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Use of MnCl₂ / 'BuOOH oxidizing system for conversion of *p*-tolyldisiloxanes to *p*-carboxyphenyldisiloxanes

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GraphicalAbstract



Abstract

The possibility of Mn-catalyzed oxidation of *p*-tolyldisiloxanes **1a-b** to the corresponding *p*-carboxyphenyldisiloxanes **2a-b** was studied using a commercially available and inexpensive system based on $MnCl_2$ / ^{*t*}BuOOH. Products **2a** and **2b** were isolated in 51% and 32% yields, respectively.

Keywords: functionalized siloxanes, peroxides, Mn-catalyzed oxidation, *p*-tolyldisiloxanes, *p*-carboxyphenyldisiloxanes

1. Introduction

Since 20th century, siloxanes (polyorganosiloxanes) were found to be very important materials in various fields of science, technology, medicine and construction due to their unique physico-chemical properties, e.g., low glass transition temperature, high thermal stability, low temperature dependence of viscosity, gas permeability, biocompatibility,etc.¹Despite all these advantages, there are two main drawbacks limiting their application fields: low mechanical strength and incompatibility with organic polymers. These issues arise from the weak intermolecular interaction of siloxane chains. These problems can be solved by introducing of "polar" functional group (e.g. -C(O)OH, $-C(O)NH_2$, -OH, $-NH_2$, etc.)into an organic polyorganosiloxane substituent leading to an increase in intermolecular interaction in a polysiloxane combined with organic polymers and, consequently, increasing the strength of siloxane-based materials.

The standard approaches to the synthesis of organosilicon compounds are not functionalgroup tolerant and cannot provide monomers with "polar" organic substituents, so polysiloxanes with "polar" edging are not readily available.²

It looks so promising to introduce "polar" groups into organic substituents of organosilicon compounds synthesized by standard procedures,²but this post-modification challenge is still of current interest despite its apparent simplicity: it was solved in only a few cases.³

The fact is that classic modification ways in organic chemistry become ineffective when applied to organosilicon compounds because of drastic reaction conditions, e.g. usage of acids, bases, oxidants, reductants, variable valency metals, and protonic solvents becomes fatal to Si-E-groups (where E is O, N, C or Cl). So these approaches are usually destructive and lead to complex mixtures of side products. Consequently, the methods for introduction of "polar" functions known from organic chemistry are not applicable to the synthesis of functionalized organosilicon substrates.³

One of the most attractive methods for synthesizingorganosilicon compounds containing "polar" groups involves the oxidation of *p*-tolylsilyl derivatives to the corresponding *p*-carboxyphenylsilylderivatives (scheme 1).⁴

Firstly, it is due to the relative ease of synthesizing *p*-tolylsilanes in laboratory.^{4,5}Furthermore, some of them are commercially available (e.g.tetra(*p*-tolyl)-, trichloro*p*-tolyl-, *p*-tolyltriethyl, triethoxy-*p*-tolylsilanes, etc.). Secondly, it was shown that it is principallypossible to use the conditions of toluene oxidation to benzoic acid in the oxidation of *p*-tolylsilanes to *p*-carboxyphenylderivatives (scheme 1, *path. A*).⁴ Thus, for example, using methods (1) and (2) bis(*p*-carboxyphenyl)tetramethyldisiloxane **2b** was prepared in the presence of 6 eq. of CrO_3 in solution of AcOH / Ac₂O / H₂SO₄ and 8 eq. of KMnO₄ in solution of Pyr / H₂O at reflux, respectively.^{4a-b} As for method (3),^{4c} despite relatively high yields of octakis[(*p*-carboxypheny)dimethylsilyl] silicate (77 - 78%), obtained from the corresponding octakis(*p*-tolyl) derivative is used up to 68 eq. of N-bromsuccinimide (NBS; 8.5 eq. per one tolyl-group) and 96 eq. of AgNO₃ (12 eq. per one tolyl-group). The number of similar works is reduced to several examples.⁴

Undoubtedly, these pioneering works made a serious contribution to the development of methods for the preparation of the above-mentioned (symmetric)*p*-carboxyphenylsiloxanes and confirmed the feasibility of this approach, but on the other hand showed the limitations of real synthetic methods, in particular on other (asymmetric)*p*-carboxyphenylsiloxanes: the stringent conditions of the process (in acid or base solution, high temperatures) lead to the formation of a hardly separable product mixtures (decay products in Si-O- and Si-C-bonds); use of excess quantities of expensive and toxic reagents and oxidants. Probably, for these reasons, these methods have not received further serious development and practical application.

Scheme 1. Approaches to *p*-tolylsilanes oxidation



Thus, the development of new synthetic methods based on milder reaction conditions, in particular catalytic ones, is required for the production of p-carboxyphenylsiloxanes, which are most important for solving the above problems.

One of the most promising oxidizing systems for the functionalization of C-H or Si-H bondsinvolves a combination of a variable valence metal (mainly 3d-metals) as a catalyst, and a peroxide as an oxidant, because of the low cost and commercial availability of the starting reagents, as well as the relatively milder process conditions.⁶ In addition, in some studies(e.g. concerning the production of silanols from the corresponding hydrosilanes using the [Cu] / ^{1}BuOOH system) it was shown that the reaction occurs without breaking the Si-O- and Si-C (sp3) bonds.⁷

2. Materials and methods

All the starting materials were purchased from Acros and Sigma Aldrich company. Solvents were dried and purified according to standard procedures. ¹H, ¹³C, ²⁹Si NMR spectra were recorded using a Bruker Avance 400 NMR spectrometer in CDCl₃, (CD₃)₂CO, chemical shifts are referenced to residual chloroform (7.26 ppm, ¹H) and acetone (2.05 ppm, ¹H).

3. Results and discussion

To evaluate the applicability of the $[M]/R^1OOR^2$ system to the oxidation of organosilicon molecules,(asymmetric)*p*-tolyldisiloxane**1a** was selected as a model substrate (Table 1, *note a*; SupportingInformation).

Table 1. Optimization of 1a-b oxidation

	[M], [x] ^t BuOOH	HO
Si Si	MeCN, T (°C), 24 h	Si Si R ²
1a-b		2a-b
a: R ¹ = Me,		a: R ² = Me,
b: R ¹ = <i>p</i> -MeC ₆ H ₄		b: R ² = <i>p</i> -HOOCC ₆ H ₄

N⁰			1/2 / side products,
	[M]		%
1.	0.0065 MnCl ₂	2,75	54 / 30 / 16 ^a
2.	0.0065 CrCl ₃	2,75	54/20/26 ^a
3.	$0.0065 \text{ MnCl}_2 + 0.0065 \text{ CrCl}_3$	9	25 / 55 / 20 ^b
4.	$0.0065 \text{ MnCl}_2 + 0.0065 \text{ AlCl}_3$	9	25 / 52 / 23 ^b
5.	0.0065 MnCl ₂	9	$20 / 58 / 22,^{b} 51^{d}$
	0.013 MnCl ₂	18	$21/56/23,^{c}32^{d}$

^a**1a** (0.151 g, 0.635mmol, 1 equiv.), ^tBuOOH (0.157 g, 1.746mmol, 2.75 equiv.,70% solution in

water),[M](0.0041mmol, 0.0065equiv.) and MeCN (1 mL)were stirred at 100 °C for 24 h. The 1/2 / side products ratio was determined by ¹H NMR ((CD₃)₂CO).

^b**1a** (0.151 g, 0.635 mmol, 1 equiv.), ^tBuOOH (0.171 g, 1.905 mmol, 3 equiv., 70% solution in water), [M] (0.0041 mmol, 0.0065 equiv.) and MeCN (1 mL) were stirred at 100 °C for 5 h. Further, after adding ^tBuOOH (0.171 g, 1.905 mmol, 3 equiv., 70% solution in water), the reaction mixture was stirred at 100 °C for 5h (2 times at 5-hour intervals). Next it was stirred at 100 °C for 14 h.

^{*c*}**1b** (0.100 g, 0.317 mmol, 1 equiv.), ^{*t*}BuOOH (0.171 g, 1.905 mmol, 6 equiv., 70% solution in water), [M](0.0041 mmol, 0.013 equiv.) and MeCN (1 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 100 °C for 5 h. Further, after adding ^{*t*}BuOOH (0.171 g, 1.905 mmol, 6 equiv., 70% solution in water), the reaction mixture was stirred at 100 °C for 5h (2 times at 5-hour intervals).Next it was stirred at 100 °C for 14 h.

At the first stage of optimization, the type of metal catalyst was varied, and ^{*t*}BuOOH was used as the oxidizing agent. It turned out that when MnCl₂or CrCl₃were used as the catalyst, a product (*p*-carboxyphenyldisiloxane) **2a** was formed in up to 30% and 20% yields respectively in an acetonitrile solution, at 100 °C, in 24 h. However, in the presence of metal catalysts such as CuCl₂, NiCl₂, CoCl₂, FeCl₃ and ceric ammonium nitrate (CAN), the yield of product **2a** was significantly lower and varied between 5 and 12% under the same conditions. Since the greatest yield of product **2a** was achieved using MnCl₂as the catalyst, further optimization of the process conditions was carried out with this metal catalyst.

Evaluation of the effect of the oxidant (peroxide) type on the yield of product **2a** showed that 'BuOOH is the most active (20%), in contrast to other peroxides: H_2O_{2aq} , $(NH_4)_2S_2O_8$ and 'BuOO'Bu which gives **2a** in yields up to 1%. The low efficiency of the latter peroxides can probably be explained by the fact that H_2O_{2aq} is decomposed relatively quickly under the reaction conditions (in comparison with 'BuOOH), while(NH_4)₂S₂O₈ and 'BuOO'Bu are rather stable and relatively less active (in comparison with H_2O_{2aq} and 'BuOOH) under appropriate reaction conditions.

Further optimization of the solvent, ratio of the initial reagents, temperature and time of the process showed no positive changes in product yields. Studying the effect of the sequence of reagent addition on the yield of the reaction product was the next key stage in optimizing the reaction. It was shown that portion-wise addition of 'BuOOH increases the yield of product **2a** from 30% to 58%. Conversion remained incomplete in this stage, so we tried some combinations of different metals as metal catalysts, but we failed to exceed the MnCl₂ activity. The yield of product **2a** was 58% under optimal conditions (Table 1, line 5, determined by ¹H NMR; conversion of substrate **1a** was 80% including 58% of product **2a** and 22% of a difficultly identifiable mixture of side products: decomposition cleavage by Si-Ar and Si-O bonds, incomplete oxidation of **1a**; no products of oxidation of Me-Si group were observed).Product **2a** was isolated in 51% yield by preparative chromatography using SiO₂ as the sorbent and a hexane / EtOAc system as the eluent.

Further, we evaluated the applicability of oxidizing conditions to substrate **1b** (bis(*p*-tolyl)disiloxane). Substrate **1b** was oxidized with a conversion of 79% to form a complex mixture of up to 56% oxidation products with two (**2b**, bis(*p*-carboxyphenyl)disiloxane) or one tolyl group and up to 23% side products. Compound **2b** was also isolated in 32% yield by

preparative chromatography using SiO_2 as the sorbent and a hexane / EtOAc system as the eluent.

4. Conclusions

Thus, the work demonstrates the principal possibility of using a catalytic approach to the conversion of *p*-tolyldisiloxanes **1a-b** to the corresponding *p*-carboxyphenyldisiloxanes **2a-b** using ainexpensive and commercially available oxidation system: $MnCl_2$ – catalyst and ^tBuOOH – oxidant. From a comparison of the conversions of the original model compounds and the yields of the target products, it follows that, as the synthesis conditions are further optimized, the achieved indices can be significantly improved. The demonstrated activity of the salts of some transition metals, in particular in $MnCl_2$, indicates the promise of further research in this direction.

5. Experimental section

<u>Method of 2a synthesis</u>: 1a (0.151 g, 0.635 mmol, 1 eq.), ^tBuOOH (0.171 g, 1.905 mmol, 3 eq., 70% solution in water), MnCl₂ (0.0005 g, 0.0041 mmol, 0.0065 eq.) and MeCN (1 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 100 °C for 5 h. Further, after adding of a ^tBuOOH (0.171 g, 1.905 mmol, 3 eq., 70% solution in water), the reaction mixture was stirred at 100 °C for 5h (2 times at 5-hour intervals). Next it was stirred at 100 °C for 14 h. Then MeCN was evaporated (150-200 mbar, Tbath = 40 °C) and reaction mixture was dried (1 mbar, 50 °C). Product 2a was isolated as white powder in a 51% yield (0.087 g) by preparative chromatography using SiO₂, as a sorbent, and a hexane / EtOAc system, as the eluent.

<u>Method of **2b** synthesis</u>: **1b** (0.100 g, 0.317 mmol, 1 eq.), ^tBuOOH (0.171 g, 1.905 mmol, 6 eq., 70% solution in water), MnCl₂ (0.0005 g, 0.0041 mmol, 0.013 eq.) and MeCN (1 mL) were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) at 100 °C for 5 h. Further, after adding of a ^tBuOOH (0.171 g, 1.905 mmol, 6 eq., 70% solution in water), the reaction mixture was stirred at 100 °C for 5h (2 times at 5-hour intervals). Next it was stirred at 100 °C for 14 h. Then MeCN was evaporated (150-200 mbar, Tbath = 40 °C) and reaction mixture was dried (1 mbar, 50 °C). Product **2a** was isolated as white powder in a 32% yield (0.037 g) by preparative chromatography using SiO₂, as a sorbent, and a hexane / EtOAc system, as the eluent.

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- Mn-catalyzed oxidation of *p*-tolyl-to *p*-carboxyphenyldisiloxanes was studied;

- The catalytic approach to the synthesis of *p*-carboxyphenyldisiloxanes was suggested.