



Synthesis, structure and application of a new class of Tr-podands derived in phase-transfer catalysis

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ABSTRACT

Triton X surfactants are used in numerous commercial and industrial products. Large amounts of such surfactants and their various residual biodegradation by-products are ultimately released into the environment. The first synthesis of the group of Tr-polypodands (Triton polypodands), with different central atoms, such as Si, B or P, is reported. Results of this study demonstrate the potential of these compounds in some organic reactions in phase-transfer catalysis (PTC) conditions. The catalytic activity of Triton X (**1**) and Tr-podands (**2–8**) has been evaluated in an ion promoted reaction under solid–liquid phase-transfer catalysis conditions and compared with that of the earlier studied Si-podands (**9–11**), used as PTC agents.

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1. Introduction

Phase-transfer catalysis (PTC) is a useful approach to synthesis because of simple and easy reaction procedure, mild conditions and inexpensive reagents. The phase-transfer catalyzed reaction systems have been studied in many research groups since the 1960s [1–5]. Syntheses of organic chemicals by phase-transfer catalysis offer such advantages as high reaction rate, high product selectivity, moderate operating temperature, and suitability for industrial-scale production. Organic reactions occur most easily in a uniform medium in which the contact between the reacting molecules is the easiest. PTC is a very important technique used in organic synthesis in chemical industry, especially if the reagents differ in physical properties (like polarity) or occur in two immiscible phases e.g. in immiscible liquids (solvents) LL-PTC (liquid–liquid phase-transfer catalysis) or in the solid and liquid phase SL-PTC (solid–liquid phase-transfer catalysis). A small addition of a catalyst would improve the reaction rate or simply permit its occurrence. Such a catalyst being most often a salt in a complex with a metal cation (e.g. a crown ether) draws out one of the reagents (frequently the anion) and transfers it to the other phase in which the reaction takes place. PTC in solid–liquid system has attracted a lot of attention. Supramolecular compounds, such as crown ethers, cryptands, cyclodextrins, etc. have for the last 20 years been among the pre-eminent catalyst of phase-transfer catal-

ysis chemistry. These macrocycles could form stable complexes with different metal ions, especially from I and II main groups of elements [6–11].

A fundamental and essential problem of the SL-PTC processes is to find an appropriate and effective catalyst. Earlier we have studied some B- and Si-podand systems as particularly suitable ligands for solid–liquid phase-transfer catalysis [12–15]. Podands are non-cyclic structures in which several polyether chains are linked to the same binding centre being either an atom (N, P, Si, S), or a multi-branched structural arrangement. The type of the central atom in the polypodand molecules, number of oxygen atoms and polyoxoalkyl chains and also different length of these chains, determine the complex forming ability of these compounds. Because of their specific properties they are called open-chain analogues of crown ethers and cryptands. In comparison with typical phase-transfer catalysts, like open-chain PEGs, cryptands or crown ethers, they are characterized by low cost and easy synthesis, practical non-toxicity and high complex forming ability [12–15]. These reasons make this type of molecular structures highly promising as anion activators in organic reactions.

In anion-promoted reactions the rate of the process mainly depends on the interaction between the anion and the solvent molecules increasing, even by several orders of magnitude, on going from polar protic media, that specifically solvate the anion through hydrogen bonds, to the solvents in which this interaction is minimized (aprotic dipolar solvents) [16].

The surfactants, such as non-ionic Triton X (molecular formula: $C_{14}H_{220}(C_2H_{40})_n$, $n = 9–10$), have many applications in a wide range of different disciplines and are widely used in numerous commer-

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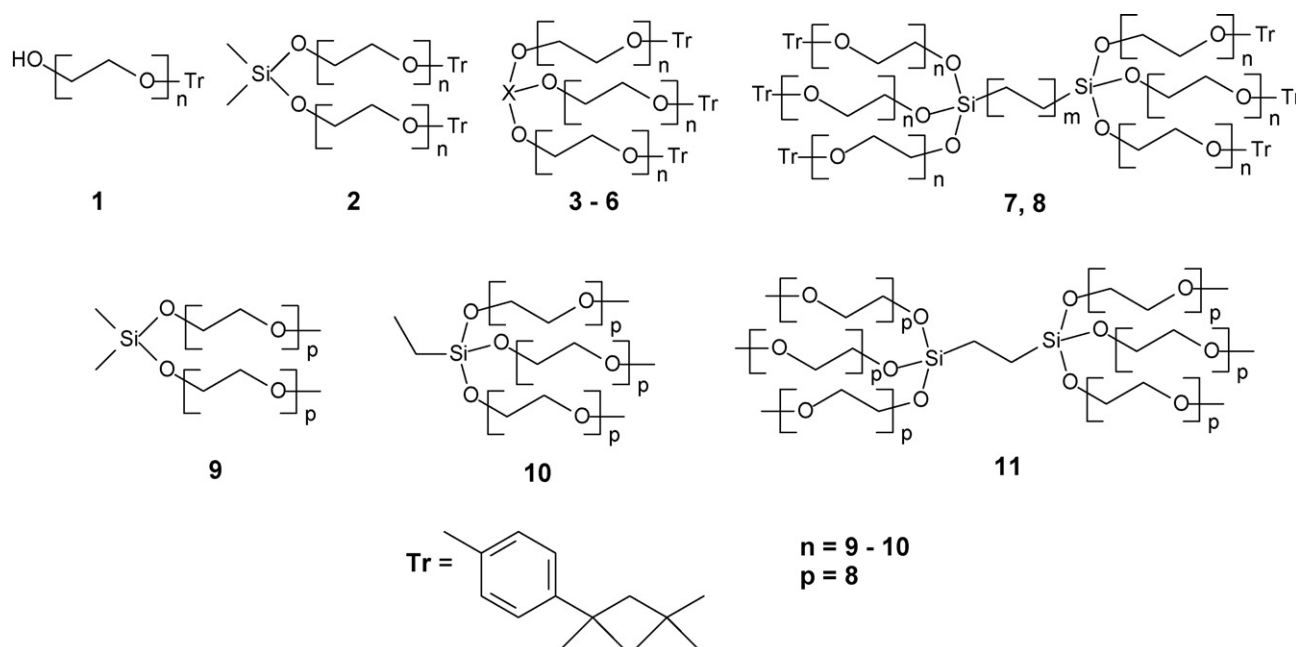
cial and industrial products, including detergents, emulsifiers, wetting agents, solubilizers and dispersants [17–21]. As wetting agent Triton X is used in the microscopy and histology laboratories, in the form of dilute solutions, it is used as a wetting agent for affecting certain staining protocols and for the cleaning of diamond knives. In the electronics industry, it is used as a wetting agent on wafers in order to enhance and speed up certain procedures and operations. Triton X-100 will leave a thin film on the surface of the wafer, which can be removed using standard resist stripping techniques or with the SPI Plasma Prep II plasma etcher using oxygen etch. Large amounts of the surfactants and their various residual biodegradation by-products are ultimately released into the environment [22–26]. In view of the above, it is important that the catalysts developed are not only effective in PTC but also easily biodegradable. In this paper we report a systematic study of Triton X as a PTC-ligand agent (**1**) and different poly podands (Tr-podands) with B, Si and P as central atoms in the molecule, obtained on the basis of Triton X (**2–8**), in high yield in the reaction presented in the Section 2 of this paper. The formulas of podands **2–8** (Scheme 1) have been confirmed by ^1H and ^{13}C NMR spectroscopy methods and elementary analyses. Tr-podands are thermally stable under the reaction conditions. We have used these podands as catalysts in some phase-transfer catalysis processes and they have been found excellent catalysts in some anion-promoted reactions (nucleophilic substi-

tution, reduction, alkylation, etc.) under solid–liquid conditions in chlorobenzene as low polarity medium and acetonitrile as polar aprotic solvent. A comparison is performed with the Si-podands studied previously by us as PTC catalysts (**9–11**). The catalytic activity results are collected in Tables 2–5. The influence of the central atom type of poly podands on the PTC reactions is also discussed.

2. Experimental

2.1. General methods

HPLC data were obtained with a Dionex ASI-100 equipped with a P680 HPLC pump using a Thermo BDS Hypersil C18 column and as well as a Dionex PDA-100 Photodiode Array Detector. As mobile phase we used mixtures of acetonitrile, methanol and water at the ratios depending on particular analysis. The reactions studied were followed by the HPLC method up to $\geq 90\%$ conversions. The percent of conversion of nucleophilic substitution reactions was determined on the basis of the substrate disappearance (**12**, **13**) and the reaction products appearance. The reduction reaction was followed by evaluating the disappearance of benzaldehyde **15** in the organic phase. In the cases of *N*- and *O*-alkylation reactions the disappearance of alkylbromide was measured.



Compound	X	m
1	-	-
2	-	-
3	B	-
4	P	-
5	PhSi	-
6	$\text{H}_2\text{C}=\text{CHSi}$	-
7	-	1
8	-	3

Scheme 1. Compounds used: **1** Triton X-100; **2–8** Tr-poly podands, **9–11** Si-podands.

Potentiometric titrations were carried on with a titrator by using a ring combined silver electrode isolated with a potassium nitrate bridge or a glass electrode isolated with a potassium chloride bridge (Metrohm).

All NMR spectra were recorded on Varian Gemini 300 spectrometer, operating at 300.076 MHz for ^1H . For ^1H , ^{13}C and ^{29}Si NMR spectra tetramethylsilane was used as internal reference. The external references were: 1 M solution of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in CDCl_3 for ^{11}B NMR measurements, 80% H_3PO_4 for ^{31}P NMR and 1 M solution of NaCl in D_2O for ^{23}Na NMR. All spectra were recorded at 293 K using CDCl_3 as a solvent (except sodium-23 measurements for which CD_3CN was used).

Elementary analyses were obtained on a Vario EL III (Elementar, USA) analyser.

2.2. Synthesis of Tr-podands

2.2.1. Triton X-100 borate (3)

To a solution of Triton X-100 (25 g, 0.04 mol) in dry benzene (250 cm^3), anhydrous boric acid (0.825 g, 0.013 mol) was added. The mixture obtained was heated using Dean-Stark apparatus until water was no longer released (about 20 h). The product obtained, by solvent evaporation under reduced pressure was a colourless, viscous liquid and was used without further purification. The ester's purity was about 92–94% (by NMR). ^1H NMR: δ 0.70 (s, 9H), 1.33 (s, 6H), 1.69 (s, 2H), 3.6–3.7 (m, ~32H), 3.82 (t, J = 4.7 Hz, 2H), 3.92 (t, J = 4.9 Hz, 2H), 4.09 (t, J = 4.7 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8, 2H). ^{13}C NMR: δ 31.5, 31.6, 32.1, 37.7, 56.7, 62.4, 67.0, 69.5, 70.3, 70.5, 71.3, 113.2, 126.6, 141.8, 156.0. ^{11}B NMR: δ 19.3. Anal. Calcd for $\text{C}_{99}\text{H}_{177}\text{O}_{31.5}\text{B}$: C, 63.19; H, 9.48; B, 0.57. Found: C, 63.40; H, 9.38; B, 0.58.

2.2.2. Triton X-100 phosphite (4)

To a vigorously stirred solution of Triton X-100 (25 g, 0.04 mol) and pyridine (3.16 g, 0.04 mol) in dry diethyl ether (250 cm^3), a solution of phosphorus trichloride (1.78 g, 0.013 mol) in the same solvent, was added dropwise over 1 h. Then the mixture obtained was heated under reflux (about 5 h). After cooling, pyridine hydrochloride precipitated was separated by filtration and the solvent was evaporated in vacuum. The residue was dissolved in dry dichloromethane and the solution obtained was filtered. Solvent evaporation gave phosphite ester as slightly yellow, viscous liquid. The product purity was about 90–91% (by NMR). ^1H NMR: δ 0.70 (s, 9H), 1.33 (s, 6H), 1.69 (s, 2H), 3.6–3.7 (m, ~30H), 3.82 (t, J = 4.7 Hz, 2H), 3.96 (dt, J_1 = 5.5 Hz, J_2 = 4.9 Hz, 2H), 4.09 (t, J = 4.7 Hz, 2H), 4.20 (dt, J_1 = 9.3 Hz, J_2 = 4.9 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8, 2H). ^{13}C NMR: δ 31.6, 31.7, 32.3, 37.7, 56.8, 61.6 (d, J = 10.6 Hz), 67.1, 69.7, 70.4, 70.68, 70.9 (d, J = 4.7), 113.5, 126.7, 141.9, 156.1. ^{31}P NMR: δ 134.12 (sp, J_1 = 9.3 Hz, J_2 = 5.5 Hz). Anal. Calcd for $\text{C}_{99}\text{H}_{177}\text{O}_{31.5}\text{P}$: C, 62.52; H, 9.38; P, 1.63. Found: C, 62.46; H, 9.41; P, 1.65.

2.2.3. Triton X-100 phenylsilyl derivative (5)

The product was obtained in a similar way as phosphate ester. Triton X-100 (25 g, 0.04 mol) and trichlorophenylsilane (2.84 g, 0.013 mol) were used for synthesis. Solvent evaporation gave the product as a colourless, viscous liquid of purity about 97–98% (by NMR). ^1H NMR: δ 0.70 (s, 27H), 1.33 (s, 18H), 1.69 (s, 6H), 3.6–3.7 (m, ~96H), 3.84 (t, J = 5.0 Hz, 6H), 3.95 (t, J = 5.2 Hz, 6H), 4.10 (t, J = 5.0 Hz, 6H), 6.80 (d, J = 8.8 Hz, 6H), 7.24 (d, J = 8.8, 6H), 7.34 (m, 3H), 7.67 (d, J = 7.7 Hz, 2H). ^{13}C NMR: δ 31.6, 31.7, 32.3, 37.9, 56.9, 62.3, 67.2, 69.7, 70.5, 70.6, 72.0, 113.6, 126.8, 127.6, 130.3, 134.5, 134.7, 142.1, 156.1. ^{29}Si NMR: δ –66.2. Anal. Calcd for $\text{C}_{105}\text{H}_{182}\text{O}_{31.5}\text{Si}$: C, 62.81; H, 9.29; Si, 1.39. Found: C, 63.05; H, 9.40; Si, 1.42.

2.2.4. Triton X-100 vinylsilyl derivative (6)

The product was obtained in a similar way as phosphate ester. Triton X-100 (25 g, 0.04 mol) and trichlorovinylsilane (2.17 g, 0.013 mol) were used for synthesis. Solvent evaporation gave the product as a colourless, viscous liquid of purity about 95–96% (by NMR). ^1H NMR: δ 0.70 (s, 27H), 1.33 (s, 18H), 1.69 (s, 6H), 3.6–3.7 (m, ~96H), 3.84 (t, J = 5.0 Hz, 6H), 3.91 (t, J = 5.3 Hz, 6H), 4.10 (t, J = 5.0 Hz, 6H), 5.83 (dd, J_1 = 20.6, J_2 = 14.0, 1H), 6.06 (dd, J_1 = 20.6 Hz, J_2 = 4.9 Hz, 1H), 6.12 (dd, J_1 = 14.0 Hz, J_2 = 4.9 Hz, 1H), 6.81 (d, J = 8.8 Hz, 6H), 7.24 (d, J = 8.8, 6H). ^{13}C NMR: δ 31.66, 31.74, 32.3, 37.9, 56.9, 62.1, 67.2, 69.7, 70.5, 70.7, 72.1, 113.6, 126.8, 129.1, 138.3, 142.1, 156.1. ^{29}Si NMR: δ –70.4. Anal. Calcd for $\text{C}_{101}\text{H}_{180}\text{O}_{31.5}\text{Si}$: C, 62.98; H, 9.42; Si, 1.44. Found: C, 63.10; H, 9.45; Si, 1.46.

2.2.5. Triton X-100 dimethylsilyl derivative (2)

The product was obtained in a similar way as phosphate ester. Triton X-100 (25 g, 0.04 mol) and dichlorodimethylsilane (2.60 g, 0.02 mol) were used for synthesis. Solvent evaporation gave product as a colourless, viscous liquid of purity about 96–97% (by NMR). ^1H NMR: δ 0.17 (s, 3H), 0.70 (s, 9H), 1.33 (s, 6H), 1.69 (s, 2H), 3.6–3.7 (m, ~32H), 3.84 (m, 4H), 4.10 (t, J = 5.0 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8, 2H). ^{13}C NMR: δ –3.0, 31.66, 31.74, 32.3, 37.9, 56.9, 61.7, 67.2, 69.7, 70.5, 70.7, 72.1, 113.6, 126.8, 142.1, 156.1. ^{29}Si NMR: δ –45.2. Anal. Calcd for $\text{C}_{68}\text{H}_{124}\text{O}_{21}\text{Si}$: C, 62.56; H, 9.58; Si, 2.15. Found: C, 62.66; H, 9.69; Si, 2.18.

2.2.6. Triton X-100 1,2-bis(silyl)ethane derivative (7)

The product was obtained in a similar way as phosphate ester. Triton X-100 (25 g, 0.04 mol) and 1,2-bis(trichlorosilyl)ethane (2.00 g, 0.007 mol) were used for synthesis. Solvent evaporation gave the product as a colourless, viscous liquid of purity about 90–92% (by NMR). ^1H NMR: δ 0.70 (s, 27H), 0.92 (s, 2H), 1.33 (s, 18H), 1.69 (s, 6H), 3.6–3.7 (m, ~96H), 3.84 (m, 12H), 4.10 (t, J = 5.1 Hz, 6H), 6.81 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8, 2H). ^{13}C NMR: δ 4.4, 31.6, 31.7, 32.3, 37.9, 56.9, 61.6, 67.2, 69.7, 70.4, 70.7, 72.0, 72.3, 113.6, 126.8, 142.1, 156.1. ^{29}Si NMR: δ –41.0. Anal. Calcd for $\text{C}_{200}\text{H}_{358}\text{O}_{63}\text{Si}_2$: C, 62.78; H, 9.43; Si, 1.47. Found: C, 63.02; H, 9.57; Si, 1.45.

2.2.7. Triton X-100 1,6-bis(silyl)hexane derivative (8)

The product was obtained in a similar way as phosphate ester. Triton X-100 (25 g, 0.04 mol) and 1,6-bis(trichlorosilyl)hexane (2.37 g, 0.007 mol) were used for synthesis. Solvent evaporation gave the product as a colourless, viscous, slightly opalescent liquid of purity about 90–93% (by NMR). ^1H NMR: δ 0.65 (b, 4H), 0.70 (s, 27H), 1.33 (s, 18H), 1.35 (b, 2H), 1.69 (s, 6H), 3.6–3.7 (m, ~96H), 3.84 (m, 12H), 4.10 (t, J = 5.1 Hz, 6H), 6.81 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8, 2H). ^{13}C NMR: δ 10.1, 22.8, 31.68, 31.71, 32.4, 33.6, 37.81, 56.8, 61.6, 67.2, 69.7, 70.5, 70.7, 72.2, 72.6, 113.6, 126.8, 142.1, 156.1. ^{29}Si NMR: δ –44.0. Anal. Calcd for $\text{C}_{204}\text{H}_{366}\text{O}_{63}\text{Si}_2$: C, 63.11; H, 9.50; Si, 1.45. Found: C, 63.28; H, 9.61; Si, 1.50.

2.3. The others materials and solvents

Silicon podands **9–11** were prepared following a previously reported procedure [27]. Their structures were confirmed by ^1H , ^{13}C and ^{29}Si NMR spectroscopy.

Octyl methanesulphonate **12**, b.p. 94–97 °C at 0.003 mmHg, n_{D}^{20} 1.4392, 78% yield was prepared according to a literature method (b.p. 98 °C at 1.5 mmHg, n_{D}^{20} 1.4390) [28].

Octylbromide **13** and benzaldehyde **15** were commercial products (Aldrich), used as purchased.

Alkali metal halides (NaI, KI), potassium carbonate (K_2CO_3), sodium borohydride (NaBH_4) and potassium phthalimide

(C₆H₄(CO)₂NK) **17** were Fluka and Aldrich commercial products, kept in a desiccator under vacuum.

Dry (Fluka) chlorobenzene, toluene (Aldrich), methanol (Aldrich) and acetonitrile (Aldrich) (H₂O ≤ 20 ppm) were kept over molecular sieves.

3. Results and discussion

3.1. Complexing ability of Triton X podands by NMR titration

²³Na NMR titration experiments were carried out at constant concentration of sodium ion, changing the ligand/metal ratio from 0.1 to 25. For compound **3**, containing three podand arms, the fitting of titration curves gave five stability constants. The values of K₁–K₄ are the same (they differ by less than the error of calculation), of 200 ± 20. The value of K₅ was measurably smaller, and amounted to 140 ± 30. Titration of compounds **4**–**6** gave very similar curves and no significant differences in the values of stability constants. Ligand **2** titration gave three stability constants: K₁ and K₂ of similar value 125 ± 10, while K₃ much smaller, of only 60 ± 10. No titration experiments were carried out for compounds **7** and **8**. For these podands, the fractions of complexes of higher stoichiometry (ion/ligand ratio more than 5) were too small in the conditions of NMR measurements, so that the calculation of K values was practically impossible.

Calculations were made using the WinEQNMR software. The number of equilibria in a model, assumed for the calculations (and, in consequence, the number of K values obtained) was increased to obtain the best fitting of the calculated titration curve to the experimental points during the iteration process. Further increase in the parameters worsened the fitting or obtaining of K values equal to 0. From 30 to 40 experimental points were used for each calculation.

3.2. Complexation extent of Triton X-100, Tr-polypodands **2**–**8** and ligands **9**–**11** under SL-PTC conditions

The complex forming abilities of ligands **1**–**11** were evaluated for a series of alkali metal salts M⁺Y⁻ (M⁺ = Na⁺, K⁺; Y⁻ = I⁻) by stirring a chlorobenzene solution of a ligand with 10–50 molar equivalents of the appropriate salt as a solid phase at 60 °C (Table 1).

The data reported in Table 1 show that the complexation extent, defined as moles of MY complexed per mole of ligand, mainly depends on the topology of the polypodand, also increasing with the number of silicon atoms (ligands: **7**, **8** and **11**) and oxygen atoms. We observed that the ligand (**1**) complexed 1.40 of Na⁺ and only 0.66 for K⁺, for the Tr-polypodand (**2**) with two polyoxaethylene chains, the result of complexation is the following: 3.00 for Na⁺ and 1.00 for K⁺. The salt being the same, the highest complexation values (up to 7.3–7.8 mol of NaI) are always obtained with the polypodands **7** and **8** having the highest number of donor atoms (60 oxygen atoms).

Interestingly, a comparison with the corresponding simple podand reveals a “cooperative effect” of the pendant arms in the complexation process. As shown in Table 1, indeed, the complexation extent of polypodand **7** and **8** (with six polyether chains) is

Table 1

Complexation extent Triton X-100 (**1**), Tr-polypodands (**2**–**8**) and Si-podands (**9**–**11**) under SL-PTC in chlorobenzene at 60 °C

Ligand (catalyst)	NaI	KI
1	1.40	0.66
2	3.00	1.00
3	4.00	1.40
4	4.15	1.10
5	4.70	1.30
6	3.44	1.20
7	7.30	3.04
8	7.60	3.11
9	2.50	1.30
10	4.00	1.70
11	5.60	3.70

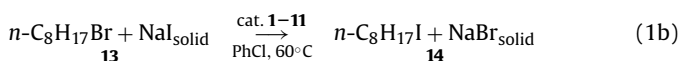
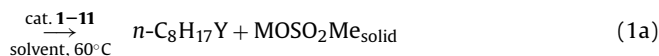
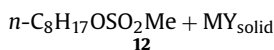
Defined as complexed MY moles/ligand mole.

about 6 (for NaI) or 5 (for KI) times higher than that of the Triton X (**1**). The complex forming ability of polypodands (**7**, **8**) is noticeably higher than that corresponding to monopodands (**3**–**6**), showing a “cooperative effect” [14].

The structure of exemplary Tr-podand (**7**) was calculated by PM5 method using MOPAC program [29] to visualize space structure of compound (Fig. 1).

3.3. Nucleophilic substitution reactions

As a continuation of our earlier studies of polypodand ligands in phase-transfer catalysis reaction, we have conducted the typical S_N2 nucleophilic substitution reactions of *n*-octyl methanesulfonate **12** or 1-bromooctane **13** in organic solvent-solid MY two-phase systems (organic solvent = chlorobenzene, acetonitrile; MY = NaI, KI) in the presence of catalytic amount (0.1 mol per mole of substrate) of Tr-various catalysts (**2**–**8**). The kinetic results (*k*_{obsd}) for the reaction with ligands **2**–**8** were compared with those earlier obtained for the same processes conducted with Triton X (**1**) and Si-ligands **9**–**11** under the same conditions (reactions: (1a) and (1b)).



The kinetic results are visualized by *k*_{obsd} data. The Tr-podands we used can be divided into three groups. The first one comprises the two-chain podands, such as **2** and **9**. The next class includes three-chain podands: **3**–**6** and **10**. The last group includes the podands with two silicon atoms and six polyoxaalkyl chains: **7**, **8** and **11**. According to the data from Table 2, under the same conditions the reaction times (at 90% conversion) decrease in the following order **7** > **8** > **11** > **4** > **3** = **10** = **5** > **6** > **9**, **2** ≫ **1**. The best results were obtained for the Tr-podands **7** and **8**, having 11 oxygen

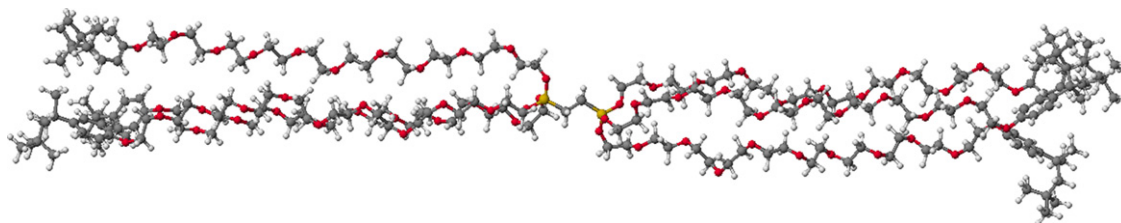


Fig. 1. The exemplary molecule of podand **7** calculated by PM5 semiempirical method. This picture shows space structure of Triton based podands.

Table 2

The catalytic efficiency of Triton X-100 (**1**), Tr-podands (**2–8**) and Si-podands (**9–11**) (**1a**): $n\text{-C}_8\text{H}_{17}\text{OSO}_2\text{Me}$; MY = NaI, KI under SL-PTC conditions in chlorobenzene at 60 °C and (**1b**) $n\text{-C}_8\text{H}_{17}\text{Br}$; NaI under SL-PTC conditions in chlorobenzene at 60 °C

Catalyst	Reaction time (min) ^a			10 ⁵ k_{obsd} (s ⁻¹)		
	NaI ^b	KI ^b	NaI ^c	NaI ^b	KI ^b	NaI ^c
–	>4300	–	–	–	–	–
1	124.2	411.0	126.7	13.4	4.1	13.2
2	55.6	201.7	56.2	30.0	8.3	29.7
3	35.0	140.0	38.4	47.6	11.9	43.4
4	27.1	109.2	30.1	61.5	15.3	55.4
5	38.2	160.2	41.9	43.6	10.4	39.8
6	45.2	165.3	46.5	36.9	10.1	35.8
7	14.2	52.3	17.1	117.4	31.9	97.5
8	16.4	55.6	18.0	101.6	30.0	92.6
9	54.0	180.0	120.5	30.9	9.3	13.8
10	36.0	140.0	105.0	46.3	11.9	15.9
11	24.0	57.0	35.4	69.4	29.2	47.1

^a Conversion = 90% (by HPLC).

^b A chlorobenzene solution.

^c For reaction (**1b**), a chlorobenzene solution.

atoms in each of the 6 chains. These results were better than those obtained for Si-ligand **11**, which has 9 oxygen atoms in the polyoxaalkyl chain. For comparison, the results of catalysis efficiency of podands in the nucleophilic substitution reaction ((**1a**) and (**1b**)), have shown that ligands **3** and **4** are more effective than ligands (catalysts) **5** and **6**, and as for the class of three-chain ligands, it is interesting to note that P and B-podands have proved much more effective catalysts than Si-podands.

It is worth noting that this tendency is observed in both nucleophilic substitution reactions, with *n*-octyl methanesulfonate **12** or 1-bromooctane **13** and NaI and KI. For these reactions we observed a dramatic decline in the reaction times from 124 min for ligand **1** ($k_{\text{obsd}} = 13.4 \times 10^{-5} \text{ s}^{-1}$) to 14.2 min for ligand **7** ($k_{\text{obsd}} = 117.4 \times 10^{-5} \text{ s}^{-1}$) or to 16.4 min for ligand **8** ($k_{\text{obsd}} = 101.6 \times 10^{-5} \text{ s}^{-1}$) (Table 2).

3.4. Reduction reactions

The reduction of benzaldehyde **15** to the corresponding benzylic alcohol **16** with NaBH₄ was performed in a chlorobenzene-solid NaBH₄ two-phase system by using catalytic amounts (0.1 mol per mole of substrate) of Tr-polypodands **1–8** and comparative ligands **9–11** (reaction (2)) at 25 °C.

Table 3

The catalytic efficiency of Triton X-100 (**1**), Tr-podands (**2–8**) and Si-podands (**9–11**) in the reduction of benzaldehyde under SL-PTC conditions in chlorobenzene at 60 °C

Catalyst	Reaction time (min) ^a	10 ⁵ k_{obsd} (s ⁻¹)
–	2900.0	0.6
1	20.0	83.3
2	10.3	161.8
3	7.6	219.3
4	9.9	168.4
5	10.4	160.3
6	10.2	163.4
7	6.8	245.1
8	8.9	187.3
9	27.0	61.7
10	18.0	92.6
11	15.0	111.1

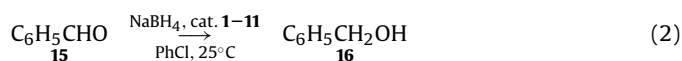
^a Conversion = 90% (by HPLC).

Table 4

The catalytic efficiency of Triton X-100 (**1**), Tr-podands (**2–8**) and Si-podands (**9–11**) in the *N*-alkylation of potassium phthalimide reactions under SL-PTC conditions in acetonitrile at 80 °C

Catalyst	Reaction time (min) ^a	10 ⁵ k_{obsd} (s ⁻¹)
–	1980.0	0.8
1	195.4	8.5
2	120.5	13.8
3	32.2	51.8
4	35.4	47.1
5	41.3	40.4
6	50.7	32.9
7	27.3	61.1
8	28.2	59.1
9	270.0	6.2
10	228.0	7.3
11	120.0	13.9

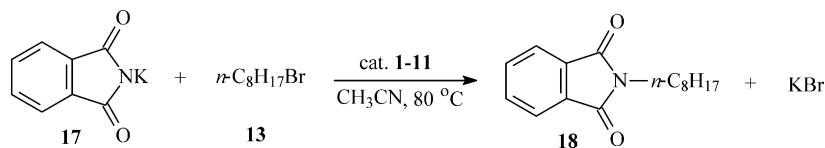
^a Conversion = 90% (by HPLC).



The results, reported in Table 3, together with those for Si-podands ligands for the sake of comparison, show that the reduction is very fast with all Tr-polypodands **1–8**, in particular with ligands: **3** ($k_{\text{obsd}} = 219.3 \times 10^{-5} \text{ s}^{-1}$), **7** ($k_{\text{obsd}} = 245.1 \times 10^{-5} \text{ s}^{-1}$) and **8** ($k_{\text{obsd}} = 187.3 \times 10^{-5} \text{ s}^{-1}$), it is less than 10 min instead of about 3000 min ($k_{\text{obsd}} = 0.6 \times 10^{-5} \text{ s}^{-1}$) (Table 3).

3.5. *N*-Alkylation reaction

The *N*-alkylation reaction of potassium phthalimide **17** by 1-bromooctane **13** was carried out at 80 °C in an acetonitrile-solid C₆H₄(CO)₂NK two-phase system in the presence of catalytic amounts (0.1 mol per mole of substrate) of ligands **1–11** and with a 1:1 molar ratio potassium phthalimide (**17**) to alkylbromide **13** (reaction (3)) in acetonitrile as a solvent.



The catalytic activities of all ligands **1–11** are collected in Table 4. Tr-polypodands **2–8** were shown to be better PT catalysts of this *N*-alkylation reaction than the other ligands **9–11**, which were studied previously in the phase-transfer processes. The Tr-podand's activity depends on the central atom type and increases with the number of donor atoms in the order: **7** > **8** > **3** > **4** > **5** > **6** (from 27.3 to 50.7 min ($k_{\text{obsd}} = 61.1 \times 10^{-5} \text{ s}^{-1}$ to $32.9 \times 10^{-5} \text{ s}^{-1}$)), while the times of the analogous reaction catalyzed by the other catalysts ligand $\gg \mathbf{2, 11} \gg \mathbf{1} \gg \mathbf{10, 9}$ and without any catalyst the reaction lasts up to 1980 min ($k_{\text{obsd}} = 0.8 \times 10^{-5} \text{ s}^{-1}$).

3.6. *O*-Alkylation reaction

We also studied the *O*-alkylation reaction of phenol **19** by 1-bromooctane **13** (at the 1:1 molar ratio) performed at 110 °C in toluene-solid K₂CO₃ two-phase system in the presence of catalytic amounts (0.1 mol per mole of substrate) of ligands **1–11** (reaction (4)). We obtained 90% conversion 5–8 times faster with some Tr-podands (**2–8**) as PT catalysts than with the other ligands (**9–11**) (Table 5).

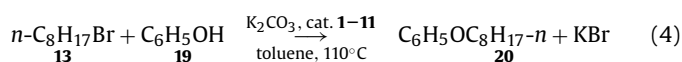


Table 5

The catalytic efficiency of Triton X-100 (**1**), Tr-podands (**2–8**) and Si-podands (**9–11**) in the O-alkylation of phenol reactions under SL-PTC conditions in toluene at 110 °C

Catalyst	Reaction time (min) ^{a,b}	10 ⁵ <i>k</i> _{obsd} (s ⁻¹)
–	>3500.0	–
1	277.0	6.0
2	202.0	8.3
3	47.4	35.2
4	51.1	32.6
5	62.6	26.6
6	71.7	23.2
7	42.4	39.3
8	45.8	36.4
9	350.3	4.8
10	259.0	6.4
11	180.1	9.3

^a Conversion = 90% (by HPLC).

^b A toluene solution and K₂CO₃ in solid phase.

It is particularly interesting to note that in the studied O-alkylation reaction of phenol under the same SL-PTC conditions, the catalytic activity of Tr-polypodands **2–8**, was much better than that of the previously studied Si-podands (**9–11**) (Table 5). The values of *k*_{obsd} were the highest for ligands **7**, **8**, **3** and **4** (from 39.3 × 10⁻⁵ to 32.6 × 10⁻⁵ s⁻¹), than with catalysts **9** (*k*_{obsd} = 4.8 × 10⁻⁵ s⁻¹) or **10** (*k*_{obsd} = 6.4 × 10⁻⁵ s⁻¹).

4. Conclusions

The kinetics of some anion-promoted organic reactions in an organic solution by phase-transfer catalysis was investigated. The rate constants obtained were higher than those in the reactions with different typical PTC catalysts [12–15].

In line with their complexation values, Tr-polypodands **1–8** are found to be excellent catalysts in a number of anion-promoted reactions ((**1**)–(**4**)) in solid–liquid two-phase systems. Their catalytic activity reflects their complexing ability, increasing in the same order. But in the case of Tr-polypodand (with B as central atom) for reduction of benzaldehyde to the corresponding benzylic alcohol with NaBH₄ in SL-PTC process (reaction (**2**), Table 3), where this ligand has been found the best catalyst than all other catalysts tested in the studies, we have not observed this described above dependence. The complexation extent of ligand **3** and NaI is 4.0 salt's moles per ligand's mole (Table 1) and it was not the best result.

The results provide strong evidence of Tr-polypodands **2–8** being powerful complexing agents of alkali metal salts in acetonitrile, toluene and in low polarity media such as chlorobenzene. The complex forming ability of this class of polypodands increases with the number of oxoethylene units. As shown in Table 1, the highest complexation values are obtained for polypodands **7** and **8** having the highest number of binding sites (six polyoxoethylene chains, each of them with 10 oxygen atoms). The catalytic effect also strongly depends on the topology and the type of the central atom (B, P or Si).

In summary, we have shown that a new class of Triton X-polypodands, combining easy availability and good stability with excellent complexing properties and high catalytic activity, make a valid alternative to more sophisticated crown ethers as catalysts in solid–liquid phase-transfer reactions, particularly in large scale processes. Tr-podands **2–8** behave as efficient phase-transfer (PT) agents under SL-PTC conditions and they are more stable and insensitive to water, with their catalytic activity being generally superior to those of Si-podands.

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