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Facile reaction of bis(tri-*n*-butyltin) oxide with silica gel

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Bis(tri-*n*-butyltin) oxide quickly reacts with chromatographic silica gel even when a solution of this oxide is filtered through silica gel, which results in stannylation of a fraction of the surface hydroxyl groups of silica gel to give n-$Bu_3SnOSi\equiv$ moieties. The calculated surface density of these moieties, 0.85 Sn groups per nm^2, corresponds to complete coverage of silica gel surface with *n*-Bu groups.

Organotin compounds (OTC), mostly di- and tri-*n*-butyltin derivatives, have already become valuable and indispensable reagents in modern organic synthesis[1(*a*),(*b*)] and found practical use in nautics and in forestry for creation of protective coatings on ships (antifoulant coatings) and on trees.[1(*c*)] In both fields of application, interest is felt in the use of OTC on carriers as a method to control OTC reactivity and release and to facilitate OTC storage, transportation and handling.[2]

The reactions of some OTC with silica gel (SG) were previously studied. It was shown that the reaction of n-Bu_3SnOMe occurred quickly (30 min) at room temperature,[3] a similar reaction with n-Bu_3SnH required 24 h or 100 °C, whereas the reaction with n-Bu_4Sn occurred only at 150–180 °C.[4] Compounds homologous to the OTC mentioned above, as well as aluminium silicate (87% SiO_2) and alumina react similarly.[3,5,6] The reactions of OTC with SG exclusively proceed on two types of silanol groups existing on SG surface, Q^2 and Q^3, as demonstrated in Scheme 1 for tributyltin derivatives.[7] These studies were carried out with Aerosil (Degussa) silica gel that has the shape of nonporous microspheres with characteristics shown in Table 1.[8] Three varieties of these SGs, namely, Aerosil 200, 500 and 1000, are obtained by dehydration *in vacuo* at temperatures matching the numeric index specified and differ in the number of surface hydroxyl groups.[8,9] However, their reactions with OTC occur almost identically.[4]

In development of a method for removal of the residues of organotin reagents and products of their conversion from reaction mixtures,[10] we became interested in the behaviour of the most popular OTC used as reagents when they come into contact with ‘chromatographic’ silica gel (ChSG) which considerably differs from Aerosil by its porous structure and a large number of hydroxyl groups on the surface.[11] It was repeatedly reported that compounds of very low polarity n-Bu_3SnH and $(n$-$Bu_3Sn)_2$ do not react with ChSG and are readily eluted with hexane, whereas n-Bu_3SnX (X = Cl, Br, I) and $(n$-$Bu_3Sn)_2O$ (TBTO) remain near the start during TLC on ChSG.[12,13]

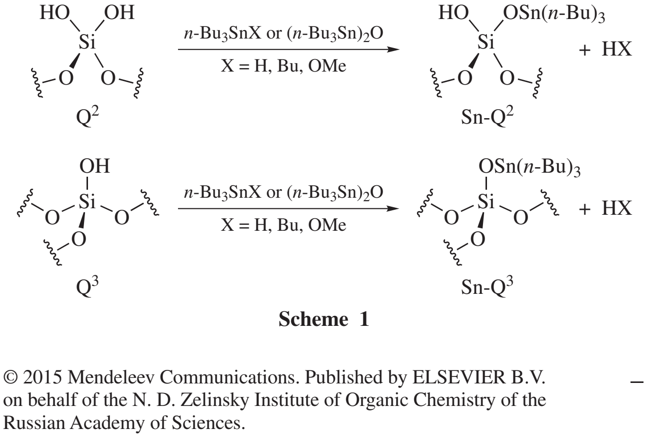
In fact, the behaviour of certain OTCs in TLC on plates with ChSG is somewhat unusual (see Table 2). The strong retention of a fraction or the entire OTC amount applied on a TLC plate on the start line and independence of this result from the eluent polarity may suggest that a chemical reaction of this OTC with ChSG occurs. In fact, filtration of an n-Bu_3SnF solution through a column with ChSG[†] resulted in irreversible sorption of a fraction of this fluoride, but the sorbed amount was no more than 11 mg per 1 g ChSG.[‡] Similarly, n-Bu_3SnCl and n-Bu_3SnI were found to react with ChSG insignificantly, or no reaction was observed at all.[§]

TBTO was found to show quite a different behaviour. TBTO in amounts of up to 150 mg per 1 g ChSG was quickly and completely grafted to ChSG. If excess TBTO was used, up to

Table 1 Characteristics of the silica gels referred to in the text and used in this study (from literature data and supplier Specification Sheets).

Silica gel	Drying temperature/°C	Content of physically bound water (%)	Grain size/μm	Pore diameter/nm	Surface area/m^2 g^{-1}	Concentration of surface hydroxyl groups/nm^{-2}
Aerosil 200	200	~0	0.012	0	200	2.35–2.60[8,9]
Aerosil 500	500	~0	0.012	0	200	1.2–1.3[8,9]
Aerosil 1000	1000	~0	0.012	0	160	0.4[8,14]
Kieselgel 60[*a*]	150	~0	25–40	6	500	4.6±0.5[*c*,11]
Silica gel L[*b*]	25	8	100–150	6	500	

[*a*] Fluka silica gel ‘for preparative column chromatography’. [*b*] Chemapol silica gel ‘for chromatography’. [*c*] $Q^2:Q^3 = 1:5.7$,[15] $1:5.3$.[16] These values and other presented here correspond to all totally hydrated SGs obtained by a similar technology rather than to particular ChSG samples used in this study.



Scheme 1

[†] Unless specified otherwise, the experiments were carried out using SG from Fluka ‘Kieselgel 60 for preparative column chromatography’. Prior to use, this SG was calcinated for 60 min at 130–140 °C and for 60 min at 150 °C in air until a constant weight was attained (mass loss 3.9–4.5%).

[‡] *Reaction of* n-*Bu₃SnF with ChSG (standard procedure).* A solution of n-Bu_3SnF (28 mg) in THF (5 ml)[10] was filtered (1 ml min^{-1}) through a short plug with ChSG (1.00 g) and additionally eluted with THF (5 ml, complete elution). The filtrate was evaporated to give 17 mg of n-Bu_3SnF crystals. Additional elution with $CHCl_3$ (20 ml) did not provide any additional amount of the compound.

[§] *Reaction of* n-*Bu₃SnCl and* n-*Bu₃SnI with ChSG.* (A) Filtration of an n-Bu_3SnCl solution (325 mg) in EtOAc (6.5 ml) through ChSG (1.00 g)

Table 2 Chromatographic mobility of Sn-containing reagents in TLC on Sorbfil plates (Sorbpolymer, Russia).

Compound	R_f in systems			
	PhMe	CH_2Cl_2	Et_2O	EtOAc
$(n\text{-}Bu_3Sn)_2$	0.84	0.84	0.82	0.71
$(n\text{-}Bu_3Sn)_2O$	~0	~0	~0	~0
$n\text{-}Bu_3SnF$[a]	~0	~0	~0	~0
$n\text{-}Bu_3SnCl$	a 'tail' from the start[b]			
$n\text{-}Bu_3SnI$	a 'tail' from the start[b]			

[a] A small amount due to low solubility. [b] The 'tail' length is proportional to the amount of the compound spotted.

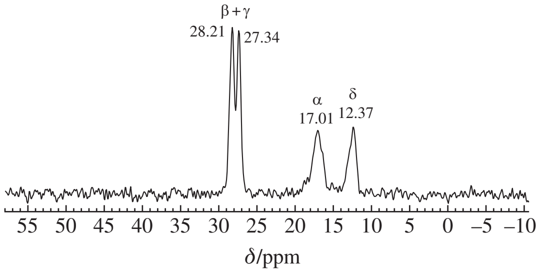


Figure 1 ^{13}C NMR CP MAS spectrum of silica gel treated with TBTO (Sn-ChSG).

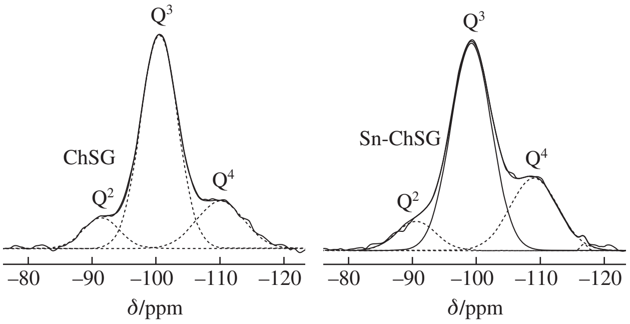


Figure 2 ^{29}Si NMR CP MAS spectra of used-up (ChSG) and TBTO-treated (Sn-ChSG) silica gel, along with the subpeaks obtained by deconvolution and their sum.

210 mg g^{-1} remained on ChSG. Given a ChSG surface area of 500 m^2 g^{-1} (see Table 1), it corresponds to 0.85 Bu_3Sn groups per 1 nm^2. This grafting amount did not depend on the polarity of the solvent (C_6H_6, CH_2Cl_2, EtOAc) and on the water content of ChSG.[¶] Furthermore, exposure of the same ChSG sample in neat TBTO for 50 days resulted in only a small increase in the grafting amount, *viz.*, up to 0.97 Bu_3Sn per 1 nm^2. Thus, the reaction of a TBTO solution with ChSG occurs by 88% (of the experimentally attainable reaction completeness) within the first few minutes and then nearly stops (*i.e.*, it slows down by a factor of $>10^4$). In this case, ~85% of ChSG hydroxyl groups (5 of 6 per 1.2 nm^2 surface containing one Bu_3Sn group) remain inaccessible for reactions due to the shielding by the Bu_3Sn groups grafted onto the surface.

The resulting tributylstannylated ChSG (Sn-ChSG) is a white hydrophobic water-resistant powder whose elementary composition agrees with the material balance of the reaction of its formation.[††] The IR spectrum of Sn-ChSG contains an intense broad peak at 3431 cm^{-1}, which confirms that the majority of hydroxyl groups in the ChSG remain unchanged. It also follows from spectral data that the chemical structure of Sn-ChSG is similar to that formed on treatment of Aerosil with $n\text{-}Bu_3SnH$ or $n\text{-}Bu_4Sn$ at elevated temperature[4,5] (see Scheme 1). The signals in the ^{13}C NMR CP MAS spectrum (Figure 1) are very narrow for this type of spectra and the δ-Me signal is not doubled,[4,17,18] which indicates that the $n\text{-}Bu_3SnO$ moieties are densely arranged and their conformations are similar. The single broad signal in the ^{119}Sn NMR MAS spectrum of Sn-ChSG (δ 115 ppm) is close to the signal for stannylated Aerosil (Sn-Aerosil, δ 102–106 ppm[4]) and differs significantly from the TBTO signal (neat, δ 81.7 ppm). The ^{29}Si NMR CP MAS spectra are more informative (Figure 2). The spectrum of the original ChSG consists of partially resolved signals of Q^2, Q^3 and Q^4 moieties [$(\equiv SiO)_2\mathit{Si}(OH)_2$, $(\equiv SiO)_3SiOH$ and $(\equiv SiO)_4Si$, δ –91.1, –100.2 and –109.8 ppm, respectively] located on ChSG surface.[19] Mathematical deconvolution of the spectrum allowed us to determine the ratio of signal areas as 10 : 70 : 20,[‡‡] respectively. Though it appears that the Q^2 signal in the Sn-ChSG spectrum is nearly missing, deconvolution gave the area ratio of the Q^2, Q^3 and Q^4 signals to be 9.0 : 64.5 : 26.5, respectively. The Q^2/Q^3 ratio is nearly the same (~1:7) before and after the reaction with TBTO, suggesting the lack of selectivity in this reaction that equals the degree of partial stannylation of both hydroxylated Q-moieties. The mean Q^2 : Q^3 ratio on ChSG surface is 1.0 : 5.5 (see notes in Table 1), hence stannylated Q^3 (Sn-Q^3) is the main Sn-containing moiety in Sn-ChSG. Based on the above and taking elementary analysis data[††] into account, the functional composition of the major part (80–85%) of Sn-ChSG can be represented as $\{(n\text{-}Bu_3SnOSiO_{1.5})[(HO)_2SiO](HOSiO_{1.5})_3(SiO_2)_{18}\}_n$.

A considerable difference between Sn-ChSG and Sn-Aerosil in terms of the level of surface stannylation was found. The Bu_3Sn per nm^2 value for Sn-Aerosil reaches 1.24,[3] which is 1.5 times higher than that for Sn-ChSG (0.85). In case of both SGs, these values correspond to the fast saturating stannylation of only 15–20% of the available surface hydroxyl groups of the SG. As it is customary in the literature, the reported Bu_3Sn per nm^2 values were calculated with respect to the SG surface areas. However, the bulky Bu_3Sn groups are arranged above the SG surface rather than on it. Hence, the degree of saturating stannylation is determined by the maximum number of *n*-Bu groups that can be placed above an SG surface. This amount also depends on the surface curvature that differs in sign and value between

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by the standard procedure followed by elution with CH_2Cl_2 returned 325 mg (100%) of $n\text{-}Bu_3SnCl$.

(B) In a similar experiment with addition of 2 equiv. of *N*-methylmorpholine and 4 equiv. of water to the original solution, the returned amount of the chloride was 95%.

(C) In an experiment with $n\text{-}Bu_3SnI$ similar to procedure (B), the returned amount of the iodide was 99%.

[¶] *Reaction of* $(n\text{-}Bu_3Sn)_2O$ *with ChSG*. Using the standard procedure, filtration of a TBTO solution (300 mg) in C_6H_6 (6 ml) through ChSG (1.00 g) followed by elution with C_6H_6 (10 ml) returned 90 mg TBTO in the filtrate, whereas the mass gain of dried ChSG from the column (Sn-ChSG) was ~210 mg. A similar extent of TBTO grafting occurred from CH_2Cl_2 and EtOAc, as well as on ChSG containing up to 8% water.

[††] *Sn-ChSG*: $(C_{12}H_{32}O_{49}Si_{23}Sn)_n$. IR (KBr, ν/cm^{-1}): 468, 801, 1099, 1467, 1629, 1638, 2858 (CH_2), 2876 (Me), 2932 (CH_2), 2962 (Me), 3431 (OH). ^{13}C NMR CP MAS (100.62 MHz, reference – the signal with δ 38.48 of solid adamantane in an external rotor) δ: 12.4 (δ-Me), 17.0 (α-CH_2), 27.3 and 28.2 (β- and γ-CH_2). ^{29}Si NMR CP MAS (79.49 MHz, reference – the ^{13}C signal with δ 38.48 ppm of solid adamantane in an external rotor) δ: –90.6 [$(SiO)_2\mathit{Si}(OH)_2$], –99.2 [$(SiO)_3\mathit{Si}OH$], –109.1 [$(SiO)_4\mathit{Si}$]. ^{119}Sn NMR MAS [149.13 MHz, reference – the signal with δ 81.68 ppm of the neat liquid $(n\text{-}Bu_3Sn)_2O$] δ: 115.0. Found (%) (mean value from 4 analyses): C, 8.46±0.05; H, 1.99±0.06; $SiO_2 + SnO_2$, 90.65±0.02. Calc. (%): C, 8.36; H, 1.87; $SiO_2 + SnO_2$, 88.85.

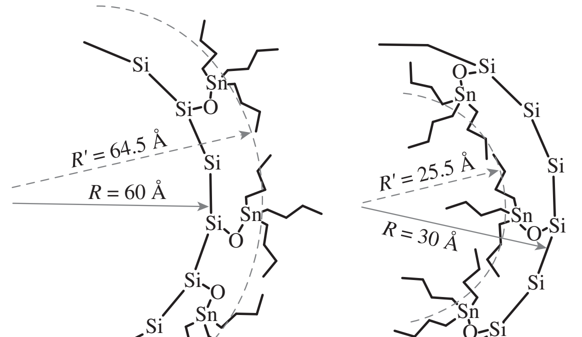
[‡‡] ^{29}Si spectra with cross polarization (CP) showed signals of only one to two surface atom layers, and that the relative signal areas are not strictly proportional to the number of the corresponding types of nuclei in these layers and are only used to compare the spectra obtained under identical conditions.

Aerosil (external surface of dense spheres) and ChSG (internal surface of cylindrical pores).

Molecular simulation (PM3 semiempirical method in the HyperChem program, version 8.0) of stannylated SG shows that the Sn atoms in the most stable conformations of *n*-Bu_3Sn groups are arranged at a distance of 3.5–4.0 Å from the SG surface and that two *n*-Bu residues in each group are nearly parallel to the surface, whereas one is almost perpendicular to it. As a result, the space at a distance of 4–5 Å from the SG surface is most populated with methylene and methyl groups. In comparison with the SG surface area, the ‘population zone’ area is larger for the convex surface (Aerosil) and smaller for the concave surface (ChSG). A simple calculation of the ‘population zone’ areas by change the surface curvature radii by +4.5 Å for Aerosil and –4.5 Å for ChSG (see Figure 3) shows that these areas differ from SG surface areas by +16% and –15%, respectively. Recalculation of the stannylation levels (1.24 and 0.85 Bu_3Sn groups per nm^2) to the ‘population zone’ areas gives 1.07 and 1.00 Bu_3Sn groups per nm^2 for Aerosil and ChSG, respectively, *i.e.*, almost equal values. Thus, the chemistry of stannylation of various SGs is the same, while the observed quantitative differences are due to the geometrical properties of the surfaces.

Only one report on TBTO reaction with SG, namely with Aerosil 1000, is available in literature.[17] In case of this strongly dehydrated SG with 0.4 OH groups per nm^2 Q^3 groups (and lack of Q^2), the French researchers obtained a stannylation degree of 1.2 Bu_3Sn groups per nm^2,[§§] *i.e.*, three times higher than the concentration of the OH groups. This was explained by the reaction of a fraction of Si–O–Si moieties in the SG with TBTO to give two Si–O–$SnBu_3$ moieties. However, this reaction was never observed with any other SGs.

In conclusion, exhaustively stannylated chromatographic SG, Sn-ChSG, can be readily obtained and has a well defined structure. This material can be used as an OTC carrier for all practical purposes mentioned in the introduction. Furthermore, given the permanently expanding application of TBTO in organic synthesis as a reagent with unique reactivity,[20] TBTO is the major, or the only, Sn-containing admixture in the products. In this case, trapping the admixture as Sn-ChSG is the simplest way to remove it. The same chemical mechanism underlies the recent chromatographic method for removal of organotin impurities from reaction mixtures.[21] Finally, a possible interesting application of the method for Sn-ChSG preparation may involve the conversion of conventional silica gel columns for preparative chromatography and HPLC to columns for reverse phase chromatography simply by filtration of a solution of TBTO or another bis(trialkyltin) oxide through the columns.



Bu_3Sn–Aerosil Bu_3Sn–Silica gel 60

Figure 3 Schematic drawing of stannylated silica gels.

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Online Supplementary Materials

Supplementary data associated with this article (the results of molecular simulations and geometrical calculations of stannylated silica gel parameters, the conditions of ^{13}C, ^{29}Si and ^{119}Sn MAS NMR experiments[22]) can be found in the online version at doi:10.1016/j.mencom.2015.01.019.

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[§§] This parameter is missing in ref. 17. It was calculated from the value reported in the paper, 4.69 wt% Sn/Aerosil in the resulting Sn-Aerosil.