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Selective Oxidation of Allylic Methyl Groups over a Solid Support under Microwave Irradiation†

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SeO_2/Bu^{t}OOH adsorbed on SiO_2 is found to be a highly selective reagent for the oxidation of allylic methyl groups to *trans*-α,β-unsaturated aldehydes under microwave irradiation.

Selective oxidation of allylic methyl groups of *gem*-dimethyl trisubstituted olefins to *trans*-α,β-unsaturated alcohols and aldehydes is an important transformation in organic chemistry. Several reagents are known[1] to achieve this goal, but selenium dioxide has been found to be a promising reagent. Some difficulties such as the removal of colloidal selenium and the formation of organoselenium as byproducts have been circumvented by the Sharpless method[2] using catalytic selenium dioxide in combination with *tert*-butyl hydroperoxide, but still it requires some modifications. By making certain changes in the above method we have been successful in obtaining *trans*-α,β-unsaturated alcohols and aldehydes[3] from allylic methyl groups and in the selective oxidation[4] of primary allylic alcohols to α,β-unsaturated aldehydes in the presence of secondary allylic alcohols.

There are a large number of reactions over solid supports with microwave irradiation reported in the literature.[5,6] These reactions generally proceed with greater selectivity, under mild, simple and safe reaction conditions than the analogues homogeneous reactions. Moreover, the reaction rate is enhanced over a solid support as it takes place in two dimensions rather than the three dimensions using an ordinary reaction method. In continuation of our earlier work in the selective iodination[7] of benzylic alcohols over a solid support with microwave irradiation, we achieved the selective oxidation of the allylic methyl groups of *gem*-dimethyl trisubstituted olefins to *trans*-α,β-unsaturated aldehydes only, probably due to the faster oxidation of allylic alcohols under these reaction conditions. However, allylic alcohols were formed when the reaction time was reduced to 2–3 min (checked by ^{1}H NMR). Compounds containing allylic methyl groups, SeO_2 and Bu^{t}OOH were adsorbed over silica and exposed to microwave irradiation, resulting in the selective conversion of the allylic methyl group to a *trans*-α,β-unsaturated aldehyde group. In most cases no intermediate α,β-unsaturated alcohol or any other product was detectable under the given experimental conditions. However, in some cases a very small amount (<5%) of the intermediate unsaturated alcohol was also obtained, depending on the reaction time. A comparison of the reaction rate with and without microwave irradiation is presented in Table 1.

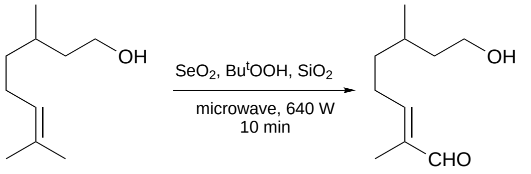
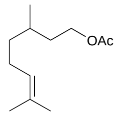
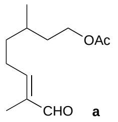
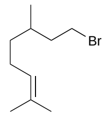
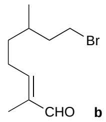
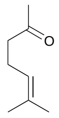
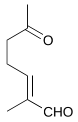
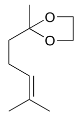
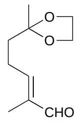
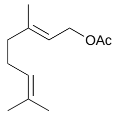
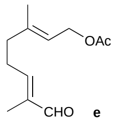
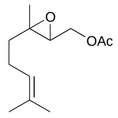
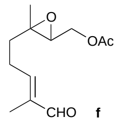


Table 1

Entry	Substrate	Reaction time[a]	Product	Yield (%)
1		10 min (24 h, 80:20)	 **a**	85 (75)
2		10 min (18 h, 70:30)	 **b**	75 (60)
3		10 min (20 h, 80:20)	 **c**	81 (60)
4		10 min (10 h, 70:30)	 **d**	77 (60)
5		10 min (24 h, 80:20)	 **e**	70 (75)
6		10 min (24 h, 80:20)	 **f**	68 (60)

[a]The figures in parenthesis are the reaction times and alcohol:aldehyde yield without microwave irradiation.[3]

Experimental

The IR spectra were recorded on a Perkin Elmer model 1430 spectrophotometer and ^{1}H NMR spectra with a Varian EM-360 (90 MHz) NMR spectrometer. Chemical shifts (δ) are reported in ppm with Me_4Si as internal standard. Elemental analyses were carried out using a Perkin-Elmer 2400 elemental analyser. Microwave induced reactions were carried out in a BPL BMO 700T (640 W) microwave oven.

General Procedure.—Citronellol (3.2 mmol, 0.500 g) SeO_6 (1.6 mmol, 0.176 g) and Bu^{t}OOH (70%, 4.48 mmol, 0.576 g) were dissolved in a small amount of dichloromethane. Silica (1 g) was then added to form a slurry and excess solvent was evaporated off to obtain free flowing silica which was then exposed to microwave irradiation at power level 9 (640 W) for 10 min. Diethyl ether was then added and the mixture filtered. The filtrate was then washed (10% KOH, brine) and then dried (anhydrous Na_2SO_4). The solvent was evaporated to furnish the pure product in 83% yield; δ_H 9.5 (s, 1 H), 6.5 (t, *J* 6 Hz, 1 H), 3.7 (t, *J* 7 Hz, 2 H), 3.3 (brs, 1 H, D_2O exchangeable), 2.4 (m, 2 H), 1.8 (s, 3 H), 1.5 (m, 5 H), 1.0 (d, *J* 7.5 Hz, 3 H); ν_{max}/cm^{-1} 3400, 2720, 1700, 1640 (Found: C, 70.38; H, 10.48. $C_{10}H_{18}O_2$ requires C, 70.54; H, 10.65%).

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*To receive any correspondence.
†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 2

			Found (required) (%)	
Compound	ν_{max}/cm^{-1}	δ_H	C	H
$C_{12}H_{20}O_3$ **a**	2710, 1740, 1690, 1640	9.5 (s, 1 H), 6.5 (t, *J* 6 Hz, 1 H), 2.5 (m, 2 H), 2.1 (s, 3 H), 1.8 (s, 3 H), 1.5 (m, 5 H), 1.0 (d, *J* 7.5 Hz, 3 H)	67.52 (67.89)	9.21 (9.49)
$C_{10}H_{17}BrO$ **b**	2710, 1690, 1640	9.5 (s, 1 H), 6.5 (t, *J* 6 Hz, 1 H), 3.5 (t, *J* 7.5 Hz, 2 H), 2.5 (m, 2 H), 1.8 (s, 3 H), 1.5 (m, 5 H), 1.0 (d, *J* 7.5 Hz, 3 H)	51.29 (51.51)	7.11 (7.34)
$C_8H_{12}O_2$ **c**	2710, 1750, 1690, 1640	9.5 (s, 1 H), 6.5 (t, *J* 6 Hz, 1 H), 2.4 (m, 4 H), 2.2 (s, 3 H), 1.1 (d, *J* 7.5 Hz, 3 H)	68.21 (68.54)	8.40 (8.62)
$C_{10}H_{16}O_3$ **d**	2710, 1690, 1640	9.5 (s, 1 H), 6.5 (t, *J* 6 Hz, 1 H), 5.4 (t, *J* 7 Hz, 1 H), 4.6 (d, *J* 7 Hz, 2 H), 2.35 (m, 4 H), 1.97 (s, 3 H), 1.75 (s, 6 H)	64.89 (65.19)	8.42 (8.75)
$C_{12}H_{18}O_3$ **e**	2720, 1750, 1690, 1650	9.5 (s, 1 H), 6.5 (t, *J* 6 Hz, 1 H), 5.4 (t, *J* 7 Hz, 1 H), 4.6 (d, *J* 7 Hz, 2 H), 2.35 (m, 4 H), 1.97 (s, 3 H), 1.75 (s, 6 H)	67.21 (68.54)	8.32 (8.62)
$C_{12}H_{18}O_4$ **f**	2720, 1750, 1690, 1640	9.5 (s, 1 H), 6.5 (t, *J* 6 Hz, 1 H), 4.0 (d, *J* 7 Hz, 2 H), 2.76 (t, *J* 7.5 Hz, 1 H), 2.4 (m, 4 H), 2.0 (s, 3 H), 1.8 (s, 6 H)	63.35 (63.69)	7.67 (8.01)

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