneous conditions (Scheme 2).

n-Butyltrimethylsilane (**4a**) reacted with dioxirane **1** mainly at C$_2$ (C$_2$/C$_3$ = 6.7, Scheme 2). C$_2$/C$_3$-regioselectivity did not match the large kinetic factors reported for the silicon β-effect in those reactions involving carbocations[16] given the lower electronic demand of electrophilic O-atom insertion in relation to heterolysis reactions. The oxygenation of *n*-butyltrimethoxysilane (**4c**, G = (CH$_3$O)$_3$Si) with dioxirane **1** also took place preferentially at C$_2$, although in this instance C$_2$/C$_3$ = 3.8 (Scheme 2), indicating a weaker electron-releasing β-effect from the substituent[18] than for **4a** (G = (CH$_3$)$_3$Si). This

dx.doi.org/10.1021/jo2019703 | J. Org. Chem. 2011, 76, 10129–10139

observation suggests that electronegative oxygen atoms slightly diminish the electron-releasing ability of the Si−C_1 σ-bond. The inductive electron-withdrawing character of the substituent[18] (σ_I = 0.04, estimated from the linear plot of the logarithm of the relative reaction rates found for this series versus the σ_I of the substituents)[31] helps diminish the C_2/C_3-regioselectivity found in relation to **4a** (G = $(CH_3)_3Si$).

Conversely, the oxygenation of 2,2-dimethylhexane (**4b**, G = $(CH_3)_3C$) took place preferentially at C_3 (C_2/C_3 = 0.12, Scheme 2) despite the inductive and hyperconjugative electron-releasing effects of the *tert*-butyl substituent. In this instance, conformations **II** with the G substituent and the ethyl group at C_2 in *gauche* fulfill the stereoelectronic requirement for the hyperconjugative activation of the C_2−H σ-bond and also allow the approach of dioxirane **1** to this position, while the most stable *anti* conformation **I** prevents both (Figure 5).

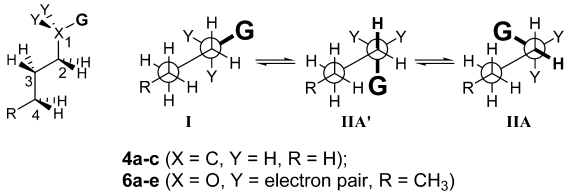


Figure 5. Conformational equilibrium of substrates **4** and **6**. C_2−H σ-bonds hyperconjugatively activated by the G−X_1 σ-bond are marked in boldface.

The regioselectivity found for **4b** (G = $(CH_3)_3C$) can then be rationalized in terms of the relative population of the conformers **I** and **II** (Figure 5), the conformational enthalpy for **4b** (G = $(CH_3)_3C$) being[32] $\Delta H^\circ \approx -3.5$ kcal mol^{-1}. By considering that the *anti* conformers react exclusively at C_3 while the *gauche* conformers react only at C_2, the Curtin−Hammett principle[33] establishes that the equilibrium constant and the population of the *anti* conformer are 184 and 99.5%, respectively. Thus, the kinetic ratio k_2/k_3 is 22, which is in agreement with the inductive and hyperconjugative electron-releasing effect of the *tert*-butyl substituent. Therefore, the steric bulkiness of the *tert*-butyl group inhibits the activation of the C_2−H σ-bonds of **4b** (G = $(CH_3)_3C$) by preventing both the *n*-butyl chain from adopting the conformation required for this interaction and dioxirane **1** from approaching this position. The magnitude of such a steric bias is lower for **4a** (G = $(CH_3)_3Si$) and **4c** (G = $(CH_3O)_3Si$) than it is for **4b** (G = $(CH_3)_3C$) since silyl substituents are smaller.[32] The results then indicate that the *tert*-butyl group (C_2/C_3 = 0.12, Scheme 2) is sterically larger than a silica nanoparticle (C_2/C_3 = 0.69−0.82, Table 1).

It is worth noting that the oxygenation at C_1 is suppressed for both **4a** (G = $(CH_3)_3Si$) and **4c** (G = $(CH_3O)_3Si$) (Scheme 2), while it occurs at a rate of 14% for **4b** (G = $(CH_3)_3C$) with a larger substituent at this position. It should be noted that the *gauche* substituents hindering the approach of dioxirane **1** to the C_2−H and C_1−H σ-bonds in 2,2-dimethylhexane (**4b**, G = $(CH_3)_3C$) are a *tert*-butyl group for the former and a methyl group for the latter. The steric preference for the C_1 position should be even stronger for **4a** (G = $(CH_3)_3Si$) and **4c** (G = $(CH_3O)_3Si$) as the Si−C σ-bonds are longer than C−C bonds. These results then evidence the destabilization exerted by the silicon atom on the electron deficiencies at the α-position (silicon α-effect).[15,23]

Homogeneous Reactions: *n*-Butoxy Chain. The set of model substrates **6** reacted with dioxirane **1** exclusively at C_2 (Scheme 3). The reaction product was butanoic acid (**7**) in all cases, which is in agreement with previously described[9i] reactions of ethers and acetals with dioxirane **1**.

The results show that the inductive electron-releasing alkyl and trimethylsilyl substituents in substrates **6a,b,e** (X = $(CH_3)_3Si$, $(CH_3)_3C$, and CH_3, respectively) actually diminished the oxygenation rate in relation to the hydrogen atom (Scheme 3), indicating a steric control of reactivity in these cases. In this instance, the most stable *anti* conformation **I** (Figure 5) permits the activation of the C_2−H σ-bonds by the oxygen lone electron pairs but prevents dioxirane **1** from approaching this position. Accordingly, the relative oxidation rates found for **6b,d,e** roughly correlate with the conformational energy values 4.9, 0, and 1.74 kcal mol^{-1} reported for the $(CH_3)_3C$, H, and CH_3 groups,[32] respectively. The reaction rate found for **6a** (X = $(CH_3)_3Si$) (Scheme 3) deviates from this trend since the conformational energy of the substituent (2.5 kcal mol^{-1})[32] would predict a reaction rate lower than for **6e** (X = CH_3). This deviation confirms that the Si−O_1 σ-bond in **6a** (X = $(CH_3)_3Si$) efficiently activates the C−H σ-bonds at β-position toward the electrophilic oxidant **1**.

The relative reaction rates $k_{Si(MeO)_3}/k_{tBu}$ for substrates **4** and **6** were 0.59 and 0.05, respectively (Schemes 2 and 3), indicating that the oxygen bridge between the alkyl chain and the trimethoxysilyl group amplifies the electron-withdrawing effect of this substituent by a factor of 11.8. However, orthosilicic acid ester **6c** (X = $(CH_3O)_3Si$) reacts exclusively at the methylene group bonded to the electron-withdrawing oxygen atom, which is in clear contrast with the efficient protection of this position toward dioxirane **1** described for aliphatic carboxylic acid esters.[9e]

Once again, these results suggest that the O-atom lone electron pairs of tetraalkoxysilanes efficiently delocalize into Si−O σ-bonds. This electronic effect increases the inductive deactivation of the *n*-butyl chain of orthosilicyc acid ester **6c** while it simultaneously renders the O_1-atom lone electron pairs less available to activate C_2−H σ-bonds toward dioxirane **1**. The strong β-activation observed for **6c** toward dioxirane **1** should thus be attributed to the hyperconjugative electron-releasing ability of the Si−O_1 σ-bond, which is boosted in this case by the electron delocalization from the three methoxy groups O-atoms into the Si−O_1 σ-bond. Conversely, the inductive deactivation dominates the reactivity of carboxylic acid esters of linear aliphatic alcohols, which react with methyl(trifluoromethyl)dioxirane (**1**) preferentially at the most distant C−H σ-bonds from the substituent.[9e] In these cases, the lower energy and polarization of the σ_{CO1} bonding orbitals compared to the σ_{SiO1}[30] prevents an efficient activation of the C_2−H σ-bond toward the electrophilic dioxirane **1**.

■ CONCLUSIONS

The oxygenation of the *n*-butyl and *n*-butoxy chains bonded to silica and trimethylsilyl, trimethoxysilyl, *tert*-butyl and methyl groups with methyl(trifluoromethyl)dioxirane (**1**) has revealed that (i) the silica matrix efficiently releases electron density toward the C_2 position of organic ligands covalently bonded to the surface; (ii) the silica surface provides a relatively large free space for conformational mobility of the surface ligands and the approach of reactants from the solution; (iii) both the silica surface's hydrophilic/hydrophobic character and the location of

dx.doi.org/10.1021/jo2019703 | J. Org. Chem. 2011, 76, 10129−10139

the organic ligands determine the reaction rates, although they do not significantly change the reaction regioselectivity; (iv) the steric inhibition of the oxygenation at the C_2 methylene group of substituted *n*-butyl chains is larger for the *tert*-butyl group than for a silica nanoparticle; (v) orthosilicic acid esters react preferentially at the methylene group adjacent to the oxygen atom, in contrast to carboxylic or sulfonic acid alkyl esters,[9e] which efficiently protect this position toward oxidation with **1**; (vi) the O-atoms lone pairs of tetralkoxysilanes and silica efficiently delocalize into the Si−O σ-bonds. These factors should be considered when performing chemical reactions on organic moieties bonded to silica surfaces.

The electronic and steric effects described herein can be readily extended to silicones, tetralkoxysilanes, and functional hybrid silicas of technological importance. Protecting the β-positions of these compounds with electronic, conformational, or steric shields would enhance their resistance to undergo oxidative degradation.

EXPERIMENTAL SECTION

General. Solvents were purified by standard procedures and distilled before use. Methyl(trifluoromethyl)dioxirane (**1**) in ketone-free dichloromethane solution was prepared as described,[34] and the peroxidic content of the solutions was determined by iodometric titration.[35] Glassware used for reactions with dioxirane **1** was carefully cleaned and washed with a solution of EDTA in bidistilled water (0.25 g L^{-1}) before use.

Tetraethoxysilane (TEOS), *n*-butyltrimethoxysilane (**4c**), *n*-butanol (**6d**), and *n*-butyl methyl ether (**6e**) are commercial products and were used as received. Commercial chromatographic silica Merck (0.040−0.063 mm particle size) was dried under vacuum at 60 °C prior to use.

Characterization of the hybrid materials **2** by ^{1}H NMR was performed by dissolving 50 mg of the solid in 1 mL of a solution of 4.9 M NaOH and 0.15 M methanol in deuterated water.[6] Nitrogen adsorption−desorption isotherms were determined at 77 K. Average pore width was derived using the BJH model[36] on the desorption branch of the nitrogen adsorption isotherms. Transmission electron micrographs were collected at an acceleration field of 200 kV. ^{29}Si MAS solid-state NMR spectra were recorded on a spectrometer equipped with a 7 mm CP-MAS BB/H probe at a resonance frequency of 79.45 MHz. Magic angle spinning speed was 4.5 kHz. A 90° single pulse of 6 μs was used with an acquisition time of 0.05 s and a relaxation delay of 20 s. Chemical shifts (δ, ppm) are relative to tetramethylsilane (TMS).

Synthesis of *n*-Butyl-Functionalized Mesoporous Silica 2A.[37,38] A stirred solution of 4.8 g (0.013 mol) of cetyltrimethylammonium bromide (CTAB) in 240 mL of bidistilled water at 27 °C was treated with 16 mL of a 32% aqueous solution of NH_4OH. Afterward, 20 mL (0.089 mol) of tetraethoxysilane (TEOS) and 0.5 mL (2.615 mmol) of *n*-butyltrimethoxysilane were added at once, and the mixture was stirred at 27 °C for 3 h and then allowed to stand unstirred overnight. The solid material was filtered, washed with bidistilled water until neutral pH, washed with a 0.1 M solution of HCl in aqueous methanol at 70 °C, filtered, and then washed at 90 °C with 0.1 M aqueous solution of HCl. After filtration, the washing cycles were repeated until ^{1}H NMR analysis[6] showed complete removal of surfactant. The solid material was dried under vacuum at 10 mbar and 60 °C, obtaining about 5 g of **2A** functionalized with 0.57 mmol of *n*-butyl ligands g^{-1}, as shown by ^{1}H NMR.[6] Nitrogen adsorption isotherms showed a BET surface area of 971.094 m^2 g^{-1} with a total pore volume of 1.176174 mL g^{-1} and an average pore width of 4.7809 nm.

Synthesis of *n*-Butyl-Functionalized Mesoporous Silica 2B.[37,38] Mesoporous silica was prepared following the same procedure described for **2A** using TEOS as the only alkoxysilane. To a suspension of 9 g of 20% hydrated mesoporous silica in 150 mL of toluene was added 0.87 mL (4.565 mmol) of *n*-butyltrimethoxysilane under stirring. The mixture was refluxed with a Dean−Stark apparatus for 12 h. The solid material was filtered, washed with toluene and dichoromethane, and dried under vacuum at room temperature. ^{1}H NMR analysis[6] of the hybrid material showed 0.5 mmol of ligands per gram of silica. Nitrogen adsorption isotherms showed a BET surface area of 964.9831 m^2 g^{-1} with a total pore volume of 0.912062 mL g^{-1} and an average pore width of 3.7273 nm.

Synthesis of *n*-Butyl-Functionalized Chromatographic Silica 2C.[38] To a suspension of 10 g of 20% hydrated chromatographic silica (Merck, 0.040−0.063 mm particle size) in 150 mL of toluene was added 0.96 mL (5.00 mmol) of *n*-butyltrimethoxysilane under stirring. The mixture was refluxed with a Dean−Stark apparatus for 12 h. The solid material was filtered, washed with toluene and dichoromethane, and dried under vacuum at room temperature. ^{1}H NMR analysis[6] of the hybrid material showed 0.5 mmol of ligand per gram of silica. Nitrogen adsorption isotherms showed a BET surface area of 438.3312 m^2 g^{-1} with a total pore volume of 0.607783 mL g^{-1} and a average pore width of 4.1655 nm.

Synthesis of *n*-Butoxy-Functionalized Chromatographic Silica 3C.[39] To a suspension of 4 g of anhydrous chromatographic silica (0.040−0.063 mm particle size) in 50 mL of toluene were added 0.19 mL (2.05 mmol) of *n*-butanol and two drops of concentrated H_2SO_4. The suspension was refluxed for 12 h. The solid material was filtered, washed with toluene and dichloromethane, and dried under vacuum at room temperature. ^{1}H NMR analysis[6] of the solid material showed 0.4 mmol of ligand per gram of silica.

Synthesis of *n*-Butyl-Functionalized Silicas 2A(OCH_3) and 2C(OCH_3). General Procedure.[39] To a suspension of the hybrid material **2** in anhydrous methanol (2.5 g in 150 mL) were added two drops of concentrated H_2SO_4, and the mixture was refluxed for 12 h. The solid material was filtered, washed with anhydrous methanol, dried under vacuum at room temperature, and analyzed by ^{1}H NMR using ethanol as internal standard.[6] N_2 adsorption isotherms showed BET surface areas of 1157.2061 m^2 g^{-1} [**2A**(OCH_3)], 976.3334 m^2 g^{-1} [**2B**(OCH_3)], and 411.5063 m^2 g^{-1} [**2C**(OCH_3)] with total pore volumes of 1.591989 mL g^{-1} [**2A**(OCH_3)], 0.912409 mL g^{-1} [**2B**(OCH_3)], and 0.617666 mL g^{-1} [**2C**(OCH_3)] and average pore widths of 4.8768 nm [**2A**(OCH_3)], 3.6393 nm [**2B**(OCH_3)], and 5.5624 nm [**2C**(OCH_3)].

Hydration of Hybrid Silicas 2A,B and 2C. The anhydrous hybrid material **2** was treated with the desired amount of bidistilled water in a tightly closed glass vial under magnetic stirring for 1 h at 20 °C.

***n*-Butyltrimethylsilane (4a) [1000-49-3].**[40] To a stirred solution of 10 mL (78.8 mmol) of trimethylchlorosilane in 40 mL of anhydrous diethyl ether at −78 °C was added 40 mL of a 2 M solution of *n*-butyllithium in pentane (80 mmol) dropwise under inert atmosphere. The reaction mixture was stirred until it reached room temperature (17 h) and then treated with 30 mL of distilled water for 10 min. The organic layer was separated, and the aqueous phase was extracted with 30 mL of diethyl ether. The combined organic phases were dried over magnesium sulfate and filtered. The solvent was removed under vacuum, and the residue was distilled, collecting the fraction distilling at 110−120 °C (4.40 g, 47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.3 (m, 4H), 0.9 (t, 3H), 0.5 (m, 2H), 0.0 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.7, 26.3, 16.5, 13.9, 0.1. EM (EI$^+$, 70 eV): *m*/*z* (rel abund) 130 (2, [M$^+$]), 115 (28), 73 (100), 59 (34), 45 (7), 43 (7).

4-Trimethylsilyl-2-butanone (5a(C3)) [13506-88-2]. A mixture of 1 g of 4-trimethylsilyl-3-butyn-2-one and 5 mg of palladium on carbon in 2 mL of pentane was allowed to react under hydrogen at normal pressure for 20 h, at room temperature and under stirring. The mixture was filtered, and the solid catalyst was thoroughly washed with pentane. The solvent was removed under vacuum to yield 1 g of a colorless liquid (97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.4 (m, 2H), 2.1 (s, 3H), 0.7 (m, 2H), 0.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 210.1, 38.3, 29.2, 10.4, 0.1. EM (EI$^+$, 70 eV): *m*/*z* (rel abund) 144 (17, [M$^+$]), 129 (85), 101 (3), 75 (100), 73 (78), 59 (7), 43 (19).

General Procedure for the Preparation of Ketones 5b(C1−3). Preparation of 2,2-Dimethyl-3-hexanone (5b(C1)) [5405-79-8].[41] A. To a stirred solution of 2.15 g (28.6 mmol) of butyraldehyde

dx.doi.org/10.1021/jo2019703 | J. Org. Chem. 2011, 76, 10129−10139

in 20 mL of anhydrous diethyl ether cooled to −78 °C was added 16.5 mL of a 2.0 M solution of *tert*-butyllithium in pentane (32.5 mmol) dropwise under inert atmosphere. The solution was stirred at −78 °C for 1 h and then at room temperature for additional 2.5 h. The mixture was poured into 75 mL of saturated aqueous ammonium chloride, the layers were separated, and the aqueous phase was extracted twice with ether. The combined organic phases were washed with water and dried over magnesium sulfate. The solvent was removed under vacuum to yield 2.8 g (75%) of 2,2-dimethyl-3-hexanol. Gas chromatography analysis of this material showed that it was 96% pure, and it was used in the next step without further purification.

B. To a stirred suspension of pyridinium chlorochromate in 50 mL of dichloromethane was added a solution of 2.8 g of 2,2-dimethyl-3-hexanol in 50 mL of dichloromethane dropwise at room temperature, and the mixture was stirred overnight. The organic layer was decanted, and the dark residue was triturated three times with diethyl ether. The combined solvents were evaporated under vacuum, and the residue was distilled to give 1.6 g (44%) of a light yellow liquid.

2,2-Dimethyl-3-hexanone (5b(C1)) [5405-79-8]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.4 (t, J = 7.35 Hz, 2H), 1.5−1.6 (m, 2H), 1.1 (s, 9H), 0.8 (t, J = 7.35 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.9, 44.0, 38.3, 26.3, 17.2, 13.7. EM (EI$^+$, 70 eV): m/z (rel abund) 128 (48, [M$^+$]), 113 (4), 71(80), 57(100), 43(62), 41(55).

5,5-Dimethyl-3-hexanone (5b(C2)) [5340-30-7]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.3 (q, J = 7.16 Hz, 2H), 2.2 (s, 2H), 0.9 (s, 9H), 0.8−0.9 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.4, 38.1, 30.9, 29.7, 7.6. EM (EI$^+$, 70 eV): m/z (rel abund) 128 (15, [M$^+$], 113 (3), 99 (21), 72 (12), 57 (100), 43 (8), 41 (10).

5,5-Dimethyl-2-hexanone (5b(C3)) [14272-73-2]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.3−2.4 (m, 2H), 2.1 (s, 3H), 1.3−1.4 (m, 2H), 0.8 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.3, 37.2, 29.7, 29.3, 29.0. EM (EI$^+$, 70 eV): m/z (rel abund) 128 (6, [M$^+$], 113 (20), 95 (25), 72 (28), 57 (63), 55 (12), 43 (100), 41 (18).

4-Trimethoxysilyl-2-butanone (5c(C3)). *A. 2-Methoxy-3-butene [17351-24-5].*[42] To a stirred suspension of 2.27 g of potassium hydride (56.8 mmol) in 40 mL of anhydrous dimethylsulfoxide was added 1.40 g of 3-buten-2-ol (19.4 mmol) dropwise under inert atmosphere. The mixture was stirred for 7 h at room temperature, and then 1.20 mL of methyl iodide (19.3 mmol) was added at once. The reaction was stirred for 24 h at room temperature, and then the volatile products were collected by distilling under vacuum at room temperature. The distillate was redistilled at 0 °C under vacuum to obtain 1.1 g of a colorless liquid (66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.6 (m, 1H), 5.0 (m, 2H), 3.6 (m, 1H), 3.2 (s, 3H), 1.2 (d, (J = 6.4 Hz), 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.0, 116.0, 78.5, 55.9, 21.1. EM (EI$^+$, 70 eV): m/z (rel abund) 86 (40, [M$^{+\cdot}$]), 85 (14), 71 (100), 59 (31), 55 (56), 41 (50).

B. 4-(Trimethoxysilyl)-2-methoxybutane.[43] A stirred mixture of 2.6 g of 2-methoxy-3-butene (30 mmol), 10 mL of trimethoxysilane (78.6 mmol), and 90 drops of a 0.03 M solution of hexachloroplatinic acid in isopropanol was allowed to react at 60 °C for 14 h under inert atmosphere. The volatile products were evaporated under vacuum, and the residue was distilled under vacuum to obtain 3.74 g of a colorless liquid (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.5 (s, 9H), 3.3 (s, 3H), 3.2 (m, 1H), 1.4 (m, 2H), 1.0 (d, (J = 6.12 Hz), 3H), 0.6 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 78.3, 56.0, 50.6, 28.8, 18.5, 4.4. EM (EI$^+$, 70 eV): m/z (rel abund) 208 (1, [M$^{+\cdot}$]), 176 (14), 161 (97), 153 (31), 121 (100), 107 (12), 91 (75), 59 (99). Exact mass calcd for $C_8H_{20}O_4Si$ 208.113088. Found: 208.114102.

C. 4-(Trimethoxysilyl)-2-butanone [5c(C3)].[44] To a stirred solution of 0.027 g of 4-(trimethoxysilyl)-2-methoxybutane (0.13 mmol) in 3 mL of methylene chloride, cooled to −15 °C, was added 2.17 mL of a 0.18 M solution of methyl(trifluoromethyl)dioxirane (**1**) in methylene chloride at once. The reaction was stirred for 21 h at −15 °C, and then the solvent was removed under vacuum to yield 0.024 g of a colorless liquid (95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.5 (s, 9H), 2.4 (m, 2H), 2.0 (s, 3H), 0.7 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.9, 50.6, 36.8, 29.4, 2.6. EM (EI$^+$, 70 eV): m/z (rel abund) 191 (1, [M$^+$-1]), 177 (7), 163 (46), 160 (23), 145 (5), 121 (100), 107 (17), 91 (42), 77 (8), 59 (10), 43 (6). Exact mass calcd for $C_7H_{16}O_4Si$ 192.081788, found 192.082551.

n-Butoxytrimethylsilane (6a) [1825-65-6]..[45] A stirred mixture of 10.1 g of hexmethyldisilazane (0.1 mol), 13.3 g of *n*-butanol (0.18 mol), and two drops of trimethylchlorosilane was heated to reflux for 12 h under inert atmosphere. After cooling to room temperature, the mixture was distilled under ambient pressure to obtain 18 g of the fraction distilling at 110 °C (68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.5 (c, 2H), 1.4 (m, 2H), 1.3 (m, 2H), 0.8 (t, 3H), 0.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 62.5, 35.0, 19.1, 14.0, −0.3. EM (EI$^+$, 70 eV): m/z (rel abund) 146 (1, [M$^{+\cdot}$], 13 (100), 115 (3), 103 (49), 89 (30), 75 (90), 73 (70), 59 (10), 45 (15).

n-Butyl-tert-butylether (6b) [1000-63-1].[46] To a stirred solution of 10 g of potassium *tert*-butoxide (89 mmol) in 100 mL of anhydrous dimethylsulfoxide was added 12.1 g of *n*-butylbromide (89 mmol) dropwise at 10 °C. The reaction mixture was allowed to warm and stand under stirring for 8 h at room temperature. The mixture was distilled under vacuum at −20 °C. The crude was redistilled at normal pressure to collect 6 g (52%) of the fraction distilled at 75−78 °C as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.4 (c, 2H), 1.6 (m, 2H), 1.4 (m, 2H), 1.3 (s, 9H), 0.9 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 72.5, 69.3, 32.9, 31.3, 19.5, 14.1. EM (EI$^+$, 70 eV): m/z (rel abund) 130 (0.1, [M$^+$], 115(40), 87 (2), 73 (1), 59 (100), 57 (75), 43 (8), 41 (20).

n-Butoxytrimethoxysilane (6c) [18395-47-6].[47] To a mixture of 41.6 g of tetramethoxysilane (0.27 mol), 0.50 g of anhydrous sodium bicarbonate, and 2 drops of concentrated sulfuric acid in 250 mL of anhydrous diethyl ether cooled to −20 °C was added a solution of 4 g of *n*-butanol (0.06 mol) in 50 mL of anhydrous diethyl ether dropwise with stirring under inert atmosphere. The reaction was stirred at −20 °C for 1 h. The mixture was distilled at ambient pressure to remove the volatile products (120 °C). After cooling to room temperature the residue was distilled at 10 mmHg to collect 7 g of the fraction distilling at 55 °C (65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.7 (c, 2H), 3.5 (s, 9H), 1.5 (m, 2H), 1.3 (m, 2H), 0.8 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 63.4, 51.2, 34.4, 18.8, 13.7. EM (EI$^+$, 70 eV): m/z (rel abund) 194 (1, [M$^+$], 193 (2), 151 (100), 139 (33), 121 (95), 107 (30), 91 (47), 61 (10).

General Procedure for Oxidation of *n*-Butyl-Functionalized Silicas 2 in Dichloromethane. The oxidation reactions were carried out in a jacketed amber flask connected to a recirculating cooling device set at −15.0 °C. A suspension of 0.1 g of hybrid silica **2** in dichloromethane was treated with a freshly prepared 0.2 M dichloromethane solution of methyl(trifluoromethyl)dioxirane (**1**) (initial molar ratio **2**:**1** 1:3). The mixture was maintained at −15 °C under stirring for 12 h. The supernatant solution was directly analyzed by gas chromatography, and then the solvent was removed under vacuum. GC−MS and GC analysis[6] of the hybrid material was performed by adding the solid in small portions to a stirred 35% aqueous solution of hydrogen fluoride (2.5 mL) contained in a propylene test tube cooled at 0 °C. To this solution was added 1.5 mL of cold dichloromethane, and the mixture was stirred at 0 °C for 10 min. The organic phase was transferred via a micropipet with a plastic tip into a cold polypropylene vial containing anhydrous magnesium sulfate and sodium hydrogenphosphate and then analyzed by GC and GC−MS. These operations were performed at 0 °C in polypropylene containers as trifluorosilanes are volatile products that efficiently stick to glass surfaces. In order to obtain reproducible results the contact of the solutions with glass must be carefully avoided along the analysis procedure. C_3/C_2 ratios were obtained from the peak areas corresponding to 2-butanone and **5**(**C3**) in the gas chromatograms.

Solventless Oxidation of *n*-Butyl-Functionalized Silicas 2. *General Procedure.* The hybrid silica material **2** (0.1 g) was placed into a 50 mL cylindrical glass column with a glass filter at the bottom, which was then connected to a 25 mL flask containing a freshly prepared dichloromethane 0.2 M solution of methyl-(trifluoromethyl)dioxirane (**1**) (initial molar ratio **2**:**1** 1:3) The system was tightly closed, protected from light, and allowed to stand at 3 °C for 6 days. GC and GC−MS analysis of the hybrid material was performed[6] as described above.

n-Butyltrifluorosilane. EM (EI^+, 70 eV): m/z (rel abund) 142 (10, [M^+]), 127 (15), 113 (100), 105 (6), 93 (30), 85 (24), 43 (62). Exact mass calcd for $C_4H_9F_3Si$ 142.042562, found 142.042752.

4-Trifluorosilyl-2-butanone. EM (EI^+, 70 eV): m/z (rel abund) 156 (11, [M^+]), 141 (4), 137 (4), 113 (20), 93 (11), 85 (15), 55 (5), 43 (100). Exact mass calcd for $C_4H_7F_3OSi$ 156.021827, found 156.021998.

Oxidation of *n*-Butoxy-Functionalized Chromatographic Silica 3C with Dioxirane 1. The oxidation reactions were carried out in a jacketed amber flask connected to a recirculating cooling device set at −15.0 °C. A suspension of 0.2 g of hybrid silica **3** in dichloromethane was treated with a freshly prepared 0.2 M dichloromethane solution of methyl(trifluoromethyl)dioxirane (**1**) (initial molar ratio **2**:**1** 1:3). The mixture was maintained at −15 °C under stirring for 12 h. The supernatant solution was directly analyzed by gas chromatography, and then the solvent was removed under vacuum. The solid material was dissolved in 1 mL of a 4.9 M NaOH solution in deuterated water containing 1,2-ethanediol (0.15 M) as internal standard and analyzed by ^{1}H NMR.[6]

Decay of Dioxirane 1 in the Oxidation of *n*-Butyl-Functionalized Hybrid Silicas 2A,B and 2A,B(OCH$_3$). The experiments were carried out in a jacketed amber flask connected to a recirculating cooling device set at −15.0 °C. To a suspension of 0.15 g of hybrid silica **2** (0.52 mmol of ligand per gram of silica) in 5 mL of a 0.015 M dichloromethane solution of methyl *p*-chlorobenzoate as internal standard was added 0.325 mL of a freshly prepared 0.11 M dichloromethane solution of dioxirane **1** at once. The initial concentration of dioxirane **1** in the reaction mixture was in all cases 0.0067 M. Aliquots of 0.1 mL withdrawn from the reaction mixture were quenched at 0 °C with 0.1 mL of a 0.023 M solution of cyclopentanol in dichloromethane. The resulting solutions were directly analyzed by gas chromatography. The concentration of dioxirane (**1**) was established from the concentration of cyclopentanone in the aliquots. The relation of peak areas were corrected by the response factor of cyclopentanone versus standard, which were obtained previously from calibration curves under the same analysis conditions.

Oxidation of Substrates 4 and 6 with Methyl(trifluoromethyl)dioxirane (1). General Procedure. To a 0.02 M solution of **4** in dichloromethane, cooled to −15 °C, was added an aliquot of a thermostatted methyl(trifluoromethyl)dioxirane (**1**) solution in dichloromethane (initial **4**:**1** molar ratio 1:2.2) at once. The reaction was stirred in the dark at −15 °C for 8−10 h. A 0.1 mL aliquot of the reaction mixture was quenched with 2,3-dimethyl-2-butene and directly analyzed by GC and GC−MS. The products were identified by comparison with authentic samples, and the regioselectivity was determined from the integration of the peak areas corresponding to each isomer. The selectivity values reported are the average of at least three independent experiments. GC and GC−MS analyses of the reaction mixtures corresponding to substrates **4a,c** were performed with an injector temperature of 150 °C in order to minimize the rearrangement of products **5a,c(C2)** to give the corresponding O-sililated enolethers. Compounds **5a,c(C2)** were characterized from the mixture of products **5a,c(C2)** and **5a,c(C3)** obtained from the reaction of **4a,c** with dioxirane **1** performed with an initial **2**:**1** molar ratio 1:4, following the same procedure. The solvent was evaporated under vacuum, and the residue was dissolved in deuterochloroform and analyzed by ^{1}H and ^{13}C NMR.

1-(Trimethylsilyl)-2-butanone [5a(C2)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.4 (q, J = 7.2 Hz, 2H), 2.1 (s, 2H), 1.0 (t, J = 7.2 Hz, 3H), 0.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 210.0, 36.9, 29.4, 7.8, 1.9. EM (EI^+, 70 eV): m/z (rel abund) 144 (10, [M^+·]), 129 (53), 115 (85), 99 (5), 75 (77), 73 (100), 59 (5), 45 (11). Exact mass calcd for $C_7H_{16}OSi$ 144.097042, found 144.097813.

1-(Trimethoxysilyl)-2-butanone [5c(C2)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.5 (s, 9H), 2.4 (q, J = 7.2 Hz, 2H), 2.2 (s, 2H), 1.0 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.6, 50.8, 37.1, 30.7, 7.9. EM (EI^+, 70 eV): m/z (rel abund) 192 (1, [M^+·]), 177 (1), 163 (68), 160 (6), 145 (1), 121 (100), 107 (7), 91 (23), 77 (6), 59 (7). Exact mass calcd for $C_7H_{16}O_4Si$ 192.081788, found 192.080890.

2-(Trimethylsililoxy)-1-butene. EM (EI^+, 70 eV): m/z (rel abund) 144 (11, [M^+·]), 129 (2), 116 (2), 101 (9), 73 (100), 59 (3), 45 (9). Exact mass calcd for $C_7H_{16}OSi$ 144.097042, found 144.096559.

2-(Trimethoxysililoxy)-1-butene. EM (EI^+, 70 eV): m/z (rel abund) 192 (1, [M^+·]), 178 (1), 149 (2), 136 (1), 121 (100), 104 (1), 91 (27), 77 (1), 61 (4). Exact mass calcd for $C_7H_{16}O_4Si$ 192.081788, found 192.080844.

Determination of the Relative Rates of Oxygenation with Dioxirane 1 for Substrates 4 and 6. *General Procedure.* To a stirred 0.02 M solution (2 mL) of substrates **4a**, **4c** and methyl *p*-chlorobenzoate in dichloromethane, thermostatted at −15 ± 0.1 °C, was added an aliquot of a thermostatted 0.1 M solution of methyl(trifluoromethyl)dioxirane (**1**) in dichloromethane. The initial molar ratio **4a**:**4c**:**1** was 1:1:1 in all cases. The reaction was carried out under air and protected from the light for 6 h. The reaction mixtures were directly analyzed by GC. The substrate conversions were obtained from the areas of the starting materials at t = 0 and after the reaction was complete, by applying the equation $k_{TMOS}/k_{TMS} = [(A_{4a}/A_{ST})_0 - (A_{4a}/A_{ST})_t]/[(A_{4c}/A_{ST})_0 - (A_{4c}/A_{ST})_t]$. The relative reaction rates were the averages of at least three independent experiments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Electron micrographs and MS and ^{1}H, ^{13}C, ^{29}Si-CP-MAS NMR spectra for starting materials and reaction products. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

Financial support from the Spanish Dirección General de Investigación (CTQ2010-21172, CTQ2007-65251/BQU, and CTQ2007-30762-E) and Consolider Ingenio 2010 (CSD2007-00006) is gratefully acknowledged. J.M.F. and A.A.A. thank the Spanish Ministerio de Educación y Ciencia for fellowships. We also thank the SCSIE (Universidad de Valencia) for their instrumental facilities.

■ REFERENCES

(1) (a) Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3216. (b) Descalzo, A. B.; Martínez-Mañez, R.; Sancenón, F.; Hoffmann, K.; Rurak, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 5924.

(2) (a) Zhang, C.; Li, H.; Jiang, D.; Yang, Q. *Chem. Commun.* **2007**, 547. (b) McMorn, P.; Hutchings, G. J. *Chem. Soc. Rev.* **2004**, *33*, 108. (c) DeVos, D. E.; Dams, M.; Sels, B. F.; Jacobs, P. A. *Chem. Rev.* **2002**, *102*, 3615.

(3) Stein, A.; Melde, B. J.; Schroden, R. C. *Adv. Mater.* **2000**, *12*, 1403−1419.

(4) (a) Copéret, C. *Chem. Rev.* **2010**, *110*, 656−680. (b) Gölzhäuser, A.; Wöll, C. *Chem. Phys. Chem.* **2010**, *11*, 3201−3213. (c) Bonifazi, D.; Mohnani, S.; Llanes-Pallas, A. *Chem. Eur. J.* **2009**, *15*, 7004−7025. (d) Kind, M.; Wöll, C. *Prog. Surf. Sci.* **2009**, *84*, 230−278. (e) Murray, R. W. *Chem. Rev.* **2008**, *108*, 2688−2720. (f) Bard, A.; Abruña, H. D.; Chidsey, C. E.; Faulkner, L. R.; Feldberg, L. R.; Itaya, K.; Majda, M.; Melroy, O.; Murray, R. W.; Porter, M. D.; Soriaga, M. P.; White, H. S. *J. Phys. Chem.* **1993**, *97*, 7147−7173.

(5) (a) Gajan, D.; Levine, D.; Zocher, E.; Copéret, C.; Lesage, A.; Emsley, L. *Chem. Sci.* **2011**, *2*, 928−931. (b) Maishal, T. K.; Boualleg, M.; Bouhrara, M.; Copéret, C.; Jeanneau, E.; Veyre, L.; Thieuleux, C. *Eur. J. Inorg. Chem.* **2010**, 5005−5010. (c) Gajan, D.; Guillois, K.; Delichère, P.; Basset, J. M.; Candy, J. P.; Caps, V.; Copéret, C.; Lesage, A.; Emsley, L. *J. Am. Chem. Soc.* **2009**, *131*, 14667−14669. (d) Wöll, C.

Angew. Chem., Int. Ed. **2009**, *48*, 8406–8408. (e) Chelmowski, R.; Käfer, D.; Köster, S. D.; Klasen, T.; Winkler, T.; Terfort, A.; Metzler-Nolte, N.; Wöll, C. *Langmuir* **2009**, *25*, 11480–11485. (f) Xie, Y.; Sharma, K. K.; Anan, A.; Wang, G.; Biradar, A. V.; Asefa, T. *J. Catal.* **2009**, *265*, 131–140. (g) Baish, B.; Raffa, D.; Jung, U.; Magnussen, O. M.; Nicolas, C.; Lacour, J.; Kubitschke, J.; Herges, R. *J. Am. Chem. Soc.* **2009**, *131*, 442–443. (h) Kidder, M. K.; Buchanan, A. C. III *J. Phys. Chem. C* **2008**, *112*, 3027–3031. (i) Dabestani, R.; Kidder, M.; Buchanan, A. C. III *J. Phys. Chem. C* **2008**, *112*, 11468–11475. (j) Sharma, K. K.; Buckley, R. P.; Asefa, T. *Langmuir* **2008**, *24*, 14306–14320. (k) Tsvelikhovsky, D.; Pessing, D.; Avnir, D.; Blum, J. *Adv. Synth. Catal.* **2008**, *350*, 2856–2858. (l) Sharma, K. K.; Anan, A.; Buckley, R; P..; Ouellette, W.; Asefa, T. *J. Am. Chem. Soc.* **2007**, *130*, 218–228. (m) Sharma, K. K.; Asefa, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 2879–2882. (n) Kidder, M. K.; Britt, P. F.; Zhang, Z.; Dai, S.; Hagaman, E. W.; Chaffee, A. L.; Buchanan, A. C. III *J. Am. Chem. Soc.* **2005**, *127*, 6353–6360. (o) Buchanan, A. C. III; Kidder, M. K.; Britt, P. F. *J. Phys. Chem. B* **2004**, *108*, 16772–16779. (p) Gelman, F.; Blum, J.; Avnir, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 3647–3649. (q) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27–36. (r) Frenkel-Mullerad, H.; Avnir, D. *Chem. Mater.* **2000**, *12*, 3754–3759. (s) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867–871. (t) Rottman, C.; Grader, G.; De Hazan, Y.; Melchior, S.; Avnir, D. *J. Am. Chem. Soc.* **1999**, *121*, 8533–8543.

(6) Mello, R.; Olmos, A.; Varea, T.; González-Núñez, M. E. *Anal. Chem.* **2008**, *80*, 9355–9359.

(7) (a) Curci, R.; D'Accolti, L.; Fusco, C. *Acc. Chem. Res.* **2006**, *39*, 1–9. (b) Adam, W.; Saha-Moller, C. R.; Ganeshpure, P. A. *Chem. Rev.* **2001**, *101*, 3499. (c) Adam, W.; Smerz, A. K. *Bull. Soc. Chim. Belg.* **1996**, *105*, 581. (d) Clennan, E. L. *Trends Org. Chem.* **1995**, *5*, 231. (e) Adam, W.; Hadjiaropoglou, L.; Curci, R.; Mello, R. *Organic Peroxides*; Wiley: Chichester, 1992; pp 195–219.

(8) (a) Freccero, M.; Gandolfi, R.; Sarzi-Amadè, M.; Rastelli, A. *J. Org. Chem.* **2003**, *68*, 811–823. (b) Shustov, G. V.; Rauk, A. *J. Org. Chem.* **1998**, *63*, 5413–5422. (c) Du, X.; Houk, K. N. *J. Org. Chem.* **1998**, *63*, 6480–6483. (d) Glukhovtsev, M. N.; Canepa, C.; Bach, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 10528–10533. (e) Bach, R. D.; Andrés, J. L.; Su, M.-D.; McDouall, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5768–5775.

(9) (a) Mello, R.; Royo, J.; Andreu, C.; Báguena-Añó, M.; Asensio, G.; González-Núñez, M. E. *Eur. J. Org. Chem.* **2008**, 455–466. (b) González-Núñez, M. E.; Royo, J.; Mello, R.; Báguena, M.; Martínez-Ferrer, J.; deArellano, C. R.; Asensio, G.; Prakash, G. K. S. *J. Org. Chem.* **2005**, *70*, 7919–7924. (c) González-Núñez, M. E.; Castellano, G.; Andreu, C.; Royo, J.; Báguena, M.; Mello, R.; Asensio, G. *J. Am. Chem. Soc.* **2001**, *123*, 7487–7491. (d) González-Núñez, M. E.; Royo, J.; Castellano, G.; Andreu, C.; Boix, C.; Mello, R.; Asensio, G. *Org. Lett.* **2000**, *2*, 831–834. (e) Asensio, G.; Castellano, G.; Mello, R.; González-Núñez, M. E. *J. Org. Chem.* **1996**, *61*, 5564–5566. (f) Asensio, G.; Mello, R.; González-Núñez, M. E.; Castellano, G.; Corral, J. *Angew. Chem., Int. Ed.* **1996**, *35*, 217–218. (g) Kuck, D.; Schuster, A.; Fusco, C.; Fiorentino, M.; Curci, R. *J. Am. Chem. Soc.* **1994**, *116*, 2375. (h) Asensio, G.; González-Núñez, M. E.; Mello, R.; Boix-Bernardini, C.; Adam, W. *J. Am. Chem. Soc.* **1993**, *115*, 7250. (i) Curci, R.; D'Accolti.; Fiorentino, M.; Fusco, C.; Adam, W.; González-Núñez, M. E.; Mello, R. *Tetrahedron Lett.* **1992**, *33*, 4225–4228.

(10) Lesaint, C.; Lebeau, B.; Marichal, C.; Patarin, J. *Microporous Mesoporous Mater.* **2005**, *83*, 76–84.

(11) (a) Zhao, X. S.; Lu, G. Q.; Millar, G. J. *Ind. Eng. Chem. Res.* **1996**, *35*, 2075. (b) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, E. M.; Cresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schelenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(12) Ossenkamp, G. C.; Kemmitt, T.; Johnston, J. H. *Chem. Mater.* **2001**, *13*, 3975–3980.

(13) (a) Asensio, G.; Boix-Bernardini, C.; Andreu, C.; González-Núñez, M. E.; Mello, R.; Edwards, J. O.; Carpenter, G. B. *J. Org. Chem.* **1999**, *64*, 4705–4711. (b) Asensio, G.; Mello, R.; Boix-Bernardini, C.; González-Núñez, M. E.; Castellano, C. *J. Org. Chem.* **1995**, *60*, 3692–3699. (c) Murray, R. W.; Gu, D. *J. Chem. Soc,. Perkin Trans.* **1993**, *2*, 2203.

(14) (a) Brindza, M. R.; Walker, R. A. *J. Am. Chem. Soc.* **2009**, *131*, 6207–6214. (b) Mamdouh, W.; Uji-i, H.; Ladislaw, J. S.; Dulcey, A. E.; Percec, V.; DeSchryver, F. C.; DeFeyter, S. *J. Am. Chem. Soc.* **2005**, *128*, 317–325. (c) Zhang, X.; Steel, W. H.; Walker, R. A. *J. Phys. Chem. B* **2003**, *107*, 3829–3836. (d) Zhang, X.; Cunningham, M. M.; Walker, R. A. *J. Phys. Chem. B* **2003**, *107*, 3183–3195.

(15) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677–2689.

(16) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L.; Liu, X.; So, J.-H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183–190.

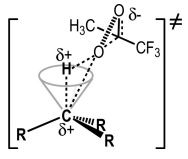
(17) (a) Tredwell, M.; Gouverneur, V. *Org. Biomol. Chem.* **2006**, *4*, 26–32. (b) Archibald, S. C.; Barden, D. J.; Bazin, J. F. Y.; Fleming.; Foster, C. F.; Mandal, A. K.; Parker, D.; Takaki, K.; Ware, A. C.; Williams, A. R. B.; Zwicky, A. B. *Org. Biomol. Chem.* **2004**, *2*, 1051–1064. (c) Fleming, I. *Chem. Rev.* **1997**, *97*, 2063–2192.

(18) (a) Brook, M. A.; Henry, C.; Jueschke, R.; Modi, P. *Synlett* **1993**, 97–104. (b) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954–4961. (c) Brook, M. A.; Neuy, A. *J. Org. Chem.* **1990**, *55*, 3609–3616. (d) Brook, M. A.; Hadi, M. A.; Neuy, A. *J. Chem. Soc., Chem. Commun.* **1989**, 957–958. (e) Mayr, H.; Hagen, G. *J. Chem. Soc., Chem. Commun.* **1989**, 91–92.

(19) The results reported by Avnir et al. on the electrophilic hydrobromination of alkenyl functionalized hybrid silicas[5r] indicated a faster reaction for C=C double bonds placed at C_2 and C_3 in relation to further positions. Although the hybrid silica materials studied by these authors had a peculiar morphology and the location of the organic ligands determined mainly the unexpected reactivity reported, probably the silicon β-effect contributed also to activate the vinyl and allyl substituents towards the electrophile.

(20) (a) Grabowsky, S.; Hesse, M. F.; Paulmann, C.; Luger, P.; Beckmann, J. *Inorg. Chem.* **2009**, *48*, 4384–4393. (b) Gibbs, G. V.; Wallace, A. F.; Cox, D. F.; Downs, R. T.; Ross, N. L.; Rosso, K. M. *Am. Mineral.* **2009**, *94*, 1085–1102. (c) Al Derzi, A. R.; Gregusová, Runge, K.; Bartlett, R. J. *Int. J. Quant. Chem.* **2008**, *108*, 2088–2096. (d) Gillespie, R. J.; Johnson, S. A. *Inorg. Chem.* **1997**, *36*, 3031–3039. (e) Nicholas, J. B.; Feyereisen, M. *J. Chem. Phys.* **1995**, *103*, 8031–8042. (f) Pauling, L. *Am. Mineral* **1980**, *65*, 321–323. (g) Oberhammer, H.; Boggs, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 7241–7244.

(21) In the theoretical description[8] of the oxygenation of saturated C–H σ-bonds by dioxirane **1**, the geometry of the transition state is determined by the interaction of the O–O antibonding σ-orbital of dioxirane **1** with the out of phase combination of the σ(CH) local orbitals of the methylene fragment. Then, the approach of dioxirane



towards the methylene C–H bonds occurs along a trajectory that minimizes the steric and torsional strain derived from the adjacent bonds, somewhat off-axis to the C-H σ-bonds (Figure 1). The lone pair on the electrophilic oxygen acts as the migration terminus for the 1,2-hydrogen shift, thus determining the relative orientation of the molecules in the concerted transition state.

(22) Brinker, C. J.; Sherer, G. W. *Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing*; Academic Press: London, 1990.

(23) (a) Bausch, M. J.; Gong, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5963–5964. (b) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806–2807. (c) Stang, P. J.; Ladika, M.; Apeloig, Y.; Stanger, A.; Schiavelli, M. D.; Hughey, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 6852–6854. (d) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715–5725.

(24) (a) Lim, M. H.; Stein, A. *Chem. Mater.* **1999**, *11*, 3285−3295. (b) Lim, M. H.; Blandford, C. F.; Stein, A. *J. Am. Chem. Soc.* **1997**, *119*, 4090−4091.
(25) (a) Prélot, B.; Lantenois, S.; Nedellec, Y.; Lindheimer, M.; Douillard, J.-M.; Zajac, J. *Colloid Surf., A* **2010**, *355*, 67−74. (b) Azais, T.; Hartmeyer, G.; Quignard, S.; Laurent, G.; Babonneau, F. *J. Phys. Chem. C* **2010**, *114*, 8884−8891. (c) Synak, A.; Gil, M.; Organero, J. A.; Sánchez, F.; Iglesias, M.; Douhal, A. *J. Phys. Chem. C* **2009**, *113*, 19199−19207. (d) Lee, C.-H.; Lin, H.-C.; Cheng, S.-H.; Lin, T.-S.; Mou, C.-Y. *J. Phys. Chem. C* **2009**, *113*, 16058−16069. (e) Bhan, A.; Iglesia, E. *Acc. Chem. Res.* **2008**, *41*, 559−567. (f) Yang, Q.; Han, D.; Yang, H.; Li, C. *Chem. Asian J.* **2008**, *3*, 1214−1229. (g) Zhang, H.; Wang, Y. M.; Zhang, L.; Gerritsen, G.; Abbenius, H. C. L. *J. Catal.* **2008**, *256*, 226−236. (h) Burt, M. C.; Dave, B. C. *J. Am. Chem. Soc.* **2006**, *128*, 11750−11751. (i) Thomas, J. M.; Raja, R. *Acc. Chem. Res.* **2008**, *41*, 708−720. (j) Santiso, E. E.; Kostov, M. K.; George, A. M.; Nardelli, M. B.; Gubbins, K. E. *Appl. Surf. Sci.* **2007**, *253*, 5570−5579.
(26) Mello, R.; Olmos, A.; Alcalde-Aragonés, A.; Díaz-Rodríguez, A.; González-Núñez, M. E.; Asensio, G. *Eur. J. Org. Chem.* **2010**, 6200−6206.
(27) (a) Dias, L. C.; Ferreira, M. A. B.; Tormena, C. F. *J. Phys. Chem. A* **2008**, *112*, 232−237. (b) Cypryk, M. *J. Organomet. Chem.* **1997**, *545-546*, 483−493. (c) Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Schereiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 697−703.
(28) (a) Song, J.; Duval, F. L.; Stuart, M. A. C.; Hillborg, H.; Gunst, U.; Arlinghaus, H. F.; Vancso, G. J. *Langmuir* **2007**, *23*, 5430−5438. (b) Sahai, N. *Environ. Sci. Technol.* **2002**, *36*, 445−452. (c) Kubicki, J. D. *J. Phys. Chem. A* **2001**, *105*, 8756−8762. (d) Nawrocki, J. *J. Chromatogr. A* **1997**, *779*, 29−71. (e) Fleischer, U.; Kutzelnigg, W.; Bleiber, A.; Sauer, J. *J. Am. Chem. Soc.* **1993**, *115*, 7833−7838. (f) Grimm, D. T.; Bartmess, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 1227−1231. (g) West, R.; Baney, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 6145−6148.
(29) (a) Beckmann, J.; Grabowsky, S. *J. Phys. Chem. A* **2007**, *111*, 2011−2019. (b) Paton, R. S.; Goodman, J. M. *Org. Lett.* **2006**, *8*, 4299−4302. (c) Blake, J. F.; Jorgensen, W. L. *J. Org. Chem.* **1991**, *56*, 6052−6059. (d) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 260−269. (e) Pitt, C. G.; Bursey, M. M.; Chatfield, D. A. *J. Chem. Soc., Perkin II* **1976**, 434−438. (f) Varma, R.; MacDiarmid, A. G.; Miller, J. G. *Inorg. Chem.* **1964**, *3*, 1754−1757. (g) Abel, E. W.; Armitage, D. A.; Willey, G. R. *Trans. Faraday Soc.* **1964**, *60* (499), 1257−1262. (h) West, R.; Whatley, L. S.; Lake, K. J. *J. Am. Chem. Soc.* **1961**, *83*, 761−764. (i) Sternbach, B.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1961**, *83*, 3384−3388. (j) Sujishi, S.; Witz, S. *J. Am. Chem. Soc.* **1954**, *76*, 4631−4636.
(30) (a) Rauk, A. *Orbital Interaction Theory of Organic Chemistry*; John Wiley & Sons: New York, 1994. (b) Albright, T. A.; Burdett, J. K.; Whangboo, M. H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985.
(31) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119−251.
(32) (a) Awwad, A. M.; North, A. M.; Pethrick, R. A. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 731−743. (b) Colle, R.; Suter, U. W.; Luisi, P. L. *Tetrahedron* **1981**, *37*, 3727−3737.
(33) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994.
(34) Adam, W.; Curci, R.; González-Núñez, M. E.; Mello, R. *J. Am. Chem. Soc.* **1991**, *113*, 7654−7658.
(35) Adam, W.; Asensio, G.; Curci, R.; González-Núñez, M. E.; Mello, R. *J. Am. Chem. Soc.* **1992**, *114*, 8345−8349.
(36) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373−380.
(37) Trens, P; Russell, M.L.; Spjuth, L.; Hudson, M.J.; Liljenzin, J.-O. *Ind. Eng. Chem. Res.* **2002**, *41*, 5220−5225.
(38) Lesaint, C.; Lebeau, B.; Marichal, C.; Patarin, J. *Microporous Mesoporous Mater.* **2005**, *83*, 76−84.
(39) Ossenkamp, G. C.; Kemmitt, T.; Johnston, J. H. *Chem. Mater.* **2001**, *13*, 3975−3980.
(40) Whitmore, F. C.; Sommer, L. H.; DiGiorgio, P. A.; Strong, W. A.; VanStrien, R. E.; Bailey, D. L.; Hall, H. K.; Pietrusza, E. W.; Kerr, G. T. *J. Am. Chem. Soc.* **1946**, *68*, 475−481.
(41) Heathcock, C. H.; Lampe, J. *J. Org. Chem.* **1983**, *48*, 4330−4337.
(42) Wiberg, K. B. *J. Am. Chem. Soc.* **1952**, *74*, 3891−3892.
(43) Effenberger, F.; Heid, S. *Synthesis* **1995**, *9*, 1126−1130.
(44) Curci, R.; Dáccolti, L.; Fiorentino, M.; Fusco, C.; Adam, W.; González-Núñez, M. E.; Mello, R. *Tetrahedron Lett.* **1992**, *33*, 4225−4228.
(45) Langer, S. H.; Connell, S.; Wender, I. *J. Org. Chem.* **1958**, *23*, 50−58.
(46) Duchon, M.; Miocque, M.; Gautier, J. A. *Bull. Soc. Chim. Fr.* **1964**, *10*, 2471−2476.
(47) George, P. D.; Ladd, J. R. *J. Am. Chem. Soc.* **1953**, *75*, 987−988.