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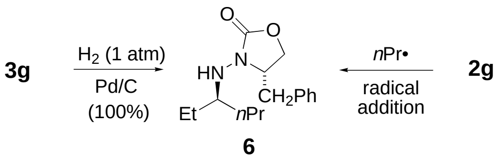

(2)

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Molecular Insight Into Surface Organometallic Chemistry Through the Combined Use of 2D HETCOR Solid-State NMR Spectroscopy and Silsesquioxane Analogues[**]

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Anne Lesage, and Lyndon Emsley*

The structural characterization of heterogeneous catalysts remains difficult. In the late eighties, Feher and later others showed that polyhedral oligomeric silsesquioxanes (POSS) can be used to model the surface structure of partially dehydroxylated silica and therefore infer information about the coordination sphere of metal complexes directly supported on oxides such as silica.[1] This approach can also provide mechanistic insights on surface chemistry processes. However, no direct comparison between these models and their related surface complexes has been reported.

We have recently shown that the reaction of tris(neopentyl)neopentylidene tantalum, [Ta(=CH*t*Bu)(CH_2*t*Bu)$_3$] (**1**) with $SiO_{2\text{-}(500)}$ gives a mixture of mono-[≡SiO-Ta(=CH*t*Bu)(CH_2*t*Bu)$_2$] and bisgrafted surface complexes [(≡SiO)$_2$Ta(=CH*t*Bu)(CH_2*t*Bu)],[2a] while its reaction with a $SiO_{2\text{-}(700)}$ provides the monografted species [≡SiO-Ta(=CH*t*Bu)(CH_2*t*Bu)$_2$] (**2**$_\mathbf{s}$) as the sole surface species. The characterization was based on elemental analysis, the evolution of neopentane during grafting of **1**, and solvolysis of **2**$_\mathbf{s}$ as well as infrared (IR) spectroscopy.[2b]

We report here the use of high-resolution solid-state one-dimensional (1D) and two-dimensional (2D) NMR spectroscopy to study **2**$_\mathbf{s}$ and the use of high-resolution solution-state 1D and 2D NMR spectroscopy of its molecular analogue [(c-C_5H_9)$_7Si_7O_{12}$Si–O–Ta(=CH*t*Bu)(CH_2*t*Bu)$_2$] (**2**$_\mathbf{m}$) to define the structure of **2**$_\mathbf{s}$ at a molecular level and to investigate the reaction pathway leading to the grafted species.

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As previously described, the surface complex $\mathbf{2}_\mathrm{s}$, was prepared by treating a solution of [Ta(=CHtBu)(CH$_2t$Bu)$_3$] in pentane (1.1 equivalents with respect to surface silanols; 0.7–0.8 accessible OH nm^{-2}) with SiO$_{2\text{-}(700)}$.[2b] After workup, $\mathbf{2}_\mathrm{s}$ was obtained as a yellow powder typically containing 4.2 % wt of Ta. Noteworthy is the rapid (within 1 min) coloration of silica and discoloration of the supernatant solution upon addition of the pentane solution of **1** to SiO$_{2\text{-}(700)}$. All the observations and chemical analyses are consistent with the proposed structure of $\mathbf{2}_\mathrm{s}$ [Eq. (1)], but further corroboration at the molecular level has been sought using both solid-state NMR spectroscopy of the grafted species and solution NMR spectroscopy of molecular model species.

$$\mathbf{1} + \underset{\text{SiO}_{2\text{-}(700)}}{\equiv\text{SiOH}} \longrightarrow \underset{\mathbf{2}_\mathrm{s}}{[\equiv\text{SiO–Ta(=CH}t\text{Bu)(CH}_2t\text{Bu)}_2]} + \text{NpH} \qquad (1)$$

To improve the signal-to-noise ratio in the solid-state NMR spectra of **2**, the complex was partially ^{13}C enriched at the α-position by reaction of [Ta(=C*HtBu)(C*H$_2t$Bu)$_3$] (**1***) with SiO$_{2\text{-}(700)}$, which yielded [≡SiO–Ta(=C*HtBu)(C*H$_2t$Bu)$_2$] ($\mathbf{2}^*_\mathrm{s}$). The solid-state ^{1}H NMR spectrum of $\mathbf{2}^*_\mathrm{s}$ shows two broad resonance signals at $\delta = 4.2$ and 1.0 (see the Supporting Information),[3] and its ^{13}C solid-state cross polarization/magic angle spinning (CP/MAS) NMR spectrum displays strong signals at $\delta = 246$, 96.5, and 33.5 (Figure 1 a). Moreover, the 2D HETCOR solid-state NMR spectra provided an unequivocal assignment for $\mathbf{2}^*_\mathrm{s}$ (see Supporting Information for experimental details). The 2D NMR spectrum, recorded with a contact time of 2 ms (Figure 1 c), shows clear correlations between the signals at $\delta = 4.2$ and 1.0 in the ^{1}H dimension (F$_1$) with those at $\delta = 246$ and 33.5, respectively, in the carbon dimension (F$_2$). The signal at $\delta = 96.5$ also correlates with the peak centered at $\delta = 1.0$, strongly suggesting that the methylene protons are buried under this massive signal (the chemical shifts of the corresponding protons for the surface model $\mathbf{2}_\mathrm{m}$ are indeed around 1 ppm, see Table 1 and below).

A reaction intermediate can be detected if the preparation of $\mathbf{2}^*_\mathrm{s}$ involves a rather short (5 min or less) or a cold (below 15–20 °C) drying step; under such conditions, an extra signal appears in the solid-state NMR spectrum at $\delta = 110$ (Figure 1 b), which readily disappears upon treating the sample under vacuum or under heat. During this step, neopentane is evolved. All these observations suggest that the intermediate observed in the reaction of [Ta(=CHtBu)(CH$_2t$Bu)$_3$] with SiO$_{2\text{-}(700)}$, is the tetraalkyl derivative [≡SiO–Ta(CH$_2t$Bu)$_4$] ($\mathbf{3}_\mathrm{s}$) which is formed under kinetic control. The intermediate $\mathbf{3}_\mathrm{s}$ rapidly releases neopentane, to finally yield $\mathbf{2}_\mathrm{s}$ as the sole surface complex.

To corroborate the assignments proposed above and to gain further insight in the reaction mechanism suggested by the detection of intermediate $\mathbf{3}_\mathrm{s}$, we have prepared a molecular model of $\mathbf{2}_\mathrm{m}$ using the silsesquioxane (c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$SiOH (**4**) a Feher-cage analogue,[1d,f] that can mimic an isolated silanol of a silica surface partially dehydroxylated at 700 °C. The thermodynamic product of the reaction between the monosilanol **4** and [Ta(=CHtBu)(CH$_2t$Bu)$_3$] is $\mathbf{2}_\mathrm{m}$ (for characteristic data, see Table 1) alongside one equivalent of neopentane.[4] The NMR spectroscopy data obtained for $\mathbf{2}_\mathrm{m}$ are in good agreement with those of its solid-state counterpart, $\mathbf{2}_\mathrm{s}$. Based on NMR spectroscopy data, the reaction is under kinetic control and reaches completion after 48 h. The kinetic monitoring of the reaction shows that a colorless intermediate, [(c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$SiOTa(CH$_2t$Bu)$_4$] ($\mathbf{3}_\mathrm{m}$) is formed immediately upon mixing of the reagents. The long-lived intermediate $\mathbf{3}_\mathrm{m}$ ($\tau_{1/2} = 9$ h) has been characterized by 1D and 2D solution NMR spectroscopy, which yields data in good agreement with those obtained for its solid counterpart $\mathbf{3}_\mathrm{s}$ (Table 1). The decomposition path of complex $\mathbf{3}_\mathrm{m}$ consists of the elimination a neopentane unit by means of α-H abstraction to yield the orange complex $\mathbf{2}_\mathrm{m}$.

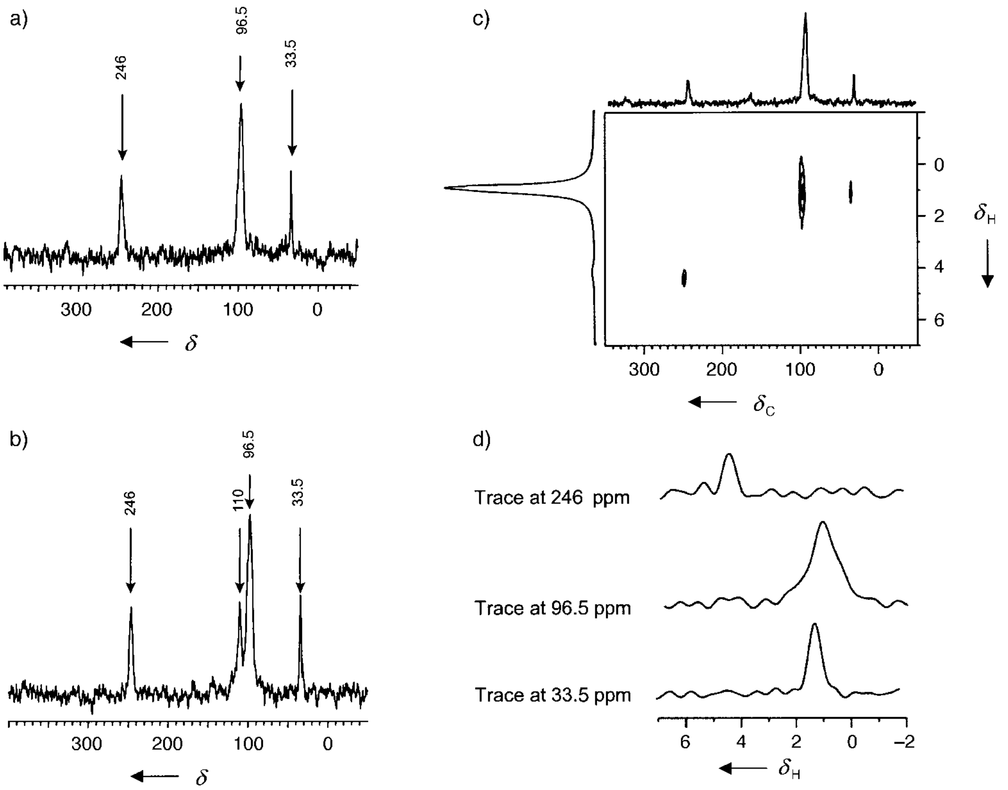

Figure 1. a) CP/MAS ^{13}C solid-state NMR spectra of $\mathbf{2}^*_\mathrm{s}$, b) $\mathbf{2}^*_\mathrm{s}$ and $\mathbf{3}^*_\mathrm{s}$, c) 2D ^{1}H-^{13}C HETCOR solid-state NMR spectra of $\mathbf{2}^*_\mathrm{s}$ (2 ms of contact time). d) Proton traces of the signals at $\delta = 246$, 96.5, and 33.5 in the 2D ^{1}H–^{13}C NMR spectrum.

The combination of the data obtained in the solid state for the synthesis of $\mathbf{2}_\mathrm{s}$ and in solution for $\mathbf{2}_\mathrm{m}$ allows a mechanistic pathway to be proposed for the reaction:

Table 1. ^{1}H and ^{13}C chemical shifts of **1**, **2_m**, and **3_m** in C_6D_6.

Complex	^{1}H NMR [δ] resonance[a]	^{1}H NMR [δ] assignement	^{13}C NMR [δ] resonance	^{13}C NMR [δ] assignement
1	0.81	$\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_3}$	34.7	$\mathrm{{=}CHC(}\mathit{C}\mathrm{H_3)_3}$
	1.14	$\mathrm{CH_2C(C}\mathit{H}_3)_3$	34.95	$\mathrm{CH_2C(}\mathit{C}\mathrm{H_3)_3}$
	1.45	$\mathrm{{=}CHC(C}\mathit{H}_3)_3$	35.05	$\mathrm{CH_2}\mathit{C}\mathrm{(CH_3)_3}$
	1.89	$\mathrm{{=}C}\mathit{H}\mathrm{C(CH_3)_3}$	47.0	$\mathrm{{=}CH}\mathit{C}\mathrm{(CH_3)_3}$
			113.75	$\mathit{C}\mathrm{H_2C(CH_3)_3}$
			249.9	$\mathrm{{=}}\mathit{C}\mathrm{HC(CH_3)_3}$
2_m	1.1–2.1(m)[b]	$(c\text{-}\mathrm{C}\mathit{H}(\mathrm{C}\mathit{H}_2)_4)$	22.6, 22.65	$(c\text{-}\mathit{C}\mathrm{H(CH_2)_4})$
			27.4, 27.45, 27.85, 27.9	$(c\text{-}\mathrm{CH(}\mathit{C}\mathrm{H_2)_4})$
	1.03(d)[c]	$\mathrm{C}\mathit{H}_a\mathrm{H_bC(CH_3)_3}$	33.95	$\mathrm{CH_2C(}\mathit{C}\mathrm{H_3)_3}$
	1.20(d)[c]	$\mathrm{CH_a}\mathit{H}_b\mathrm{C(CH_3)_3}$	34.4	$\mathrm{{=}CHC(}\mathit{C}\mathrm{H_3)_3}$
	1.20	$\mathrm{CH_2C(C}\mathit{H}_3)_3$	34.75	$\mathrm{CH_2}\mathit{C}\mathrm{(CH_3)_3}$
	1.41	$\mathrm{{=}CHC(C}\mathit{H}_3)_3$	45.55	$\mathrm{{=}CH}\mathit{C}\mathrm{(CH_3)_3}$
	4.77	$\mathrm{{=}C}\mathit{H}\mathrm{C(CH_3)_3}$	95.6	$\mathit{C}\mathrm{H_2C(CH_3)_3}$
			245.2	$\mathrm{{=}}\mathit{C}\mathrm{HC(CH_3)_3}$
3_m	1.1–2.1(m)[b]	$(c\text{-}\mathrm{C}\mathit{H}(\mathrm{C}\mathit{H}_2)_4)$	22.7, 22.6,	$c\text{-}\mathit{C}\mathrm{H(CH_2)_4})$
	1.34	$\mathrm{CH_2C(C}\mathit{H}_3)_3$	22.55	
	1.87	$\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_3}$	27.45, 27.55, 27.75, 27.9	$(c\text{-}\mathrm{CH(}\mathit{C}\mathrm{H_2)_4})$
			–[d]	$\mathrm{CH_2}\mathit{C}\mathrm{(CH_3)_3}$
			35.2	$\mathrm{CH_2C(}\mathit{C}\mathrm{H_3)_3}$
			108.7[b]	$\mathit{C}\mathrm{H_2C(CH_3)_3}$

[a] multiplicity in parenthesis; singlets are not specified. [b] broad signal. [c] $J = 14.0$ Hz. [d] Not detected.

addition of the silanol to the alkylidene moiety of **1** (**1**→**3_s**) followed by an α-H abstraction (**3_s**→**2_s**; Scheme 1).[5]

The reactivities of **4** and $SiO_{2\text{-}(700)}$ are relatively similar (immediate reaction of **1** with silanols and a subsequent slower α-H abstraction step), which is probably because of similar pKa values[6] and steric crowding. Finally, 2D HETCOR solid-state NMR spectroscopy is an important tool to unequivocally assign ^{1}H and ^{13}C chemical shifts for surface complexes, and will be important in the future development of surface organometallic chemistry. In conclusion, these data taken together show, besides the analogy between surface and solution chemistry, that the combined use of high-resolution solid state NMR and solution NMR spectroscopy to investigate molecular analogues, is a powerful tool in surface organometallic chemistry, and enables the identification of end products, and determination of the grafting-reaction mechanism. Moreover, we have shown that the Feher cage analogue **4**, is a good model for $SiO_{2\text{-}(700)}$, a silica partially dehydroxylated at 700 °C, which contains mainly isolated silanols, and provides a good estimation of the chemical shifts for surface complexes and can help in understanding elementary steps of surface reactions.

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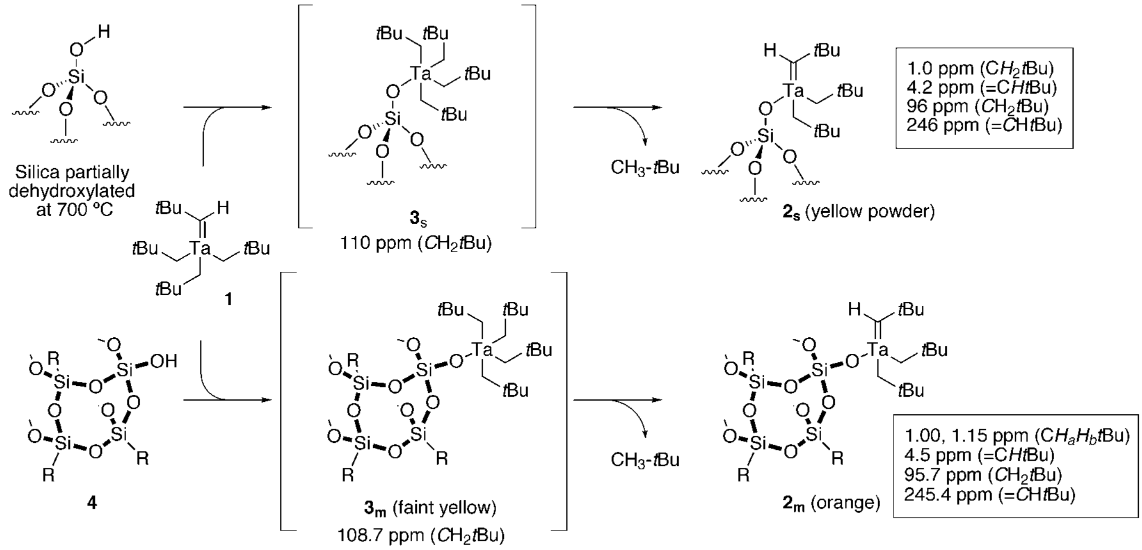

Scheme 1. Comparison of the reaction of silica partially dehydroxylated at 700 °C ($SiO_{2(\text{-}700)}$) versus $(c\text{-}C_5H_9)_7Si_7O_{12}SiOH$.

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[3] The natural abundance ^{13}C NMR spectrum displays three signals at δ = 33.5 (C(CH_3)$_3$), 96.5 ($CH_2C(CH_3)_3$), and 246 (=CH–C(CH_3)$_3$), albeit with a poor signal/noise ratio, especially for the latter. Therefore, **2_s** was partially ^{13}C enriched at the α-position to the metal, **2_s^***, by reaction of [Ta(=C*HtBu)(C*H_2tBu)$_3$] (**1***) with $SiO_{2\text{-}(700)}$.

[4] These values are different from those obtained by Wolczanski and coworkers for [(tBu)$_3$SiOTa(=CHtBu)(CH_2tBu)$_2$]:R. E. Lapointe, P. T. Wolczanski, G. D. Van Duyne, *Organometallics* **1985**, *4*, 1810. This illustrates the dramatic effects on the NMR data of substituents on Si and the necessity of the oxygen atoms around the Si centers.

[5] This was in fact indirectly shown in the studies of the formation of the surface complexes, see ref. [2a]. Noteworthy is the reaction of HCl on

[Ta(=CHtBu)(CH$_2t$Bu)$_3$] which yields Cl−Ta(CH$_2t$Bu)$_4$: R. R. Schrock, J. D. Fellmann, *J. Am. Chem. Soc.* **1978**, *100*, 3359.

[6] a) For comprehensive information on the pK_a values of silicas, see: *The Surface Properties of Silicas* (Ed.: A. P. Legrand), Wiley, New York, **1998**, chapter 4B; b) for related comments on **4**, see ref. [1f].

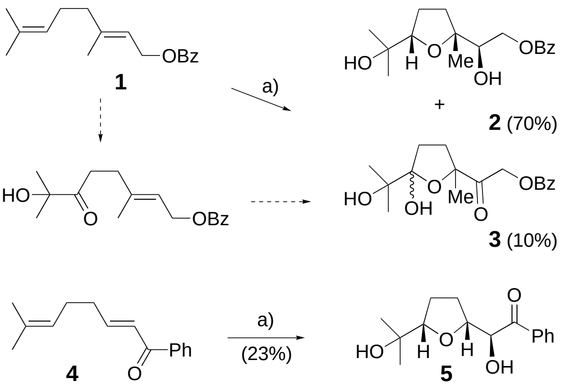
Asymmetric Permanganate-Promoted Oxidative Cyclization of 1,5-Dienes by Using Chiral Phase-Transfer Catalysis**

Richard C. D. Brown* and John F. Keily

2,5-Bis(hydroxymethyl)-substituted tetrahydrofurans (THF diols) are an important structural unit found in many natural and synthetic, biologically active molecules.[1] An elegant approach to the synthesis of THF diols is by the permanganate-promoted oxidative cyclization of 1,5-dienes, which leads to the stereospecific formation of up to four new stereocenters and the THF ring.[2–6] The same transformation has been carried out using other metal–oxo reagents and catalysts.[7, 8] In the permanganate-promoted oxidative cyclization reaction, control of absolute stereochemistry has been achieved with chiral auxiliaries;[4a,b] however, preparation of enantiomerically enriched THF diols by oxidative cyclizations of achiral 1,5-dienes has not been reported. Herein we report the novel high-yielding phase-transfer permanganate-promoted oxidation of geranyl benzoate (**1**) to the corresponding THF diol **2** (Scheme 1), and a procedure for the asymmetric oxidative cyclization of phenone dienes to produce enantiomerically enriched THF diols.

The use of phase-transfer conditions in permanganate-promoted oxidations is well known,[9] although we were not aware of application to the oxidative cyclization of 1,5-dienes. Therefore before attempting to develop an asymmetric process, we investigated the phase-transfer oxidative cyclization of a readily available substrate **1** using achiral tertiary ammonium salts (Scheme 1).[10]

Oxidation of diene **1** with potassium permanganate (2 equiv) in diethyl ether buffered with ethanoic acid gave the best yield of THF diol **2** (70%) when Adogen 464 (0.1–1 equiv) was employed (entry 4, Table 1). Oxidation of enone **4** under the same conditions gave the desired THF diol **5**, albeit in lower yield (Scheme 1). We then returned to our primary goal of developing an asymmetric oxidative cyclization.



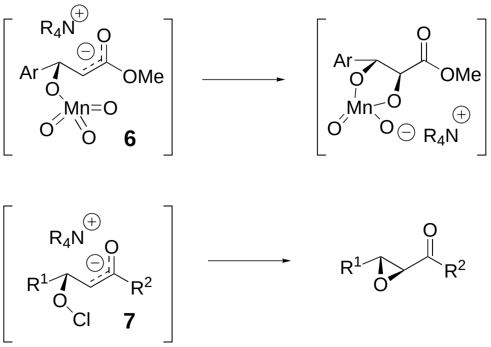
Scheme 1. Oxidative cyclization of dienes **1** and **4**. a) 0.4 M KMnO$_4$ (2 equiv), AcOH (4 equiv), Adogen 464 (0.4 equiv)/Et$_2$O. Bz = benzoyl.

Table 1. Oxidative cyclization of geranyl benzoate (**1**) (see Scheme 1).[a]

Entry	Solvent	Phase-transfer agent	Yield of **2** [%]	Yield of **3** [%]
1	CH$_2$Cl$_2$[b]	TBAB	8[c]	not recorded
2	CH$_2$Cl$_2$	TBAB	44[d]	21[d]
3	Et$_2$O	TBAB	40[d]	7[d]
4	Et$_2$O	Adogen 464	70[d]	10[d]

[a] Reactions were conducted on a 0.19 mmol scale. TBAB = tetrabutylammonium bromide. [b] No AcOH added to the reaction mixture. [c] Yield estimated by HPLC. [d] Yields represent analytically pure isolated material.

Studies on the oxidation of cinnamate esters by quaternary ammonium permanganates led Lee et al. to conclude that the transition state was electron-rich, and they proposed an enolate-like structure **6** with stabilization due to interaction with the ammonium ion (Scheme 2).[11] The similarity of **6** and the initial adduct **7** formed in the phase-transfer-catalyzed nucleophilic epoxidation of enones suggested that chiral catalysts developed for the epoxidation reaction might also be applied to the oxidative cyclization.[12]



Scheme 2. Possible reaction pathways for the permanganate-promoted oxidation of electron-poor olefins (top), and the nucleophilic epoxidation of α,β-enones with ClO$^-$ (bottom).

Oxidative cyclization of geranyl benzoate (**1**) in the presence of **8** in dichloromethane/water/ethanoic acid at

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