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Scope and Limitations of Sodium and Potassium Trimethylsilanolate as Reagents for Conversion of Esters to Carboxylic Acids

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Sodium or potassium trimethylsilanolate act as versatile and very powerful reagents for conversion of a wide variety of esters to carboxylic acids. The reactions were performed in tetrahydrofuran under mild reaction conditions with high to quantitative yields.

INTRODUCTION

Conversion of esters to carboxylic acids is an important reaction with wide-spread applications in both research and industry.[1] Typically, the reaction is performed by saponification with sodium or potassium hydroxides in water, lower alcohols, or their mixtures.[2] An additional accelerating effect can be achieved by using various phase-transfer catalysts.[2,3] Alternatively, in the cases of extreme sterical hindrances, saponification can be conducted with highly reactive, finely dispersed potassium hydroxide *in situ* generated by addition of a stoichiometric amount of water to the etheral (or THF) solution of potassium *tert*-butoxide.[4] Besides saponification, esters can be hydrolyzed with various protic or Lewis acids, *e.g.*, CH_3SO_3H,[5] *p*-TsOH,[6] BCl_3.[7] However, both saponification and acid-catalyzed hydrolysis of esters can be limited in the cases of acid- or base-sensitive substrates. Apart from numerous methods based on saponification/hydrolysis reaction pathways, this conversion can be carried out with various strong nucleophilic reagents capable to cleave the esters by the dealkylation (S_N2-type) reaction.[8]

Among them, LiCl,[9] LiBr,[9] LiI,[9–11] NaCN,[8] $NaSC_6H_5$,[8] LiS*n*-Pr[8] and KO*t*-Bu[8] have been described as effective reagents for conversion of esters derived from primary and secondary alcohols. Concerning the activity and versatility, lithium iodide and thio-n-propoxide in refluxing polar aprotic solvents, *e.g.*, DMF, are the most popular and widely used reagents.[8,10] Still, these methods have serious drawbacks, including relatively harsh reaction conditions and lack of sensitive functional groups. Possibly, the most powerful reagents for cleavage of esters to carboxylic acids are boron trihalides, *e.g.,* BCl_3, BBr_3,[12] and $(CH_3)_3SiI$.[13] These reagents are highly reactive and are not tolerant to many functional groups, which seriously limits their utility.

Laganis and Chenard reported that sodium or potassium trimethylsilanolate efficiently cleave methyl hepta-

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noate and *p*-chlorobenzoate to the corresponding acids in high yields under mild reaction conditions (THF/r. t.).[14] Unfortunately, these were the only two examples of employing alkali metal silanolates as the reagent for this reaction. Some other authors recognized these potentially powerful reagents and used them successfully in some instances in the cleavage of two methyl esters of aliphatic acids,[15–18] two methyl esters of aromatic acids,[19,20] one ethyl ester of aliphatic acid,[21] *p*-nitrobenzoyl esters of secondary aliphatic alcohol.[22] There is an evident lack of information about the real scope and limitation of this kind of reagents. No such study has been published to date. Since we have been very successful with the application of sodium trimethylsilanolate in some very specific esters, we decided to study the scope and limitation of the reaction of sodium and potassium trimethylsilanolates with various classes of esters: esters of aliphatic and aromatic acids of primary, secondary, and tertiary alcohols, as well as phenols, allyl, and benzyl alcohols; esters of α,β-unsaturated acids; esters of acids functionalyzed with acidic functional groups, *etc*.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a AV Bruker (600 MHz) spectrometer, and shifts are given in ppm downfield from TMS as an internal standard. TLC analyses were performed on Merck's (Darmstadt, Germany) DC-alufolien with Kieselgel 60F_{254}. Melting points were determined using a Büchi B-540 instrument.

Preparation of Sodium and Potassium Trimethylsilanolate

To a stirred solution of 16.24 g hexamethyldisiloxane (0.1 mol) in 100 cm^3 of 1,2-dimethoxyethane (DME), 8.0 g of sodium hydroxide (0.2 mol) (or 11.22 g of potassium hydroxide (0.2 mol)) was added. The reaction mixture was vigorously stirred at reflux temperature for 72 h. After that, the mixture was filtered and the crude residue was washed with 2 x 50 cm^3 of boiling DME. The filtrate and washings were evaporated to dryness. Crude product was azeotropically dried with 2 x 100 cm^3 of toluene and 11.18 g (49.8 %) sodium trimethylsilanolate was obtained as almost white hygroscopic crystals (or 7.94 g (20.6 %) of potassium trimethylsilanolate was obtained as 3 $KOSi(CH_3)_3 \cdot DME$ solvate as a slightly yellow semi-solid hygroscopic mass).

$NaOSi(CH_3)_3$

M.p.: > 395 °C; ^{1}H NMR (DMSO-d_6) δ/ppm: –0.22 (s, 9H, CH_3Si); ^{13}C NMR (DMSO-d_6) δ/ppm: 5.42 (*C*H_3Si); IR (KBr) ν_{max}/cm^{-1}: 3648, 3399, 2952, 2897, 2322, 1910, 1666, 1444, 1284, 1252, 1239, 948, 883, 832, 747, 669, 650, 542. The content of sodium trimethylsilanolate determined by volumetric titration (0.1 M HCl; methyl orange) was 90.1 %.

$3KOSi(CH_3)_3 \cdot DME$

^{1}H NMR (DMSO-d_6) δ/ppm: –0.20 (s, 27H, CH_3Si), 2.78 (s, 6H, CH_3O), 2.93 (s, 4H, CH_2O); ^{13}C NMR (DMSO-d_6) δ/ppm: 14.46 (*C*H_3Si), 69.00 (*C*H_3O), 76.90 (*C*H_2O); IR (KBr) ν_{max}/cm^{-1}: 3188, 2950, 2897, 1906, 1627, 1467, 1382, 1251, 1193, 982, 884, 831, 778, 744, 704, 671, 644, 593. The content of potassium trimethylsilanolate determined by volumetric titration (0.1 M HCl; methyl orange) was 87.4 %.

Sodium Silanolate-mediated Cleavage of Esters to Carboxylic Acids – Typical Procedure

To a suspension of ester (2 mmol) in dried tetrahydrofuran, sodium trimethylsilanolate (2.4 mmol) was added – amount ratio ("mole ratio") of ester with respect to sodium trimethylsilanolate (*r*(ester, sodium trimethylsilanolate) = *n*(ester) / *n*(sodium trimethylsilanolate)) is 1 : 1.2. The reaction mixture was stirred at room temperature for the time indicated in Tables I and II. After the reaction mixture was evaporated to dryness, distilled water was added to the residue. Concentrated hydrochloric acid was added dropwise until the pH reached 3.0. The suspension was then filtered, crude residue was washed with water, and dried under high vacuum to a constant mass (or crude product was isolated by extraction with dichloromethane, organic layers were dried over Na_2SO_4, and evaporated). The crude product was additionally purified by preparative chromatography.

The analytical results (M.p., IR, ^{1}H-, ^{13}C-NMR) of all products **2a**-**k** were in good agreement with the literature data.[23–26]

N-*Carbobenzoxy-L-leucine*[27] (**2g**, $C_{14}H_{19}O_4N$)

Yield: 0.48 g (90 %); R_f (5 % CH_3OH/CH_2Cl_2): 0.57; ^{1}H NMR ($CDCl_3$) δ/ppm: 0.92–0.94 (m, 6H, (CH_3)$_2$CH), 1.50–1.60 (m, 1H, (CH$_3$)$_2$C*H*), 1.62–1.69 (m, 2H, CH_2CH), 4.34–4.40 (m, 1H, C*H*N), 5.04–5.17 (m, 2H, CH_2Ph), 5.29 (s, 1H, N*H*), 7.26–7.60 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ/ppm: 16.91 ((*C*H$_3$)$_2$CH), 18.20 ((*C*H$_3$)$_2$CH), 20.03 ((CH$_3$)$_2$*C*H), 36.64 (*C*H$_2$CH) 47.98 (*C*HN), 62.37 (*C*H$_2$Ph), 122.36, 122.88, 123.32, 123.43, 123.79, 131.03, 151.79 (O*C*ON), 173.06 (*C*OOH); IR (KBr) ν_{max}/cm^{-1}: 3322, 3091, 3066, 3034, 2959, 2872, 2606, 1952, 1875, 1863, 1804, 1723, 1712, 1609, 1587, 1531, 1469, 1455, 1413, 1388, 1369, 1344, 1265, 1228, 1172, 1121, 1080, 1049, 1029, 1004, 981, 910, 861, 843, 823, 777, 737, 697, 678, 623, 614, 576. HPLC analysis of enantiomeric purity of *N*-carbobenzoxy-L-leucine (**2g**) was performed on Chiralpak AD-RH column using a mobile phase 0.2 M KH_2PO_4, pH = 2.0 / ACN 7/3; t_R(*S*-) = 12.21 min, t_R(*R*-) = 14.40 min.

N-*Carbobenzoxy-L-isoleucine*[27] (**2h**, $C_{14}H_{19}O_4N$)

Yield: 0.50 g (95 %); R_f (10 % CH_3OH/CH_2Cl_2): 0.49; ^{1}H NMR ($CDCl_3$) δ/ppm: 0.90–0.98 (m, 6H, CH_3CH$_2$, CH_3CH), 1.13–1.22 (m, 1H, CH$_3$CH_2), 1.40–1.51 (m, 1H, CH$_3$CH_2), 1.92–1.94 (m, 1H, CH$_3$C*H*), 4.36–4.41 (m, 1H, C*H*N), 5.11

(s, 2H, CH_2Ph), 5.29–5.35 (m, 1H, N*H*), 7.30–7.36 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ/ppm: 11.49 (*C*H_3CH$_2$), 15.36 (*C*H_3CH), 24.72 (CH$_3$*C*H_2), 37.66 (CH$_3$*C*H), 58.14 (*C*HN), 67.07 (*C*H_2Ph), 128.04, 128.13, 128.44, 136.00, 156.16 (O*C*ON), 176.57 (*C*OOH); IR (KBr) ν_{max}/cm^{-1}: 3416, 3326, 3091, 3066, 3035, 2966, 2936, 2878, 2611, 1711, 1587, 1523, 1456, 1414, 1387, 1342, 1216, 1127, 1092, 1043, 1028, 980, 912, 844, 825, 776, 738, 698, 664, 626, 615. HPLC analysis of enantiomeric purity of *N*-carbobenzoxy-L-isoleucine (**2h**) was performed on Chiralpak AD-RH column using a mobile phase 0.2 M KH_2PO_4, pH = 2.0 / ACN 7/3; t_R(*S*-) = 12.30 min, t_R(*R*-) = 14.94 min.

N-*Carbobenzoxy-L-phenylglycine*[27] (*2i, $C_{16}H_{15}O_4N$*)

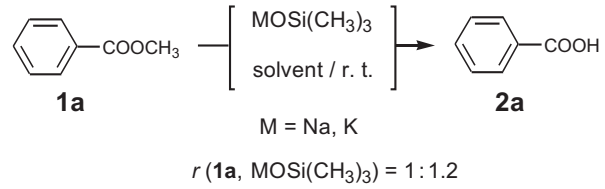
Yield: 0.56 g (98 %); R_f (5 % CH$_3$OH/2 % CH$_3$COOH/CH$_2$Cl$_2$): 0.62; M.p.: 131.9–133.1 °C; ^{1}H NMR (CD_3OD) δ/ppm: 5.06–5.11 (m, 2H, O*C*H$_2$Ph), 5.26 (s, 1H, *C*HN), 7.31–7.42 (m, 10H, Ph); ^{13}C NMR (CD_3OD) δ/ppm: 59.78 (*C*HPh), 67.89 (O*C*H$_2$Ph), 128.71, 128.95, 129.10, 129.42, 129.56, 129.85, 138.22, 138.54, 158.21 (O*C*ON), 174.10 (*C*OOH); IR (KBr) ν_{max}/cm^{-1}: 3403, 3036, 2959, 1745, 1669, 1587, 1533, 1498, 1455, 1441, 1399, 1351, 1311, 1290, 1248, 1203, 1173, 1155, 1085, 1054, 1029, 1007, 978, 927, 905, 872, 802, 776, 764, 741, 720, 696. HPLC analysis of enantiomeric purity of *N*-carbobenzoxy-L-phenylglicine (**2i**) was performed on Chiralcel OJ-RH column using a mobile phase 0.2 M KH_2PO_4, pH = 2.0 / ACN 6/4; t_R(*S*-) = 5.38 min, t_R(*R*-) = 5.68 min.

N-Carbobenzoxy-L-*phenylalanine*[27] (*2j, $C_{17}H_{17}O_4N$*)

Yield: 0.58 (96 %); R_f (5 % CH$_3$OH/2 % CH$_3$COOH/CH$_2$Cl$_2$): 0.69; M.p.: 130–132°C; ^{1}H NMR (CD_3OD) δ/ppm: 2.89–2.96 (m, 1H, C*H*$_2$Ph), 3.16–3.30 (m, 1H, C*H*$_2$Ph), 4.38–4.42 (m, 1H, C*H*N), 5.00–5.10 (m, 2H, OC*H*$_2$Ph), 7.15–7.37 (m, 10H, Ph); ^{13}C NMR (CD_3OD) δ/ppm: 38.98 (*C*H$_2$Ph), 57.46 (*C*HN), 67.53 (O*C*H$_2$Ph), 127.73, 128.77, 129.01, 129.46, 129.53, 130.10, 130.50, 138.93, 158.36 (O*C*ON), 176.18 (*C*OOH); IR (KBr) ν_{max}/cm^{-1}: 3324, 3062, 3033, 2949, 1733, 1695, 1604, 1538, 1497, 1455, 1261, 1084, 1049, 823, 747, 696. HPLC analysis of enantiomeric purity of *N*-carbobenzoxy-L-phenylalanine (**2j**) was performed on Chiralcel OJ-RH column using a mobile phase 0.2 M KH_2PO_4, pH = 2.0 / ACN 6/4; t_R(*S*-) = 5.23 min, t_R(*R*-) = 5.80 min.

RESULTS AND DISCUSSION

Here we wish to report that sodium or potassium trimethylsilanolate act as very efficient reagents for conversion of several classes of esters to the corresponding carboxylic acids. The reagents were prepared by heating sodium or potassium hydroxide with hexamethyldisiloxane in refluxing 1,2-dimethoxyethane (see Experimental). First, we probed the reaction of the model ester methyl benzoate (**1a**), with sodium and potassium trimethylsilanolate, where benzoic acid[23] (**2a**) was isolated in high yields (Scheme 1). Among the various solvents examined, tetrahydrofuran has been proved to be the most suitable (Table I).



Scheme 1.

TABLE I. Solvent effect in the reaction of methyl benzoate (**1a**) with sodium or potassium trimethylsilanolate (Scheme 1)[a]

Entry	Solvent	Time / h[b]	Yield / %[c]
1	CH_2Cl_2	3	92
2	CH_2Cl_2[d]	3	88
3	toluene	3	90
4	DMF	1.5	90
5	DMF[d]	1.5	87
6	CH_3CN	2.5	89
7	THF	1	97
8	THF[d]	1	90

[a] All reactions were performed at room temperature in dried reaction solvents with the amount ratio, r(**1a**, $NaOSi(CH_3)_3$) = n(**1a**) / $n(NaOSi(CH_3)_3$ = 1 : 1.2) unless otherwise noted.

[b] Determined by TLC analysis.

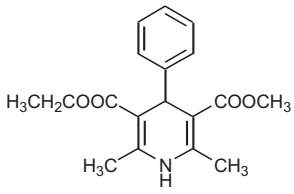
[c] Yields of pure products isolated by preparative chromatography.

[d] Amount ratio, r(**1a**, $KOSi(CH_3)_3$) = 1 : 1.2.

Hereafter, several classes of esters **1b-q** were subjected to reaction with sodium (or potassium) trimethylsilanolate where the respective carboxylic acids **2a-f** were obtained in high yields (Scheme 2). In all cases, excellent conversions were observed, giving practically pure carboxylic acids (Table II).

Both sodium and potassium trimethylsilanolate showed similar activity. Esters of both aliphatic and aromatic acids derived from primary and secondary alcohols smoothly react with sodium or potassium trimethylsilanolate, affording the corresponding carboxylic acids in fair yields. Phenolic (Entry 7), allylic (Entries 5 and 14), benzylic (Entries 6 and 15) esters also undergo the reaction.

However, esters of tertiary alcohols do not react even after a prolonged reaction time (Entry 3). Unfortunatelly, all attempts to carry out the dealkylation of methyl or ethyl esters of 2,6-dimethyl-4-phenyl-1,4-dihydropyridinecarboxylic acids (**1r**, Hantzsch type compounds), known as very unreactive esters,[28,29] completely failed despite rather harsh reaction conditions (refluxing THF or dioxane / 24 h).



1r

Furthermore, we studied the effect of sodium trimethylsilanolate on reactions of benzyl esters of *N*-carbobenzyloxy-protected L-leucine (**1s**), isoleucine (**1t**), phenylglycine (**1u**), phenylalanine (**1v**), as well as L-tryptophan-methyl ester (**1x**) to check whether the reaction can be preformed with preserving optical purity (Scheme 3). Dealkylation of these model chiral esters under optimized conditions proceeds smoothly, giving the expected acids **2g**-**k** in very high yields. In contrast to the only literature report dealing with polymerically bound amino acid methyl ester,[15] HPLC analysis of products **2g**, **h**, **k** using chiral stationary phases showed that partial racemization takes place to give approx. 0.3–3.5 % of the opposite enantiomer (Table III). However, the amounts of opposite (unwanted) enantiomers allow further purification (recrystallization) to furnish optically pure acids **2g**, **h**, **j** in good yields. Unfortunately, phenylglycine and phenylalanine esters **1u**, **v** underwent extensive racemization.

The reaction presumably proceeds via the $B_{AL}2$ (S_N2-type) reaction mechanism by nucleophilic attack of the trimethylsilanolate anion (as highly nucleophilic reagent) on the carbon atom of alkyl-group with carboxylate anion as the leaving group (Scheme 4). The small amounts of benzoic acid isolated from the reaction of *tert*-butyl benzoate (**1d**) probably come from the side-reaction of sodium

TABLE II. Sodium or potassium trimethylsilanolate-mediated cleavage of esters **1b–q** to carboxylic acids **2a–f** (Scheme 2)[a]

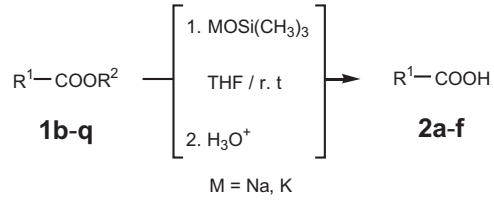
Entry	Ester	R^1	R^2	Carbox. acid	Time[b] h	Yield[c] %
1	**1b**	Ph	Et	**2a**[23]	3	92
2	**1c**	Ph	*i*-Pr	**2a**	48	74 (86)[d]
3	**1d**	Ph	*t*-Bu	**2a**	26	30
4	**1e**	Ph	n-C_5H_{11}	**2a**	6	90
5	**1f**	Ph	CH_2=$CHCH_2$	**2a**	3	97
6	**1g**	Ph	Bn	**2a**	45	96
7	**1h**	Ph	Ph	**2a**	70	75 (70)[d]
8	**1i**	2-IC_6H_4	Me	**2b**	18	93
9	**1j**	2-HOC_6H_4	Me	**2c**[24]	18	94
10	**1k**	2-$H_2NC_6H_4$	Me	**2d**[25]	30	92
11	**1l**	$PhCH_2CH_2$	Me	**2e**[26]	2	95
12	**1m**	$PhCH_2CH_2$	Et	**2e**	6	99
13	**1n**	$PhCH_2CH_2$	*i*-Pr	**2e**	48	99 (97)[d]
14	**1o**	$PhCH_2CH_2$	CH_2=$CHCH_2$	**2e**	5	99
15	**1p**	$PhCH_2CH_2$	Bn	**2e**	72	95 (91)[d]
16	**1q**	PhCH=CH	Et	**2f**	20	94

[a] All reactions were performed at room temperature in dried reaction solvents with the amount ratio of esters with respect to $NaOSi(CH_3)_3$ equal to 1 : 1.2 unless otherwise noted.

[b] Determined by TLC analysis.

[c] Yields of pure products isolated by preparative chromatography.

[d] Amount ratio, *r*(ester, $KOSi(CH_3)_3$) = 1 : 1.2

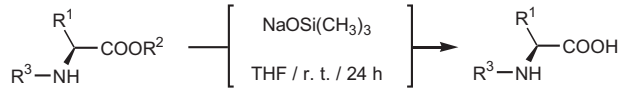


r (**1b–q**, $MOSi(CH_3)_3$) = 1 : 1.2

1b: R^1= Ph, R^2= Et
1c: R^1= Ph, R^2= *i*-Pr
1d: R^1= Ph, R^2= *t*-Bu
1e: R^1= Ph, R^2= *n*-C_5H_{11}
1f: R^1= Ph, R^2= allyl
1g: R^1= Ph, R^2= Bn
1h: R^1= Ph, R^2= Ph
1i: R^1= 2-IC_6H_4, R^2= Me
1j: R^1= 2-HOC_6H_4, R^2= Me
1k: R^1= 2-$H_2NC_6H_4$, R^2= Me
1l: R^1= $Ph(CH_2)_2$, R^2= Me
1m: R^1= $Ph(CH_2)_2$, R^2= Et
1n: R^1= $Ph(CH_2)_2$, R^2= *i*-Pr
1o: R^1= $Ph(CH_2)_2$, R^2= allyl
1p: R^1= $Ph(CH_2)_2$, R^2= Bn
1q: R^1= PhCH=CH, R^2= Et

2a: R^1= Ph
2b: R^1= 2-IC_6H_4
2c: R^1= 2-HOC_6H_4
2d: R^1=2-$H_2NC_6H_4$
2e: R^1= $Ph(CH_2)_2$
2f:R^1= PhCH=CH

Scheme 2.



1s-x **2g-k**

r (**1s–x**, $MOSi(CH_3)_3$) = 1 : 1.2

1s: R^1= $(CH_3)_2CHCH_2$, R^2= Bn, R^3= COOBn

1t: R^1= $CH_3CH_2(CH_3)CH$, R^2= Bn, R^3= COOBn

1u: R^1= Ph, R^2= Bn, R^3= COOBn

1v: R^1, R^2= Bn, R^3= COOBn

1x: R^1= indole-3-ylmethyl, R^2= CH_3, R^3= H

2g: R^1= $(CH_3)_2CHCH_2$, R^3= COOBn

2h: R^1= $CH_3CH_2(CH_3)CH$, R^3= COOBn

2i: R^1= Ph, R^3= COOBn

2j: R^1, R^3= COOBn

2k: R^1= indole-3-ylmethyl, R^3= H

Scheme 3.

TABLE III. Sodium or potassium trimethylsilanolate-mediated dealkylation of chiral esters **1s–x** to carboxylic acids **2g–k** (Scheme 3)[a]

R^1	R^2	Product	Time[b] / h	Yield[c] / %	Opt. purity[d] / %
$(CH_3)_2CHCH_2$	Bn	**2g**	4.5	90	96.5:3.5 (96.0:4.0)[e]
$CH_3CH_2(CH_3)CH$	Bn	**2h**	3.5	95	96.7:3.3
Ph	Bn	**2i**	1.5	98	55.1:44.9
Bn	Bn	**2j**	0.5	96	81.4:18.6
indole-3-yl	Me	**2k**	2.5	98[f]	99.7:0.3

[a]All reactions were performed at room temperature in dried reaction solvents with the amount ratio of esters with respect to $NaOSi(CH_3)_3$ equal to 1 : 1.2 unless otherwise noted.

[b]Determined by TLC analysis.

[c]Yields of pure products isolated by preparative chromatography.

[d]Determined by HPLC.

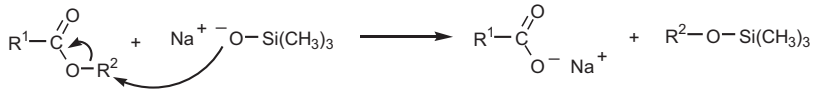
[e]Using NaOH in MeOH (r.t. / 4 h).

[f]With *r*(ester, $NaOSi(CH_3)_3$) = 1 : 2.2.

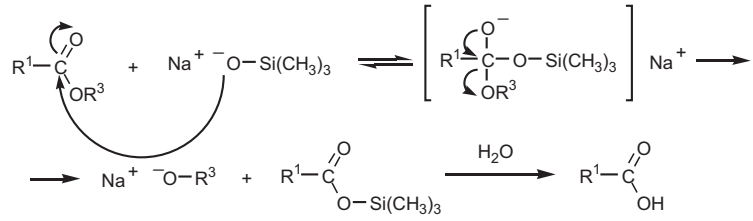
hydroxide present in small amounts (<10 %) in sodium trimethylsilanolate reagent, rather than from trimethylsilanolate-mediated dealkylation. However, an alternative $B_{AC}2$ (tetrahedral) reaction pathway involving the nucleophilic attack of trimethylsilanolate anion on the ester acyl-carbon atom has to be also taken into account at substrates derived from highly acidic alcohols, *e.g.,* phenols. Yield in the reaction of phenyl benzoate (**1h**) was much higher than one could expect from the possible saponification side-reaction of the starting ester with traces of sodium hydroxide present in sodium trimethylsilanolate reagent. Since nucleophilic substitution at the aromatic position of these substrates is rather unlikely, the only reasonable alternative explanation is the nucleophilic substitution pathway at the acyl-position (Scheme 4). Less basic phenolates are significantly better leaving groups than alkoxides providing this alternative reaction pathway.

The substantial racemization of phenylglycine ester **1u** presumably proceeds via enolate **3** with double bond

S_N2-type ($B_{AL}2$)-reaction pathway:



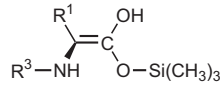
$B_{AC}2$ tetrahedral reaction pathway:



R^1 = alkyl, aryl; R^2 = primary, secondary alkyl, allyl, benzyl; R^3 = aryl

Scheme 4.

present at the parent chiral position. Subsequent protonation gave a racemic product.



3

R^1= Ph, R^3= COOBn

Since the shift of the double bond in the corresponding enolate of the phenylalanine ester **1v** is much less favored, the degree of racemization at this particular model ester is much lower.

In conclusion, sodium or potassium trimethylsilanolate are very powerful, versatile and efficient reagents for dealkylation of esters derived from variously functionalized aliphatic, aromatic, or α,β-unsaturated acids with primary or secondary aliphatic, allylic, and benzylic alcohols, as well as phenols, in tetrahydrofuran as solvent under mild reaction conditions (r.t. / possibly reflux) giving high to quantitative yields of the respective carboxylic acids. Esters of tertiary alcohols, and 1,4-dihydropyridine esters (Hantzsch compounds) do not provide the reaction. The reaction has a limitation at esters with the chiral center at α-position because partial racemization takes place. However, these products with smaller amounts of the opposite enantiomer (approx. 0.3-3.5 %) can be purified by crystallization to furnish optically pure materials. We believe that sodium or potassium trimethylsilanolate are primary reagents for this conversion, providing a useful contribution to already existing methodology based on saponification and dealkylation. We think that this work will encourage chemists to use these rather neglected, but very powerful, selective and reliable reagents for this conversion.

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SAŽETAK

Upotrebljivost i ograničenja reagensa natrijevog i kalijevog trimetilsilanolata u konverziji estera u karboksilne kiseline

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Natrijev i kalijev trimetilsilanolat djeluju kao univerzalni i vrlo snažni reagensi za konverziju širokog spektra estera u karboksilne kiseline. Reakcije se provode u tetrahidrofuranu kao otapalu u vrlo blagim uvjetima s visokim do kvantitativnim iskorištenjem.