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New Access to Organoacyloxytrialkylsilanes

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Abstract: In this article, we present the synthesis of acetoxytributylsilane, obtained from methoxytributylsilane and acetic anhydride, under different conditions (catalyst, temperature, reaction time). Access to other acyloxytributylsilanes from different anhydrides is also presented.

Keywords: acetoxytributylsilane, acyloxytributylsilane, catalyst, silane

INTRODUCTION

In organic chemistry, silanes have been used for years as protecting group reagents. They can protect various functions,^[1] such as alcohols, amines, and acids. Silanes are still intermediates in organic synthesis, or specialty products of agro and pharmaceutical chemistry. Among numerous silylated derivatives, halosilanes and silanols are the most frequently used. Acetoxyalk-ylsilanes constitute an alternative to those compounds and are often very sensitive to experimental conditions. For instance, Schuyen et al.^[2] have

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Address correspondence to Michèle Sindt, Laboratory of Chemistry and Methodology for the Environment (LCME), Paul Verlaine-Metz University, Metz, France. E-mail: sindt@univ-metz.fr shown that acetoxysilanes could replace dimethyldichlorosilanes when used as a water-repellent coating on cotton textile. By hydrolysis, acetoxysilane forms less corrosives acids than hydrochloric acid produced by halosilanes, which weaken seriously clothes.

Those compounds, beside their use as protecting groups, find application as reticulating agents at room temperature in vulcanization of silicon rubber in single-component systems.^[3]

Organoacyloxytrialkylsilanes are generally prepared by reaction of chlorosilane with acid or acid anhydride.^[3] Papers describe the preparation of acyloxysilane from trialkylsilanes by reaction with carboxylic acid and catalyzed by mineral acid, iodine, copper complex,^[4] or palladium acetate.^[5] Disiloxanes are also good precursors, by reaction with acid anhydride in presence of zinc chloride as catalyst.^[6] This reaction failed with maleic and succinic anhydride.

In this article, we present the synthesis of acetoxytributylsilane (1a, R = Me). The reaction between methoxytributylsilane and acetic anhydride has been studied under different conditions (catalyst, temperature, reaction time). Access to other acyloxytributylsilanes 1 from different anhydrides is also presented (Scheme 1).

RESULTS AND DISCUSSION

In the literature, acetoxytrialkylsilanes are often prepared by reaction between trialkylsilane and carboxylic acid or their mercury salt because of the lability of hydrogen in the Si-H bond, subject to hydrolysis cleavage.^[7] In this case, the use of a catalyst is necessary, such as strong mineral acids (H₂SO₄, HI), aluminium, iodine, or colloidal nickel; recent works show the efficiency of copper complex^[4] or palladium acetate.^[5] Substitution of hydrogen in the Si-H bond by the acetoxyl group is described in the case of trialkoxysilane^[8] (Scheme 2).

In equimolar quantities of acetic anhydride and triethoxysilane, the reaction leads to the interchange of acetate and ethoxyl group; only an excess causes the substitution of hydrogen.

To obtain acetoxytributylsilane (1a, R = Me), we first explore the reaction of tributylsilane with acetic anhydride in presence of different catalysts (Table 1).

The reaction is carried out without solvent under nitrogen at 90° C. This temperature was found to be better than 80 and 85° C. Three catalysts among those tested gave relatively good yields (entries 1, 4, and 7).

Bu₃SiOMe + (RCO)₂O → RCOOSiBu₃ + RCOOMe

Scheme 1. Synthesis of acyloxytributylsilanes.

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(EtO)₃SiH + (MeCO)₂O excess (EtO)₂Si(OCOMe)₂ + MeCHO + MeCOOEt

Scheme 2. Synthesis from triethoxysilane.

Amberlyst 15 is less efficient than zinc chloride with the same reaction time. K10 montmorillonite gives about 60% yield in only 4.5 h. During the reaction, some by-products are formed, such as hexabutyldisiloxane $[(Bu_3Si)_2O]$ (<8%) and tributylsilanol (Bu_3SiOH) (<2%), observed by gas chromatography-mass spectroscopy (GC-MS).

We turned to the synthesis of acetoxytributylsilane (1a, R = Me), using methoxytributylsilane instead of H-tributylsilane. Results are reported in Table 2.

With 1-methylimidazole (entry 3), Amberlyst 15 (entry 4), and K10 montmorillonite (entry 7), yields are up to 80%. Moreover, we can see that the use of methoxytributylsilane gave better results than the use of H-tributylsilane. Amberlyst 15 has been chosen as catalyst of the reaction of methoxytributylsilane with other anhydrides (Table 3).

The access to new acyloxytributylsilanes is possible from propionic, butyric, or benzylic anhydride with relatively good yields (49-77%). However, the conditions of the reactions did not permit us to obtain the same result with succinic or phtalic anhydride (yields: 8-14%). This is probably because in those two cases, compounds are solid and cause heterogeneity in the media.

Table 1.	Influence of	catalyst in	the	synthesis	of	acetoxytributy	lsilane	1 a	from	tribu-
tylsilane ^a										

Entry	Catalyst	Time (h)	Yield (%)
1	ZnCl ₂	24	58
2	4-Dimethylaminopyridine (DMAP)	24	4.5
3	1-Methylimidazole (1-MIM)	24	4
4	Amberlyst 15	24	46.5
5	Triphenylphosphine	72	<1
6	KSF Montmorillonite	24	<1
7	K10 Montmorillonite	4.5	59
8	2-Chloro-1-methylpyridinium iodide (CMPI)	24	<1
9	Imidazole	24	0
10	Acetylacetonate de zirconium	24	0
11	Trimethylchlorosilane	24	0
12	- 	28	0

Bu ₃ SiH + (MeCO) ₂ O		Bu ₃ SiOCOMe	+	MeCHO
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^{*a*}Reaction conditions: tributylsilane: 10 mmol, acetic anhydride: 10 mmol, catalyst: 5% wt, temp.: 90°C.

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Table 2. Influence of catalyst in the preparation of acetoxytributylsilane 1a from methoxytributylsilane^{*a*}

Catalyst	Time (h)	Yield (%)
ZnCl ₂	2	72
4-Dimethylaminopyridine (DMAP)	6	66
1-Methylimidazole (1-MIM)	24	85
Amberlyst 15	2	86
Triphenylphosphine	24	5.5
KSF Montmorillonite	3.5	72
K10 Montmorillonite	1.75	79
2-Chloro-1-methylpyridinium iodide	72	68
(CMPI)		
Imidazole	24	36
N,N'-Dicyclohexylurea	12	0
1,1'-Carbonyldiimidazole	24	61
Trimethylchlorosilane	12	50
	288	30
	Catalyst ZnCl ₂ 4-Dimethylaminopyridine (DMAP) 1-Methylimidazole (1-MIM) Amberlyst 15 Triphenylphosphine KSF Montmorillonite K10 Montmorillonite 2-Chloro-1-methylpyridinium iodide (CMPI) Imidazole N,N'-Dicyclohexylurea 1,1'-Carbonyldiimidazole Trimethylchlorosilane	CatalystTime (h)ZnCl224-Dimethylaminopyridine (DMAP)61-Methylimidazole (1-MIM)24Amberlyst 152Triphenylphosphine24KSF Montmorillonite3.5K10 Montmorillonite1.752-Chloro-1-methylpyridinium iodide72(CMPI)24Imidazole24N,N'-Dicyclohexylurea121,1'-Carbonyldiimidazole24Trimethylchlorosilane12—288

Bu₃SiOMe + (MeCO)₂O _____ Bu₃SiOCOMe + MeCOOMe

^{*a*}Reaction conditions: methoxytributylsilane: 5 mmol, acetic anhydride: 5 mmol, catalyst: 5%wt, temp. 90°C.

EXPERIMENTAL

¹H NMR and ¹³C NMR spectra were recorded on a Brucker AC-250 (250-MHz) spectrometer with deuterated chloroform (CDCl₃) as solvent with chloroform (7.26 ppm) as internal reference. Chemical shifts are reported in parts per million (ppm): s: singlet, d: doublet, t: triplet, q: quartet, and m: multiplet, and coupling constants (J) are in Hertz. Mass spectra were

Table 3. Preparation of acyloxytributylsilane 1 from methoxytributylsilane^{*a*}

Bu ₃ SiOMe	+ (RCO) ₂ O	^{yst} ► Bu ₃ SiOCOR	→ Bu ₃ SiOCOR + RCOOMe			
Entry	Product no.	Acid anhydride	Yield (%)			
1 2 3	1b 1c 1d	Propionic Butyric Benzylic	70 77 49			

^{*a*}Reaction conditions: methoxytributylsilane: 5 mmol, acid anhydride: 5 mmol, catalyst: 5%wt, temp. 90°C, catalyst: Amberlyst 15.

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recorded on a Hewlett-Packard (model 5971 A) in electronic impact (70 eV) coupling with a gas chromatograph equipped with a capillary column (WCOT fused silica, $25 \text{ m} \times 0.25 \text{ mm}$), whose stationary phase is CPSil5CB (0.12 μ m). Helium is used as gas carrier, detector temperature is 300°C, and injector temperature is 280°C.

Typical Procedure

A mixture of methoxytributylsilane (5 mmol), acid anhydride (5 mmol), and catalyst (5% wt) is stirred at 90°C under nitrogen. The catalyst is filtered, and the product is purified by distillation under low pressure.

1a: Bp: 102°C (8.7 10⁻² torr) ¹H NMR (CDCl₃): δ 2.05 (3H, s), 1.33 (6H, m), 0.89 (9H, t, J = 6.6 Hz), 0.76 (6H, m); ¹³C NMR (CDCl₃): δ 171.53, 26.51, 24.68, 22.68, 13.91, 13.41; GC-MS (70 eV): 43 (15), 85 (5), 145 (10), 210 (100). **1b**: Bp: 115°C (8.7 10⁻² torr); ¹H NMR (CDCl₃): δ 2.32 (2H, q, J = 7.5 Hz), 1.29 (12H, m), 1.09 (3H, t, J = 7.6 Hz), 0.87 (9H, t, J = 6.9 Hz), 0.76 (6H, m); ¹³C NMR (CDCl₃): δ 174.84, 29.16, 26.31, 25.07, 13.6, 13.2, 9.27; GC-MS (70 eV): 57 (10), 73 (6), 159 (12), 199 (2), 215 (100). **1c**: Bp: 122°C (6.2 10⁻² torr). ¹H NMR (CDCl₃): δ 2.27 (2H, t, J = 7.3 Hz), 1.63 (2H, st), 1.30 (12H, m), 1.02 (3H, t, J = 7.2 Hz), 0.94 (9H, m), 0.73 (6H, m); ¹³C NMR (CDCl₃): δ 174.03, 37.88, 26.26, 25.1, 18.55, 13.7, 13.25; GC-MS (70 eV): 43 (10), 71 (11), 173 (4), 199 (5), 229 (100). **1d**: Bp: 153–156°C (5.7 10⁻² torr) ¹H NMR (CDCl₃): δ 8.09 (2H, m), 7.59 (1H, m), 7.46 (2H, m), 1.31 (12H, m), 0.91 (9H, m), 0.77 (6H, m); ¹³C NMR (CDCl₃): δ 162.24, 132.69, 130.04 (2C), 129.60, 128.47 (2C), 26.26, 25.40, 13.77, 13.27; GC-MS (70 eV): 105 (65), 205 (5), 263 (100).

CONCLUSION

We have presented here a new route to synthesize organoacyloxytrialkylsilanes and particularly acetoxytributylsilane by reaction between H-tributylsilanes or methoxytributylsilane and acetic anhydride with different catalysts. The reaction with H-tributylsilane did not take place except with the use of three catalysts: ZnCl₂, Amberlyst 15, and montmorillonite K10, but yields still remained average. Better results were obtained with methoxytributylsilane and reached to 86% with Amberlyst 15. This method has been extended to other anhydrides with success.

REFERENCES

1. Cooper, B. E. Silylation as a protective method in organic synthesis. *Chem. Ind.* **1978**, 794–797.

- 2. Schuyten, H. A.; Weaver, J. W.; Reid, J. D. Preparation of substituted acetoxy silanes. J. Am. Chem. Soc. 1947, 69, 2110.
- 3. Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York and London, 1968, pp. 108–111.
- 4. Schubert, U.; Lorentz, C. Conversion of hydrosilanes to silanols and silyl esters catalysed by [Ph₃PCuH]₆. *Inorg. Chem.* **1997**, *36*, 1258–1259.
- 5. Chauhan, M.; Chauhan, B. P. S.; Boudjouk, P. An efficient Pd-catalysed route to silyl ester. *Org. Lett.* **2000**, *8*, 1027–1029.
- Valade, J. Chimie organique: Dérivés siliciés: Scission de monosiloxanes symétrique. Comptes rendus de l'Académie des sciences 1958, 952–954.
- Dolgov, B. N.; Kharitonov, N. P.; Voronkov, M. G. Reciprocal reaction of trialkylsilanes with monocarboxylic acids: A new method of synthesizing trialylacyloxysilanes and their physical properties. *J. Gen. Chem. URSS (Engl. transl)* 1954, 24, 859–865.
- 8. Reilly, A. F.; Post, H. W. Studies in silico-organic compounds XIII: Additional chemical properties of trialkylsilanes. J. Org. Chem. 1951, 16, 387–390.

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