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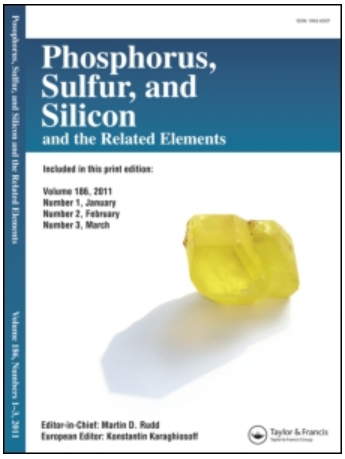

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Publication details, including instructions for authors and subscription information:
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EFFECTIVE SILYLATION OF CARBOXYLIC ACIDS UNDER SOLVENT-FREE CONDITIONS WITH *tert*-BUTYLDIMETHYLSILYL CHLORIDE (TBDMSCL) AND TRIISOPROPYLSILYL CHLORIDE (TIPSCL)

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To cite this Article Firouzabadi, Habib , Iranpoor, Naser and Shaterian, Hamid Reza(2000) 'EFFECTIVE SILYLATION OF CARBOXYLIC ACIDS UNDER SOLVENT-FREE CONDITIONS WITH *tert*-BUTYLDIMETHYLSILYL CHLORIDE (TBDMSCL) AND TRIISOPROPYLSILYL CHLORIDE (TIPSCL)', Phosphorus, Sulfur, and Silicon and the Related Elements, 166: 1, 71 — 81
To link to this Article: DOI: 10.1080/10426500008076532
URL: http://dx.doi.org/10.1080/10426500008076532

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Phosphorus, Sulfur and Silicon, 2000, Vol. 166, pp. 71-81
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Printed in Malaysia

EFFECTIVE SILYLATION OF CARBOXYLIC ACIDS UNDER SOLVENT-FREE CONDITIONS WITH *tert*-BUTYLDIMETHYLSILYL CHLORIDE (TBDMSCL) AND TRIISOPROPYLSILYL CHLORIDE (TIPSCL)

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(Received April 4, 2000; In final form June 6, 2000)

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Various types of carboxylic acids can be converted effectively to their corresponding **TBDMS** and **TIPS** esters using **TBDMSCl** and **TIPSCl** in the presence of imidazole under solvent-free conditions. The advantage of this modified method in comparison with that reported by Corey is the elimination of DMF, which eliminates aqueous work-up. The method is not a time-consuming process and the reactions proceed spontaneously. By this method, absolute chemoselectivity for the protection of carboxylic acid functions in the presence of 2°, 3° hydroxyl groups are observed.

Keywords: Silylation; Protecting groups; TBDMS carboxylate; TIPS carboxylate; Solvent-Free reaction; Imidazole

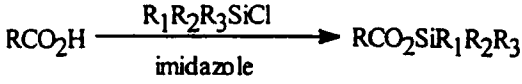
INTRODUCTION

Protection of functional groups via chlorosilanes plays an important role in modern synthetic reactions for the synthesis of complex organic molecules[1]. Protection of hydroxyl functions with chlorosilanes such as **TBDMSCl** and **TIPSCl** show their own useful properties in the total synthesis of organic molecules[2]. They can be deprotected easily under mild conditions[3] and on the other hand, they are stable towards certain oxida-

* Corresponding Author.

tion, reduction, and mild solvolytic conditions[4]. Corey has reported that the use of imidazole as a catalyst in DMF as a solvent proved to be an excellent condition for the conversion of alcohols to *tert*-butyldimethylsilyl ethers. This procedure suffers from tedious aqueous work-up and also long reaction times. Since **TBDMSCl** / IM /DMF method does not apply well to carboxylic acids[5], many variation method therefore have been reported [6]. Recently, we have reported a modified procedure for the protection of alcohols by **TBDMSCl** in the presence of imidazole by elimination of DMF. This simple modification has provided an effective media for the efficient and chemoselective protection of alcohols. By this new method, the reaction times are decreased to a few minutes. The yield of silyl ethers for the highly hindered alcohols such as adamantanol is increased to 54% whereas, by the previously reported method we were not able to isolate the related silyl ether in more than 10%[7]. Protection as well as activation of carboxylic acids is an important operation in organic synthesis therefore, introduction of a new procedure for the high yield and efficient preparation of highly stable hindered trialkylsilyl esters is of value in organic synthesis. Preparation of **TIPS**esters[8] from a carboxylic acid and **TIPSCl** in DMF in the presence of imidazole proceeds at 60°C in 48h[9] or in THF in the presence of Et_3N at room temperature in 1h[10]. The effect of **TIPS** and **TBDMS** groups on the chemical behavior of their related esters is quite different. For example, **TIPS** esters of α,β- unsaturated carboxylic acids do not undergo Michael addition reaction with alkylcuprates and C=C bond remains intact whereas, such an effect has not been observed in the corresponding **TBDMS** esters which undergo addition reaction with cuprates normally[11] **TIPS** esters are useful in nucleotide synthesis because the **TIPS** group is more stable than the **TBDMS** against hydrolysis[12].

Now, in this report we introduce efficient preparation of **TBDMS** and **TIPS** esters of carboxylic acids by using imidazole as a catalyst in the absence of solvent at room temperature in excellent yields (**Scheme**).



R = phenyl, allyl, alkyl

$R_1 = R_2$ = Me, R_3 = *tert*-butyl

$R_1 = R_2 = R_3$ = *i*-Pr

SCHEME

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RESULTS AND DISCUSSION

In this paper we report a simple, high yield and efficient conversion of carboxylic acids to their corresponding silyl esters by heating the mixture of the appropriate amount of the **TIPSCl** or **TBDMSCl** and imidazole in a wide-neck round bottomed flask until a melt results which is cooled to room temperature. By this process formation of *N*-silyl imidazole, as an effective silylating agent, is facilitated. To the resulting mixture the appropriate carboxylic acid is added and then is thoroughly mixed by a glass rod at room temperature. The reaction is exothermic and a paste results spontaneously. To the resulting paste, petroleum ether (60–80°C) is added and the mixture is purified by using a short column of silica gel to give the desired silyl esters in high purity. The results for the preparation of **TBDMS** and **TIPS** esters are summarized in the Tables (1,2) respectively.

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TABLE I Preparation of TBDMS Carboxylates with TBDMSCl/Imidazole under Solvent-Free Conditions

Entry	*Substrate*	*Subst./ TBDMS-Cl / Imidazole*	*Yield (%)*[a]
1	$PhCO_2H$	1/ 1.4/ 1.5	93
2	$4\text{-}MeOC_6H_4CO_2H$	1/ 1.5/ 1.7	90
3	$4\text{-}MeC_6H_4CO_2H$	1/ 1.4/ 1.6	92
4	$3\text{-}BrC_6H_4CO_2H$	1/ 1.3/ 1.5	89
5	$3\text{-}ClC_6H_4CO_2H$	1/ 1.2/ 1.5	90
6	$PhCH_2CO_2H$	1/ 1.3/ 1.5	92
7	$PhCH=CHCO_2H$	1/ 1.3/ 1.5	91
8	$CH_2=CH(CH_2)_8CO_2H$	1/ 1.4/ 1.5	85
9	$CH_3(CH_2)_{16}CO_2H$	1/ 1.5/ 1.7	87
10	$H_2OC(CH_2)_4CO_2H$	1/ 2 5/ 2.7	88
11	$H_2OCCH=CHCO_2H$	1/ 2.5/ 2.7	89

a. Reaction was completed spontaneously at room temperature and the yield refers to the isolated pure product.

Selectivity of the reaction is a criterion, which is important for its application in the multi-step synthesis of organic molecules. Therefore, we investigated the selectivity of the presented method for the protection of carboxyl functions in the presence of hydroxyl groups with both **TBDMSCl** and **TIPSCl** reagents. The results show that primary alcohols in the

presence of carboxylic acids are protected easily with almost absolute chemoselectivity with **TBDMSCl** (Entries 1–3, Table III). In the case of secondary and tertiary alcohols, the carboxylic function is protected almost exclusively in excellent yields with this reagent (Entries 4–7, Table III). Selectivity for the protection of phenolic hydroxyl group with **TBDMSCl** in the presence of carboxyl groups was also investigated. The reaction of phenol in the presence of benzoic acid with **TBDMSCl** results in the formation of 70% of the phenol silyl ether and 30% of the corresponding silyl ester respectively. In order to show the selectivity behavior of the method for the protection of – OH *vs* – COOH groups in a single molecule, three isomeric hydroxyl benzoic acids, as model compounds, were studied. Carboxyl functional group of 2-hydroxy benzoic acid is protected and the corresponding ester is obtained in 92% yield. 3-Hydroxy benzoic acid does not show a promising selectivity and both functional groups are protected equally in the presence of 1.2 equivalent amounts of **TBDMSCl** and 1.5 molar equivalents of Imidazole. Therefore, with 2.2 equivalents of **TBDMSCl** and 2.5 equivalents of imidazole, high yields of the protected functional groups are obtained. The same results are also observed for 4-hydroxy benzoic acid (Table IV). **TIPSCl** shows quite different behavior and the carboxylic acid function is protected more easily than 1°, 2°, and 3° hydroxyl functional groups. Therefore, this method is quite useful for the selective protection of -COOH in the presence of -OH functionality (Table V). Protection of phenolic hydroxyl groups in the presence of carboxylic acid functional groups was also investigated. In contrast to **TBDMSCl**, which protects phenolic groups easier than carboxyl groups, **TIPSCl** protects carboxyl functionality much easier. In a mixture of benzoic acid and phenol, silyl carboxylate is formed in 95% whereas; silyl phenol ether is produced in only 5% yield. Phenols substituted with electron-withdrawing groups show more reactivity towards silylation with TIPSCl and selectivity of the reaction decreases drastically (Entry 2, Table VI). In order to show the effect of steric hindrance upon the chemoselectivity of the method; the reaction of three isomeric hydroxy benzoic acids was investigated. 2-Hydroxy benzoic acid gives the corresponding silyl ester in 90% yield. 3- and 4- Hydroxy benzoic acids do not show such selectivity and both functional groups are protected equally (Entries 4–5, Table VI). In this study, we have shown that steric factors play an important role for chemoselectivity observed in these reactions. Therefore, in the case of 2-hydroxy benzoic acid in which, the two func-

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tional groups are close together the more reactive -COOH functional group is protected first and there is not enough room for the second bulky **TBDMSCl** and **TIPSCl** reagents to enter and attack the phenolic – OH group.

TABLE II Preparation of TIPS Carboxylates with TIPSCl/Imidazole under Solvent-Free Conditions

Entry	*Substrate*	*Subst/ TIPS-Cl / Imidazole*	*Yield (%)*[a]
1	$PhCO_2H$	1/ 1.3/ 1.5	95
2	$4\text{-}MeOC_6H_4CO_2H$	1/ 1.3/ 1.5	93
3	$4\text{-}MeC_6H_4CO_2H$	1/ 1.3/ 1.5	92
4	$3\text{-}BrC_6H_4CO_2H$	1/ 1.3/ 1.5	92
5	$2\text{-}ClC_6H_4CO_2H$	1/ 1.3/ 1.5	90
6	$PhCH_2CO_2H$	1/ 1.3/ 1.5	93
7	$PhCH = CHCO_2H$	1/ 1.3/ 1.5	94
8	$CH_2 = CH(CH_2)_8CO_2H$	1/ 1.4/ 1.5	92
9	$CH_3(CH_2)_{16}CO_2H$	1/ 1.5/ 1.6	91
10	$ClCH_2CO_2H$	1/ 1.6/ 1.6	85
11	$H_2OC(CH_2)_4CO_2H$	1/ 2.4/ 2.6	89
12	$H_2OCCH = CHCO_2H$	1/2.4/2.6	90
13	H_2OCCO_2H	1/ 2.5/ 2.6	87
14	$1,4\text{-}C_6H_4(CO_2H)_2$	1/ 2.4/2.5	90

a. Reaction was completed after mixing at room temperature and the yield refers to the isolated product.

CONCLUSION

In conclusion, high rates of the reactions, high yields of the desired products accompanied with a promising selectivity, easy non-aqueous work-up (elimination of DMF) are the strong practical points of the presented method. The absence of water eliminates the formation of silanol and the excess of **TBDMSCl**, **TIPSCl** and imidazole that makes the purification process very easy and not time-consuming. The method is not also harmful to heat sensitive compounds. In this study, we have found that the chemoselectivity behavior of **TBDMSCl** and **TIPSCl** is quite different for the protection of- OH and – COOH under solvent-free conditions.

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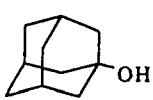
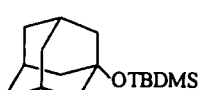
TABLE III Selective Silylation of 1°, 2°, 3° Alcohols and Carboxylic Acids with TBDMSCl /Imidazole under Solvent-Free Conditions

Entry	*Substrate*	*Product*	*Subst. 1/Subst. 2/ TBDMS- Cl /Imidazole*	*Yield(%)*[a]
1	$4\text{-MeOC}_6\text{H}_4\text{CO}_2\text{H}$	$4\text{-MeOC}_6\text{H}_4\text{CO}_2\text{TBDMS}$	1/1/1.1/1.3	0
	$4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{OH}$	$4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{OTBDMS}$		100
2	$\text{PhCH}_2\text{CO}_2\text{H}$	$\text{PhCH}_2\text{CO}_2\text{TBDMS}$	1/1/1.1/1.3	0
	$\text{PhCH}_2\text{CH}_2\text{OH}$	$\text{PhCH}_2\text{CH}_2\text{OTBDMS}$		100
3	$\text{PhCH}_2\text{CO}_2\text{H}$	$\text{PhCH}_2\text{CO}_2\text{TBDMS}$	1/1/1.1/1.3	0
	$\text{PhCH}_2\text{CH}_2\text{CH}_2\text{OH}$	$\text{PhCH}_2\text{CH}_2\text{CH}_2\text{OTBDMS}$		100
4	$\text{PhCH}_2\text{CO}_2\text{H}$	$\text{PhCH}_2\text{CO}_2\text{TBDMS}$	1/1/1.1/1.3	93
	$\text{PhCH}(\text{CH}_2\text{CH}_3)\text{OH}$	$\text{PhCH}(\text{CH}_2\text{CH}_3)\text{OTBDMS}$		7
5	$\text{PhCH}_2\text{CO}_2\text{H}$	$\text{PhCH}_2\text{CO}_2\text{TBDMS}$	1/1/1.1/1.3	100
	Ph_2CHOH	$\text{Ph}_2\text{CHOTBDMS}$		0
6	$\text{PhCH}_2\text{CO}_2\text{H}$	$\text{PhCH}_2\text{CO}_2\text{TBDMS}$	1/1/1.1/1.3	100
	$\text{Ph}_2\text{C(Me)OH}$	$\text{Ph}_2\text{C(Me)OTBDMS}$		0
7	$\text{PhCH}_2\text{CO}_2\text{H}$	$\text{PhCH}_2\text{CO}_2\text{TBDMS}$	1/1/1.1/1.3	100
				0

a. Reactions were completed at room temperature and the yields are based on the ^{1}HNMR spectra of the isolated mixtures.

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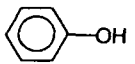
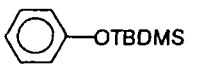
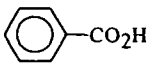
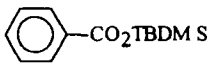
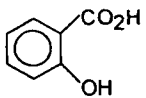
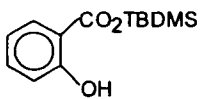
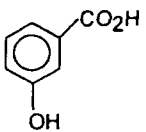
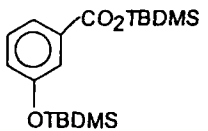
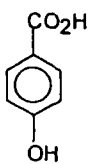
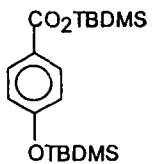
TABLE IV Selective Silylation of Phenols and Carboxylic acids with TBDMS-Cl /Imidazole under Solvent-Free Conditions

Entry	*Substrate*	*Product*	*Subst. 1/Subst. 2/ TBDMS-Cl /Imidazole*	*Yield(%)*
1/			1/ 1.2/ 1.5	70[a]
				30[a]
2			1/ 1.2/ 1.5	92[b]
3			1/ 2.2/ 2.5	87[b]
4			1 /2.2/ 2.5	89[b]

a. Reactions were completed after mixing at room temperature and the yields are based on ^{1}HNMR spectra of isolated mixtures.
b. Yields refer to isolated products.

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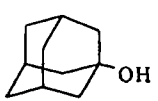
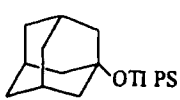
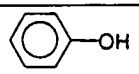
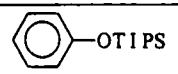
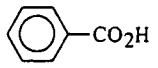
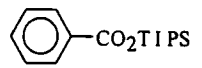
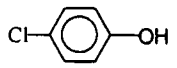
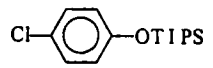
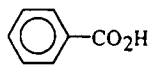
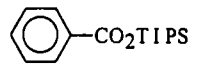
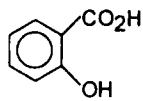
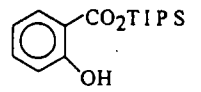
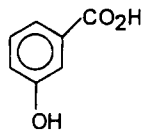
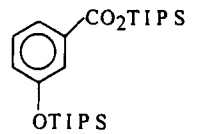
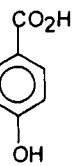
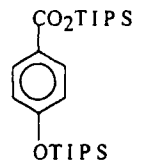
TABLE V Selective Silylation of 1°, 2°, 3° Alcohols and Carboxylic Acids with TIPSCl /Imidazole under Solvent-Free Conditions

Entry	*Substrate*	*Product*	*Subst. 1/Subst. 2/ TIPS- Cl /Imidazole*	*Yield(%)*[a]
1	$PhCH_2CO_2H$	$PhCH_2CO_2TIPS$	1/1/1.2/1.5	78
	$C_6H_5CH_2OH$	$C_6H_5CH_2OTIPS$		12
2	$PhCH_2CO_2H$	$PhCH_2CO_2TIPS$	1/1/1.2/1.5	80
	4-$MeOC_6H_4CH_2OH$	4-$MeOC_6H_4CH_2OTIPS$		20
3	$PhCH_2CO_2H$	$PhCH_2CO_2TIPS$	1/1/1.2/1.5	90
	4 $ClC_6H_4CH_2OH$	4-$ClC_6H_4CH_2OTIPS$		10
4	$PhCH_2CO_2H$	$PhCH_2CO_2TIPS$	1/1/1.2/1.5	88
	$PhCH_2CH_2OH$	$PhCH_2CH_2OTIPS$		12
5	$PhCH_2CO_2H$	$PhCH_2CO_2TIPS$	1/1/1.2/1.5	75
	$PhCH_2CH_2CH_2OH$	$PhCH_2CH_2CH_2OTIPS$		25
6	$PhCH_2CO_2H$	$PhCH_2CO_2TIPS$	1/1/1.2/1.5	100
	$PhCH(CH_2CH_3)$ OH	$PhCH(CH_2CH_3)OTIPS$		0
7	$PhCH_2CO_2H$	$PhCH_2CO_2TIPS$	1/1/1.2/1.5	100
	Ph_2CHOH	$Ph_2CHOTIPS$		0
8	$PhCH_2CO_2H$	$PhCH_2CO_2TIPS$	1/1/1.2/1.5	100
				0

a. Reactions were completed spontaneously after mixing at room temperature and the yields are based on the ^{1}HNMR spectra of the isolated mixtures.

TABLE VI Selective Silylation of Phenols and Carboxylic Acids with TIPSCl /Imidazole under Solvent-Free Conditions

Entry	*Substrate*	*Product*	*Subst. 1/Subst. 2/ TIPSCl /Imidazole*	*Yield(%)*
1			1/ 1/ 1.2/ 1.5	5[a]
				95[a]
2			1/ 1/ 1.2/ 1.5	40[a]
				60[a]
3			1/ 1.2/ 1.5	90[b]
4			1/ 2.2/ 2.5	91[b]
5			1 /2.2/2.5	94[b]

a. Reactions were completed after mixing at room temperature and the yields are based on the ^{1}HNMR spectra of isolated mixtures.
b. Yields refer to isolated products.

EXPERIMENTAL

General

All yields refer to isolated pure products unless otherwise stated. Most of products were purified by short column chromatography. They were identified by the comparison of their physical data with those reported for the authentic samples. The purity of the products was determined with TLC on

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silica-gel polygram SIL G/UV 254 plates. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. The NMR spectra were recorded on a Bruker Avance DPX instrument (250 MHz).

Preparation of tert-butyldimethylsilyl and triisopropylsilyl carboxylates with TBDMSCl and TIPSCl in the Presence of Imidazole under Solvent-Free Conditions

General Procedure

A mixture of TBDMSCl or TIPSCl (1.2–2.5 mmol) and imidazole (1.5–2.5 mmol) was heated in a wide-neck round bottomed flask (25ml) until a melt resulted. The resulting melt was cooled to room temperature. Then, the appropriate carboxylic acid (1 mmol) was added and mixed thoroughly by a glass rod at room temperature. The formation of a homogeneous paste is an indication of the completion of silylation reaction. To the resulting paste, petroleum ether (20 ml, 60–80 °C) was added and the mixture was magnetically stirred for a few minutes. The supernatant liquid was separated and the residual mixture was washed with petroleum ether (3×20 ml). The petroleum solutions were mixed and were applied on a short silica-gel column for further purification. Petroleum ether was evaporated under reduced pressure to give the desired pure silyl carboxylates in excellent yields (Tables I, II).

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A Typical Procedure for the Preparation of tert-Butyldimethylsilyl Benzoate with TBDMSCl in the Presence of Imidazole under Solvent-Free Conditions

A mixture of TBDMSCl (210 mg, 1.4 mmol) and imidazole (100 mg, 1.5 mmol) was heated in a wide-neck round bottomed flask (25 ml) until a melt resulted. The resulting melt was cooled to room temperature. Benzoic acid (122 mg, 1 mmol) was added and was mixed thoroughly by a glass rod at room temperature until a homogeneous paste was obtained. To the resulting paste, petroleum ether (20 ml, 60–80 °C) was added and the mixture was magnetically stirred for a few minutes. The supernatant liquid was separated and the residual mixture was washed with petroleum ether (3×20 ml). The petroleum solutions were mixed and were applied on a short silica-gel column for further purification. Petroleum ether was evaporated under reduced pressure to give the desired pure *tert*-butyldimethylsilyl benzoate in 93% yield. (Tables I).

Acknowledgements

The authors are grateful to the Shiraz University Research Council for the partial support of this work and we are also thankful to National Research Council of I.R. Iran for the grant no 464 for the support of this project.

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