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DIRECT CONVERSION OF ACYLSILANES TO ESTERS MEDIATED BY IRON (III) AND NITRATE IONS

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Abstract: Acylsilanes, RC(O)SiMe$_3$ (R = C_6H_5, *p*-MeOC$_6$H$_4$ and C_5H_{11}), can be converted into their corresponding carboxylic acids, when water is used as solvent, and esters when alcohol is used as solvent. This oxidation is mediated by iron (III) ions in 20-24 h or nitric acid diluted in alcohol in 2-10 h at room temperature.

Acylsilanes are potential intermediates in organic chemistry for the synthesis of more complex molecules. These compounds are important due to their unique properties and reactivity, as observed in comprehensive reviews.[1] The oxidation potentials of acylsilanes (1.45 V) are lower than ketones (> 2.5 V),[2] therefore acylsilanes are more likely to suffer oxidation.

Thus, acylsilanes can be converted to carboxylic acid by peroxide[3] and ozone.[4] The synthetically useful conversion of acylsilanes to esters is currently carried out by oxidation to carboxylic acid followed by esterification,[5] even though this conversion can be accomplished directly by electrochemistry.[2]

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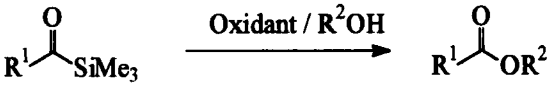
Even though of the electrochemical method afforded reasonable to good yields, this methodology is not readily available to the majority of organic synthetic laboratories. So, we sought to enhance the scope and versatility of this transformation by looking for reagents that could oxidize acylsilanes[6] directly to esters (Scheme 1).



Scheme 1

We found that iron (III) ions (reduction potential of 0.770 V) can mediate this oxidation to give carboxylic acid when water is used as solvent or esters when alcohol is the solvent.[7] The production of ester is almost quantitative when aroylsilanes are reacting with $Fe(NO_3)_3$ in methanol or ethanol (entries 5, 7 and 8 of Table 1). When the alkyl group of alcohol is isopropyl or butyl there is a significant reduction in yield and there is formation of aldehyde (entries 6 and 10 of Table 1). The same result was observed when hexanoyltrimethylsilane reacted with $Fe(NO_3)_3$ in ethanol (entry 11 of Table 1). On the other hand, the nitrate ion seems to be better than other counter ions to mediate oxidation of benzoyltrimethylsilane to afforded benzoic acid when water is used as solvent (entries 1-3 of Table 1) but nitrate ion is not effective by itself (entry 4 of Table 1).

Having in mind that the reduction potential of nitrate ion is 0.01 V at neutral pH and 0.94 V at acidic pH,[8] we used nitric acid diluted in alcohol to perform the oxidation to obtain the corresponding esters.[9] In general, the reactions using HNO_3 were faster than those using Fe(III) ions and the conversion was quantitative even using n-propanol, n-butanol, n-hexanol and benzenemethanol (entries 1, 2, 4, 5, 8, 10, 12 and 13 of Table 2), and increased up to 88% when the hexanoyltrimethylsilane was oxidized (entry 14 of Table 2). Using $Al(NO_3)_3$, a less acidic reagent, there was a significant reduction in the reactivity (entry 3 of Table 2). It seems that the

Table 1. Conversion of acylsilanes to esters mediated by iron (III) ions at 27 °C.

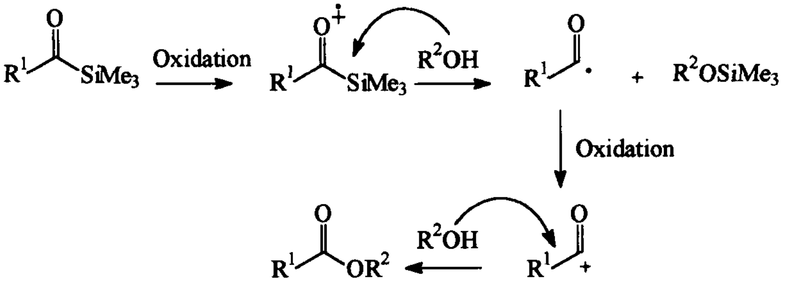
Entry	Acylsilane (R^1)	Solvent	Reagent [mol ratio]^a	Reaction time (h)	Acid or ester onversion (%)
1	C_6H_5	water	$Fe(NO_3)_3/K10^{(*)}$ [1.5]	20	82
2			$FeCl_3/K10$ [2.0]	20	72^b
3			$Fe_2(SO_4)_3/K10$ [3.0]	24	50^b
4			$KNO_3/K10$ [2.0]	20	0
5		Ethanol	$Fe(NO_3)_3$ [1.5]	20	85
6		*n*-Butanol	$Fe(NO_3)_3$ [2.0]	24	10^b
7	*p*-$MeOC_6H_4$	Methanol	$Fe(NO_3)_3$ [1.5]	20	96
8		Ethanol	$Fe(NO_3)_3$ [1.5]	20	98
9			$Fe_2(SO_4)_3/HCl$ [2.0]	8	90
10		Isopropanol	$Fe(NO_3)_3$ [2.5]	24	45^b
11	C_5H_{11}	Ethanol	$Fe(NO_3)_3$ [2.0]	20	55^b

a- mol of salt/mol of acylsilane; b- unreacted acylsilane was recovered and 10-20% of aldehyde was detected. (*) montmorillonite K10 (support)

Table 2. Conversion of acylsilanes to esters mediated by nitric acid diluted in alcohol at 27 °C.

Entry	Acylsilane (R^1)	Alcohol	Reagent [mol ratio]^a	Reaction time (h)	Ester onversion (%)
1	C_6H_5	Methanol	HNO_3 [1.5]	2	100
2		Ethanol	HNO_3 [1.5]	2	100
3			$Al(NO_3)_3$ [1.5]	20	98
4	*p*-$MeOC_6H_4$	Methanol	HNO_3 [1.5]	3	100
5		Ethanol	HNO_3 [1.5]	2	100
6			HCl [2.0]	8	0^b
7			H_2SO_4 [2.0]	8	0^b
8		*n*-Propanol	HNO_3 [2.0]	3	100
9		Isopropanol	HNO_3 [2.0]	20	50^b
10		n-Butanol	HNO_3 [2.0]	8	100
11		*tert*-Butanol	HNO_3 [2.0]	10	$10^{b,c}$
12		*n*-Hexanol	HNO_3 [1.5]	10	100
13		Benzenemethanol^d	HNO_3 [1.5]	6	100
14	C_5H_{11}	Ethanol	HNO_3 [2.0]	20	88

a- mol of salt/mol of acylsilane; b- unreacted acylsilane was recovered; c- some quantity of acid was detected; d- a solution of benzenemethanol/ethyl acetate (1:1) was used.



Scheme 2

reaction rate is dependent on acid concentration even for the oxidation mediated by Fe(III) salts (entry 9 of Table 1). The yields are reduced when the bulk of the alkyl groups of the alcohols are increased (entries 9 and 11 of Table 2).

The mechanism probably occurs by electron transference to Fe^{+3} or NO_3^- ions and may be similar to that one proposed for electrochemical oxidation[2] (Scheme 2) where cationic intermediates $[RC(O)SiMe_3]^{+\bullet}$ and $[RC(O)]^+$ may be involved, since we found the reactivity order to be p-$MeOC_6H_4C(O)SiMe_3 \cong C_6H_5C(O)SiMe_3 > C_5H_{11}C(O)SiMe_3$. The silyl ether that is proposed as a by-product could be detected by GC/MS when *p*-methoxybenzoyltrimethylsilane was allowed to react with nitric acid in the presence of benzenemethanol (entry 13 of Table 2).

In summary, the direct conversion of acylsilanes to esters, presented in this work, provides an efficient and versatile methodology. It can be accomplished by nitric acid diluted in alcohol or by alcoholic solutions of Fe(III) salts, in cases where mild oxidation is required.

Acknowledgements.

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[7] **General procedure for oxidation with Fe (III) salts**: a) **when water is used as solvent**: A mixture of 10-15 mL of water, 2 g of montmorillonite K10, 0.10 mmol of acylsilane and 0.1-0.3 mmol of salt (see Table 1) was stirred during 20-24 h at temperature of 27 °C. The products were extracted with 5-10 mL of ethyl acetate, the organic phase dried with $MgSO_4$ and analyzed by GC/MS comparing with genuine samples. b) **when alcohol is used as solvent**: A mixture of 10-15 mL of alcohol, 0.10 mmol of acylsilane and 0.1-0.25 mmol of salt (see Table 1) was stirred during 20-24 h at temperature of 27 °C. After addition of 10 mL of water the products were extracted with 5-10 mL of ethyl acetate, the organic phase dried with $MgSO_4$ and analyzed by GC/MS as mentioned above.

[8] Weast, R. C.; CRC Handbook of Chemistry and Physics, **1978**, p. D-141,

[9] **General procedure for oxidation with nitric acid:** a solution of 10 mL of alcohol, 0.1 mmol of acylsilane and 0.15-0.2 mmol concentrated nitric acid was stirred during 2-20 h (see Table 2) at temperature of 27°C. After addition of 10 mL of water the products were extracted with 5-10 mL of ethyl acetate, the organic phase dried with $MgSO_4$ and analyzed by GC/MS as mentioned above.

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