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METAL SILANOLATES: ORGANIC SOLUBLE EQUIVALENTS FOR O^{-2}

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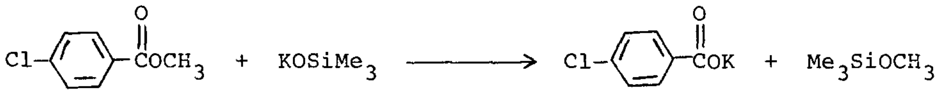
SUMMARY Alkali metal trimethylsilanolates, $M^{\oplus}\,{}^{\ominus}OSiMe_3$, convert carboxylic acid derivatives into their corresponding anhydrous acid salts under mild non-aqueous conditions.

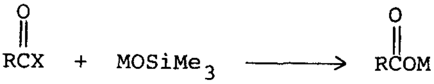
Metal silanolates have seen limited use in organic synthesis.[2] We believe these compounds, some commercially available,[3] possess a rich chemistry which has not been fully exploited. The silanolate salts have two unique advantages over other oxygen anions. They have appreciable solubility in organic solvents (ether, THF, toluene, methylene chloride) and the silicon oxygen bond may be easily cleaved, often under reaction conditions. These features allow a silanolate to function as an organic soluble equivalent of O^{-2}. We report here the use of alkali metal silanolates (particularly potassium trimethylsilanolate) to convert acid derivatives directly to their anhydrous salts.

The following procedure for the preparation of anhydrous acid salts is typical. Methyl 4-chlorobenzoate (13.65 g, 80 mmol) was added in one portion to a stirred slurry of potassium trimethylsilanolate (10.26 g, 80 mmol) in dry ether (500 ml) at ambient temperature under nitrogen. The reaction mixture was stirred for 4 hr. The white solid was filtered under nitrogen, washed with ether, and dried under a stream of nitrogen to afford analytically pure potassium 4-chlorobenzoate (13.1 g, 84%).[4]

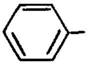
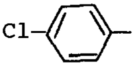
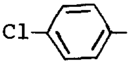
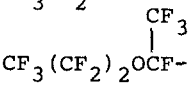


This mild procedure has clear-cut advantages over aqueous hydrolysis followed by drying in vacuo to prepare anhydrous acid salts. It has been shown in one case that the anhydrous salt prepared by the silanolate method absorbs more moisture than the same salt prepared by conventional procedures.[5] This suggests that the chemistry of salts prepared by our procedure may be different.

Table. Preparation of Anhydrous Salts



$$\overset{O}{\overset{\|}{\mathrm{RCX}}} + \mathrm{MOSiMe_3} \longrightarrow \overset{O}{\overset{\|}{\mathrm{RCOM}}}$$

Entry	R	X	M	Solvent	Temp. (°C)	Time[a,b] (h)	% Yield[c]
1	$(CF_3)_2CF-$	F	K	ether	25	3	61[d]
2	$CF_3(CF_2)_6-$	Cl	K	ether	25	1/3	77[d]
3		Cl	K	ether	25	2/16	75
4	$CH_3(CH_2)_5-$	Cl	K	ether	25	1/16	87[d]
5	$CH_3(CH_2)_5-$	OCH_3	K	THF	25	16	82
6	$CH_3(CH_2)_5-$	OCH_3	Li	toluene	110	2.5	51
7		OCH_3	K	ether	25	4	84[d]
8		OCH_3	Na	toluene	80	4	86
9	CH_3-	$OSiMe_3$	K	ether	25	2	95[d]
10	CF_3-	$OSiMe_3$	Na	THF	25	16	98
11	CF_3CF_2-	OCH_3	Na	CH_2Cl_2	25	1	92[d]
12	 $CF_3(CF_2)_2O\overset{CF_3}{\overset{\mid}{C}}F-$	F	Na	toluene	110	1.5	66[d]

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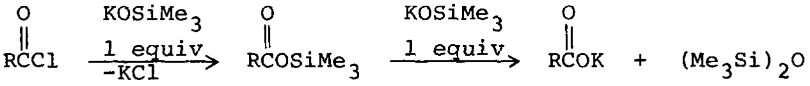
a) For X=Cl two sequential equivalents of $MOSiMe_3$ were required, with the time for each addition noted.

b) Reaction times of 16 h refer to overnight run made for convenience and do not reflect the minimal time needed to reach completion.

c) Yields are not optimized.

d) Obtained analytically pure.

The reaction described is general (table) and not limited to methyl esters. Acid fluorides are similarly converted to their acid salts in high yield. With acid chlorides, however, the reaction follows a different course. When an acid chloride and potassium trimethylsilanolate are combined in equimolar amounts, potassium chloride not the acid salt, is precipitated in nearly quantitative yield.[6] The supernatant liquid contains a trimethylsilyl ester. The addition of a second equivalent of $KOSiMe_3$ to the filtrate precipitates the pure acid salt leaving hexamethyldisiloxane in solution. In separate experiments it was demonstrated that trimethylsilyl esters are converted in high yield to acid salts under the



$$\mathrm{R\overset{\overset{O}{\|}}{C}Cl} \xrightarrow[\mathrm{-KCl}]{\overset{\mathrm{KOSiMe_3}}{\text{1 equiv}}} \mathrm{R\overset{\overset{O}{\|}}{C}OSiMe_3} \xrightarrow{\overset{\mathrm{KOSiMe_3}}{\text{1 equiv}}} \mathrm{R\overset{\overset{O}{\|}}{C}OK} + \mathrm{(Me_3Si)_2O}$$

reaction conditions. These observations are consistent with the $KOSiMe_3$ being much more reactive with an acid chloride than a silyl ester. Otherwise, the reaction of an acid chloride should lead to a co-precipitation of KCl and acid salt as the increasing concentration of silyl ester competed with the remaining acid chloride for unreacted $KOSiMe_3$. The difference in reactivity between acid chlorides and silyl esters is presumably due to different modes of reaction (carbonyl attack versus S_N2-Si displacement)[6] although other factors cannot be ruled out at this time.

As entries 4 and 5 illustrate, α-protons do not interfere with the desired reaction. Particularly with entry 4, we were concerned with the possibility of ketene formation. At least in this case, $KOSiMe_3$ behaves as a nucleophile rather than a base.[7]

While we have routinely used $KOSiMe_3$ for this chemistry, the sodium and lithium salts are equally effective. Ether, THF, toluene, and methylene chloride are all suitable solvents for the transformation.

The simple chemistry described above clearly demonstrates that metal silanolates are synthons for O^{-2} which are soluble in organic solvents. We are currently exploring other facets of the organic chemistry of silanolates and will report shortly on these developments.

References

1. Contribution No. 3251 from the Department.

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c. V. S. Chugunov, *Zh. Obshch. Khim*. **1957** 27, 494-6; C.A. **1957** 51, 15441d.

3. $KOSiMe_3$ and $NaOSiMe_3$ are available from Petrarch Systems, Inc. We sublime $NaOSiMe_3$ prior to use. $KOSiMe_3$ was used as received. $LiOSiMe_3$ is prepared according to: D. Seyferth and D. L. Alleston, *Inorg. Chem*., **1963** 2, 418-20.

4. Trimethylmethoxysilane, the volatile byproduct, was identified by G.C. comparison with an authentic sample on 20% FS-1265 60/80 Gaschrome R, 6 ft. x 1/8 in column T=50°C R_t=1.48 min.

5. $CF_3(CF_2)_6CO_2K$ absorbed 3 times as much water when prepared by the silanolate route. We thank Dr. W. E. Barnette for performing these experiments.

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