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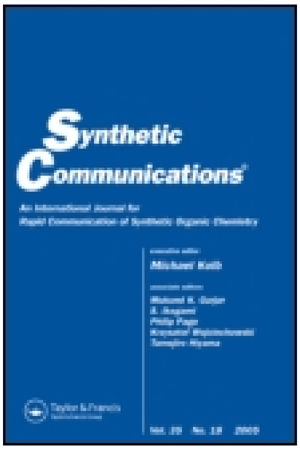

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A SIMPLE METHOD FOR MILD OXIDATION OF α-HYDROXYSILANES TO PROVIDE AROYLSILANES

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A SIMPLE METHOD FOR MILD OXIDATION OF α-HYDROXYSILANES TO PROVIDE AROYLSILANES

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ABSTRACT

Potassium permanganate supported onto alumina in hexane-water is a good oxidizing agent to convert α-hydroxysilanes into acylsilanes. This mild oxidation afforded aroylsilanes having electron-donating groups attached to the aromatic ring, in 70–86% yield.

The versatile employment of acylsilanes in organic synthetic routes such as cyclizations,[1] radical reactions,[2] stereocontrol induction,[3] bioreduction[4] and others,[5] has stimulate a search for new methodologies for their synthesis.[6]

Different from various routes for the acylsilanes synthesis that employ expensive reagents or numerous steps, the oxidation of α-hydroxysilanes **1** is simple and practical. Moreover, the preparation of acylsilanes via oxidation of α-hydroxysilanes is sometimes the sole option specifically when a silyl alcohol is a critical intermediate of a synthetic route, for example in chiral

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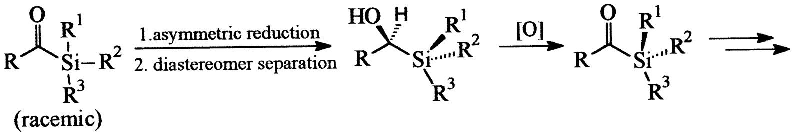
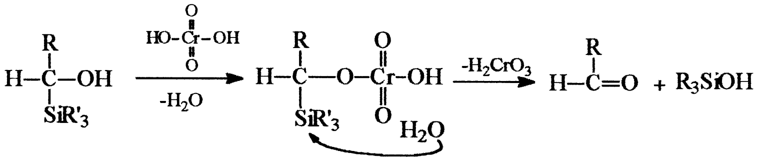
induction[7] and racemate resolution (Scheme 1).[3a] However, the drawback of this protocol is that ordinary oxidizing agents like aqueous permanganate



Scheme 1.

and chromic acid in general lead to silanols and aldehydes as major products (Scheme 2).[5a] Accordingly, the oxidation of α-silyl alcohols to acylsilanes is



Scheme 2.

restrict to some mild conditions, such as Swern-oxidation.[8]

In this communication, we present the results for the oxidation of secondary α-hydroxysilanes **1**[9] to acylsilanes **2** by a mild procedure using potassium permanganate supported[10] onto neutral alumina. Since acylsilanes are easily converted into ester or carboxylic acid by oxidizing reagents,[11] a biphasic mixture of hexane-water was used as solvent in order to limit contact between the inorganic reagent and the produced acylsilane.

Aryl-α-hydroxysilanes having electron-donating groups attached to the aromatic ring (as **1b–d**) were rapidly converted into acylsilanes **2** without significant C-Si cleavage. The replacement of CH_3 by C_6H_5 groups attached to the silicon in the silyl alcohols **1a–c** has not great influence on the yield. On the other hand, the alkyl-α-hydroxysilanes **1f** and **1g** are practically inert toward $KMnO_4$ under these reaction conditions (see Table). As a comparative study, the oxidation of **1f** was carried out by $K_2Cr_2O_7$-H_2SO_4 in water-hexane. Although this reaction is very fast (10 min.), it afforded more than 50% of products from C-Si bond cleavage.

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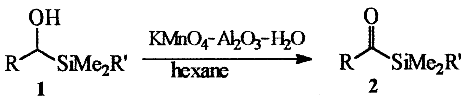
Table. Oxidation of α-Hydroxysilanes into Acylsilanes[12,13]



α-hydroxysilane **1**			acylsilane **2**
R group	R' group	Reaction time (h)[a]	yield (%)[b]
a C_6H_5	CH_3	4.0	55[c]
	C_6H_5	4.0	65[c]
b 4- $CH_3OC_6H_4$	CH_3	2.0	80
	C_6H_5	2.0	70
c $3,4(OCH_3)_2C_6H_3$	CH_3	1.0	86
	C_6H_5	1.5	83
d. $3,4\text{-}(OCH_2O)C_6H_3$	CH_3	2.0	80
e $4\text{-}ClC_6H_4$	CH_3	4.0	40[d,c]
f C_5H_{11}	C_6H_5	3.0[e]	05[d] ; 40[f]
g $(CH_3)_3C$	C_6H_5	4.0[e]	02[d]

[a]Total α-hydroxysilane conversion (except when indicated); [b]Isolated yield (except when indicated); [c]Around 15% of cleavage was detected; [d]Estimated by GC/MS; [e]The α-hydroxysilane was recovered; [f]Oxidation by $K_2Cr_2O_7$-H_2SO_4-H_2O.

In summary, we have reported a mild and practical method of α-hydroxysilanes oxidation, which enlarges the choice of methodologies available to prepare aroylsilanes.

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13. Physical data of the aroylsilane 4-methoxybenzoyldimethylphenylsilane 2b ($R'=Ph$), yellow oil, ν_{max} (KBr)/cm^{-1} 1588 ($C=O$), 1423, 1511, 1253, 836. NMR ^1H (300 MHz, $CDCl_3$): 0.61 (s, 6H, $SiMe_2$); 3.82 (s, 3H, OMe); 6.86 (d, $J=9.4$ Hz, $1H_{meta}$); 7.30–7.61 (m, 5H, SiPh); 7.75 (d, $J=9.4$ Hz, $1H_{ortho}$). m/z: 270 ($M^{\bullet+}$, 10%); 269 (31); 255 (5); 239 (16); 135 (100). HRMS found m/z 269.09961; calcd. for $C_{16}H_{17}O_2Si$ $[M\text{-}H]^+$: 269.09978. Physical data of the aroylsilane 3,4-dimethoxybenzoyldimethylphenylsilane **2c** ($R'=Ph$), yellow oil, ν_{max} (KBr)/cm^{-1} 1573 ($C=O$), 1506, 1413, 1259, 826. NMR ^1H (300 MHz, $CDCl_3$): 0.61 (s, 6H, $SiMe_2$); 3.78 (s, 3H, OMe); 3.88 (s, 3H, OMe); 6.80 (dd, $J=14.5$ and 1.9, lH_{meta}); 7.30–7.41 (m, 5H, SiPh); 7.57–7.63 (m, $2H_{ortho}$). m/z: 300 ($M^{\bullet+}$, 10%); 299 (22); 285 (5); 269 (41); 135 (100). HRMS found m/z 300.11814; calcd. for $C_{17}H_{20}O_3Si$ $[M]^+$: 300.11817. The other acylsilanes **2** were analyzed by GC/MS comparing the retention time and MS spectra with genuine samples. The physical data of these acylsilanes are found in Ref. 4a, 4e, 5a and references cited therein.

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