Tetrahedron Vol 47, No 35, pp 7477-7488, 1991
Printed in Great Britain

0040-4020/91 $3 00+00

CATALYTIC ACTIVITY OF CYCLOPHOSPHAZENIC POLYPODANDS IN PHASE-TRANSFER REACTIONS. COMPARISON WITH OPEN-CHAIN ANALOGUES.

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(*Received in UK* 14 *May* 1991)

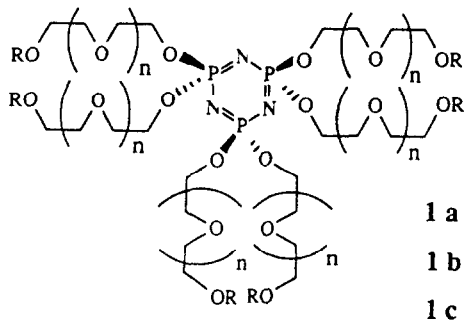
Abstract. The catalytic activity of cyclophosphazenic polypodands **1a-c** was evaluated in typical reactions performed under solid-liquid (SL) and liquid-liquid (LL) phase-transfer catalysis (PTC) conditions Such activity is largely determined by the complexation extent of **1a-c**, which is, in turn, related to the number of binding sites of the ligand (**1a** < **1b** ≤ **1c**) and to the nature of the inorganic salt M^+Y^- ($Na^+ > K^+ \gg Rb^+$ and $SCN^- \sim I^- > Br^-$) Also the presence of water was found to play an important role Comparison with open-chain analogues PEG **2** and TRIDENT **3** showed that polypodands **1a-c**, due to their excellent stability, simplicity of preparation and high complexing ability, can be considered promising phase transfer catalysts, especially under SL-PTC conditions

Polypodands, acyclic ligands in which several polyether chains are linked to the same binding centre, are efficient complexing agents of alkali and alkaline-earth metal salts.[2] In these systems the larger number of donor atoms combined with a suitable conformation permits greater complexation extents than with the corresponding simple podands [2] The cyclophosphazenic polypodands **1a-c**, recently synthesized by some of us,[3] are of particular interest in this line In fact these ligands, due to their particular topology, are powerful metal cation complexing agents even in low polarity media, and this makes them particularly attractive as phase-transfer catalysts

Preliminary data[4] showed that the complexation extent increases in the order **1a** < **1b** ≤ **1c** and is largely determined by both the size of the cation and the nature of the counter anion, in agreement with these results we found that the polypodands **1a-c** are very efficient catalysts in anion promoted reactions (e g nucleophilic substitution, alkylation, reduction, oxidation reactions) under phase-transfer catalysis (PTC) conditions [4]

Their catalytic activity is evaluated here together with the complexing ability in typical reactions performed under solid-liquid (SL-PTC) and liquid-liquid PTC (LL-PTC)

conditions The results are compared with those obtained by using other open-chain ligands **i.e.** the simple podand (PEG) (**2**) and the tris(polyoxaalkyl)amine "TRIDENT" (**3**), this latter generally being considered the catalyst of choice in SL-PTC reactions.[5]

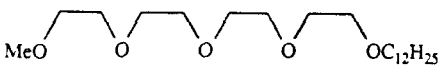


1a n = 2, R = - C_4H_9

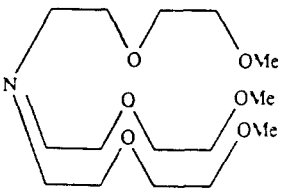
1b n = 3, R = - $C_{12}H_{25}$

1c n = 4, R = - C_6H_4-C_8H_{17} - *p*

1a-c



(**2**)



(**3**)

Results.

Complexation extent of 1a-c, 2, and 3, under SL-PTC conditions.

The complex-forming capability of **1a-c**, PEG **2** and TRIDENT **3** was evaluated for a number of alkali metal salts M^+Y^- (M^+ = Na^+, K^+, Rb^+, Y^- = I^-, Br^-, Cl^-, SCN^-) by stirring a chlorobenzene solution of the ligand with 100 molar equivalents of inorganic salt as the solid phase (Table I)

As shown in Table I the complexation extent, defined as complexed MY moles per mole of ligand, increases in the order **2<3~1a<1b~1c** for all the salts examined The ligand being the same the complexing ability decreases by increasing the size of the cation (Na^+> K^+>Rb^+). The highest values correspond to NaI and NaSCN with polypodands **1b** and **1c** and, for both ligands,an unusual stoichiometry of 4 and 5 moles of inorganic salt per mole of ligand was found [6] The complexation extent also depends on the nature of the counter anion in fact, it decreases, from 5 4-5 6 to 0 12, on changing from SCN^- to Cl^-

Catalytic activity of 1a-c, 2 and 3 in SL-PTC reactions.

All reactions were carried out in a chlorobenzene-solid salt two-phase system by

using 0 05 molar equivalents of ligand and a 5 1 molar ratio inorganic salt/substrate The reaction progress (up to 95-98% of conversion) was monitored by GLC analysis of the organic phase with respect to an internal standard

a) Nucleophilic substitution reactions

Catalytic activity of **1a-c**, **2** and **3** was measured in typical nucleophilic substitution reactions 1 (Tables II and III).

$$n\text{-}C_8H_{17}X + M^+Y^-_{solid} \xrightarrow[C_6H_5Cl,\ 60°C]{\mathbf{1a\text{-}c,2,3}_{(\ cat\ )}} n\text{-}C_8H_{17}Y + M^+Y^-_{solid} \qquad (1)$$

X = $MeSO_3$, Br
M^+ = Na^+, K^+, Rb^+
Y^- = I^-, Br^-, SCN^-

The catalytic efficiency of these ligands (Tables II and III) is most likely related to their complexing ability under the same conditions (Table I). Indeed the reaction times increase, in the order $Na^+ < K^+ \ll Rb^+$, according to the decreasing complexation extent. Also in the case of $NaSCN^-$ (Table II) the different catalytic activity found in the sequence **3** $\lesssim$ **1a** $<$ **1b** $\sim$ **1c** is in agreement with the increasing complex-forming capability of these ligands (Table I)

b) Reduction reactions

Reduction of 2-octanone to the corresponding 2-octanol was performed in a chlorobenzene-solid $NaBH_4$ two-phase system by using the same ligands **1a-c**, **2** and **3** as catalysts (reaction 2)

$$\underline{n}\text{-}C_6H_{13}COCH_3 \xrightarrow[C_6H_5Cl,\ 60°C]{NaBH_4,\ \mathbf{1a\text{-}c,2,3}_{(cat\ )}} \underline{n}\text{-}C_6H_{13}CHOHCH_3 \qquad (2)$$

Also in this case (Table IV) the catalytic activity of the polypodands **1a-c** is very noticeably higher than that of the open-chain ligands PEG **2** and "TRIDENT" **3**, as can be seen from their reaction times (3-8 h for **1a-c**, 22 and 38 h for **2** and **3**)

c) Other SL- and LL-PTC reactions

The alkylation reaction of phenol by 1-bromooctane was performed at 110°C in a toluene-solid K_2CO_3 two-phase system in the presence of catalytic amounts of **1a-c** and **3** (reaction 3)

$$C_6H_5OH + \underline{n}\text{-}C_8H_{17}Br \xrightarrow[\text{toluene, 110°C}]{K_2CO_3,\ \mathbf{1a\text{-}c},\ \mathbf{3}\ (cat.)} C_6H_5OC_8H_{17}\text{-}\underline{n} + KBr \qquad (3)$$

As shown in Table V, **1a-c** are better catalysts than "TRIDENT" **3**, in fact even in the presence of the least effective of the three polypodands, **1a**, reaction 3 reaches the same conversion as that with **3** but in about half time (4 and 7 h for **1a** and **3** respectively) (Table V)

The alkylation of benzyl methyl ketone with n-butylbromide was carried out in the chlorobenzene-50% aqueous NaOH two-phase system in the presence of catalytic amounts of ligands **1b**, **1c** or **3** at 20°C (reaction 4). The catalytic activity of **1b,c** is higher than that of TRIDENT **3** (Table IV).

$$C_6H_5CH_2COCH_3 + \underline{n}\text{-}C_4H_9Br \xrightarrow[C_6H_5Cl\text{-}50\%aq.\ NaOH,20°C]{\mathbf{1b},\ \mathbf{1c},\ \mathbf{3}\ (cat.)} C_6H_5CH(C_4H_9)COCH_3 + NaBr \qquad (4)$$

By using catalytic amounts of **1b** and **1c**, 1-octene in benzene solution was oxidized to heptanoic acid in the presence of a saturated aqueous solution of $KMnO_4$ at room temperature (40 min, $\geq$95%) (reaction 5)

$$\underline{n}\text{-}C_6H_{13}CH{=}CH_2 \xrightarrow[C_6H_6,\ r\ t]{KMnO_4 aq.,\ \mathbf{1b,c}\ (cat.)} \underline{n}\text{-}C_6H_{13}COOK + HCO_2K + MnO_2 \qquad (5)$$

Wet SL-PTC reactions.

Catalytic activity of **1b** and **1c** (reaction 1) and their complexation extent were determined under wet SL-PTC conditions by adding increasing quantities of water to the two-phase system chlorobenzene-solid NaY, for Y= I, Br In the case of **1c** and NaI the addition of water, up to 6 moles per mole of salt, progressively reduces the extent of complexation of the ligand, from 3.6 to 2.3, and consequently reduces its catalytic activity in fact the reaction time increases from 0 3 to 2 5 h On the other hand under LL-PTC conditions, in a chlorobenzene-aqueous NaY system, the complexation extent of **1c** further diminishes (up to 0.72) as does the catalytic activity (98% conversion in 6 h) The same results were obtained by using NaBr, also in the case of **1b**

Stability of polypodands.

Polypodands **1b** and **1c** were found to be stable in the presence of concentrated bases a benzene solution of the ligand, stirred with a 50% aqueous NaOH solution or over solid NaOH at 60°C, was recovered unchanged, as shown by TLC and NMR (^{1}H and ^{31}P) analyses, after more than three days. The same results were obtained when ligands **1b** and **1c** were heated at 110°C or refluxed in chlorobenzene (130°C) for 2 days. Only partial decomposition was observed on heating these ligands neat or in o-dichlorobenzene solution at 160-170°C for 2 days.

Kinetic measurements of nucleophilic substitution reactions under SL-PTC conditions.

Rate of displacement of the methanesulphonic group in n-octylmethanesulphonate by NaI (reaction 1) was measured at 60°C in a SL NaI-chlorobenzene two-phase system, in the presence of the same catalytic amount of **1b**, **1c**, **2** or **3** (0.1 mol equiv) and with a 5 1 molar ratio inorganic salt/substrate by stirring the heterogeneous mixture at 1100±100 rpm Kinetics were performed by following (GLC analysis) the disappearance of the n-octyl methanesulphonate and/or the appearance of the n-octyliodide with respect to tetradecane as an internal standard They were found to obey, in all cases, a kinetic equation of pseudo-first order (6), up to at least 70% conversion

$$\text{rate} = k_{obsd}[\text{substrate}] \qquad (6)$$

The observed rate constants (k_{obsd}) are reported in Table VI

Discussion.

Cyclophosphazenic polypodands **1a-c** are found to behave as efficient solid-liquid and liquid-liquid PTC catalysts in the series of reactions examined (Tables II-V) The catalytic activity exhibited reflects these polypodands complex-forming ability under the same reaction conditions Such activity increases with the number of donor atoms in the order **1a** < **1b** ≲ **1c** and, the ligand being the same, by decreasing the size of the cation ($Rb^{+} \ll K^{+} < Na^{+}$) (Table I) The nature of the anion and the presence of water have also been demonstrated to greatly influence the complexation power of these ligands and hence their catalytic ability On using I^{-} instead of Br^{-}, the complexation extent of **1b** with sodium halides NaI and NaBr decreases, from 3 9 to 0.17 (Table I), and thus the conversion time of reaction 1 increases from 0.75 to 32 h (Table III)

The presence of small amounts of water, previously found to be beneficial for many SL-PTC reactions,[7] slightly reduces the catalytic efficiency of **1a-c** Such effect[8],

mainly due to the lower complexation extent, is even more pronounced under LL-PTC conditions In spite of their diminished complexing ability, nowever, these lipophilic ligands, unlike "TRIDENT" **3**,[5] can be successfully used as PTC catalysts also under these conditions. Owing to their higher complexing power, cyclophosphazenic polypodands **1a-c** are better phase-transfer catalysts than the open-chain analogues **2** and **3** (Tables I-VI). Comparison of the catalytic efficiency (reaction 1 with NaI) shows that, under the same conditions, the reaction rates (k_{rel} in Table VI) with **1b** and **1c** are twice that with "TRIDENT" **3** and more than thirteen fold higher than that of the simple podand **2** (Table VI).[14] These results clearly evidence the involvement of a "synergic effect" of the six pendant arms of the polypodand in the complexation process.

Their chemical and physical stability, ease of preparation and high complexing ability make polypodands **1a-c** particularly promising SL- and LL-phase transfer catalysts. This new class of open-chain ligands can be considered a valid alternative to the use of the more expensive cyclic analogues, crown ethers

Table I. Complexation extent[a,b] of polypodands **1a-c**, PEG **2** and TRIDENT **3** under SL-PTC conditions, at 60°C

	Ligand				
MY	**1a**	**1b**	**1c**	**2**	**3**
NaI	0 70	3 9	4 2	0 16	0 95
NaBr	-	0 17	0 18	-	-
NaCl	-	0.12	0 12	-	-
NaSC N	1 7	5.4	5 6	0 32	1 0
KI	0 06	0 82	0.97	0 02	0 09
RbI	0 03	0.47	0 58	-	0 03

[a]Defined as complexed MY moles/ligand mole [b]Average of at least four determinations The error in these values is estimated to be 10%. [c]A chlorobenzene solution (25 mL) of ligand (0 5-4x10^{-2}M) and 100 molar equivalents of inorganic salt MY, as solid phase

Table II. Catalytic activity of polypodands **1a-c**, PEG **2** and TRIDENT **3** in the reaction 1, where X= Br, Y^-= I^-, SCN^-, M^+= Na^+, K^+, Rb^+, under SL-PTC conditions, at 60°C [a]

	Reaction time[b] (h)				
MY	**1a**	**1b**	**1c**	**2**	**3**
NaI	12	6	5	10	6
KI	12	7	7	20	12
RbI	28	12	12	-	48
NaSCN	2.3[c]	1.3[c]	1.3[c]	-	2.5[c]

[a]A chlorobenzene solution (5 mL) of 1-bromooctane (5 mmol), catalyst (0.25 mmol) and internal standard (2.5 mmol), with 25 mmol of MY as solid phase. [b]Conversions ≥95%, by GLC analysis [c]Reaction time at 100°C for conversions ≥95%, by GLC analysis.

Table III. Catalytic activity of polypodands **1a-c**, PEG **2** and TRIDENT **3** in the reaction 1 where X= OSO_2Me, Y^-= I^-, Br^-, M^+= Na^+, K^+, Rb^+ under SL-PTC conditions, at 60°C [a]

	Reaction time[b] (h)				
MY	**1a**	**1b**	**1c**	**2**	**3**
NaI	1.5	0.75	0.5	12	2.3
NaBr	-	32	32	-	-
KI	4	2	2	18	7
RbI	12	3	2.5	-	22

[a]Same amounts of substrate, catalyst and inorganic salt as reported in Table II, footnote a [b]Conversions ≥95%, by GLC analysis.

Table IV. Catalytic activity of polypodands **1a-c**, PEG **2** and TRIDENT **3** under SL-(reduction reaction 2)[a] and LL-(alkylation reaction 4)[b]-PTC conditions

Catalyst	Reaction time[c] (h)	
	Reduction reaction (2)	Alkylation reaction (4)
1a	8	-
1b	4	4 5
1c	3	5
2	22	-
3	38	8

[a]Same amounts of substrate and catalyst as in Table II, footnote a, but 2 1 $NaBH_4$/substrate molar ratio. [b]A chlorobenzene solution (1 mL) of benzyl methyl ketone (1 mmol), n-butyl bromide (1 5 mmol), catalyst (0.05 mmol) and 50% aqueous NaOH (1 mL), at 20°C [c]Conversions $\geqslant$ 98%, by GLC analysis

Table V. Catalytic activity of polypodands **1a-c**, and TRIDENT **3** in the alkylation reaction 3 under solid-liquid PTC conditions, at 110°C [a]

Catalyst	Reaction time (h)	Conversion[b] (%)
1a	4	72
1b	4	78
1c	4	89
3	7[c]	73

[a]A toluene solution (1 mL) of 1-bromooctane (1 mmol), phenol (1 mmol), catalyst (0 04 mmol) and solid K_2CO_3 (0 5 mmol). [b]By GLC analysis Not isolated product [c]Ref 5.

Table VI. Comparison of catalytic efficiency of **1b**, **1c**, PEG **2** and TRIDENT **3** in the nucleophilic substitution reaction 1 (X= OSO_2Me, MY= NaI), at 60°C [a]

Catalyst	$10^5 xk_{obsd}$ [b] (s^{-1})	k_{rel}
1b	86	13 4
1c	85	13.3
PEG **2**	6.4	1
TRIDENT **3**	38	5 9

[a] A chlorobenzene solution (10 mL) of substrate (0.2 M), catalyst (0.02 M) and internal standard (0 1 M) with 20 mmol of NaI. [b] Average of at least two determinations. The error in these values is estimated to be 5%

Experimental Section.

General Methods. Potentiometric titrations were carried out with a Metrohm 670 Titroprocessor by using silver and calomel electrodes, the latter isolated with a potassium sulphate bridge ^1H NMR spectra were recorded at 200 or 300 MHz using TMS as external standard ^{31}P NMR spectra were performed at 200 or 300 MHz by using 85% H_3PO_4 as an external reference . GLC data were obtained with a Alltech RSL-150 column (10m x 0 35 mm, polydimethylsiloxane, 0 25 μm thickness) or Superox II column (10 m x 0 35 mm) polyethylene glycol, 0.25 μm thickness) TLC was performed on Merck silica gel 60F 254 precoated plates

Materials and Solvents. Inorganic salts were Analar grade commercial products used without further purification, n-Octylbromide, 1-octene, 2-octanone, benzyl methyl ketone were commercially available compounds used as purchased, n-Octyl methanesulphonate, bp 112-114°C (2 mm), n_D^{20} 1 4398, was prepared according to literature [lit [15] bp 110-114°C (2 mm), n_D^{20} 1 4392] Tris(3,6-dioxaheptyl)amine, "TRIDENT" (**3**), is a commercially available product Cyclophosphazenic polypodands **1a** and **1b** were prepared according to a previously reported procedure [3] Commercial benzene, chlorobenzene, o-dichlorobenzene and toluene were used without further purification.

Synthesis of the hexakis [(p-octyl)phenoxypentabis(etoxy)] cyclophosphazene (1c) Polypodand **1c** was prepared according to the general method used for **1a** and **1b** [3] Yield

37%, n_D^{20} 1 5054 (Found C= 64 16, H= 9 32 $C_{144}H_{246}N_3C_{36}P_3$ requires C= 64.32, H= 9.22%) ^{1}H NMR (C_6D_6) δ 0 65-1 8 (m, 102 H), 3 30-4 40 (m 120 H), 6 80-7.40 (m, 24H), ^{31}P NMR[16,17] (C_6D_6) δ 19 48 (s, $P(OR)_2$)

Synthesis of the tetraethylene glycol methyl dodecyl ether (2). To a THF solution (15 mL) of the preformed sodium salt of the commercially available tetraethylene glycol mono dodecyl ether (11 5 g, 40 mmol) a THF solution (10 mL) of MeI (5 7 g, 40 mmol) was added dropwise under stirring and heated at 60°C overnight The precipitate NaI was filtered off and washed with CH_2Cl_2 The combined organic phases were evaporated and the oil residue was purified by column chromatography (silica gel, eluant CH_2Cl_2) affording 14 3g (95%) of the tetraethylene glycol methyl dodecyl ether (**2**) (Found C= 66.73, H= 11 75 $C_{21}H_{44}O_5$ requires C= 66.98, H= 11 75%) ^{1}H NMR ($CDCl_3$) δ 0 63-1 77 (m, 23H), 3.03-4 00 (m, 21H).

Extent of complexation. The extent of complexation of polypodands **1a-c**, and ligands **2** and **3** under SL-PTC conditions was determined by stirring 25 mL of a standardized chlorobenzene solution of **1a-c**, **2** or **3** (0 5-4x10^{-2}M) with 100 molar equivalents of inorganic salt MY, as solid phase, in a flask thermostatted at 60°C The system was stirred for 1-2 h, then kept without stirring for an additional 10 min to allow good separation of the two phases Aliquots (4-5 mL) of the organic phase were centrifuged, samples (2-3 mL) were withdrawn and titrated with 0 01 N silver nitrate (potentiometric titration)

General procedure for the nucleophilic substitution reactions under SL- or LL-PTC conditions. Solid inorganic salt MY (25 mmol) was added to a chlorobenzene solution (5 mL) of substrate (5 mmol), catalyst (0 25 mmol) and an internal standard (2 5 mmol) The heterogeneous mixture was heated at the appropriate temperature (see Tables II and III) under vigorous magnetic stirring. The reaction progress was monitored by GLC analysis of the organic phase, with respect to an internal standard Tetradecane was used as the reference compound in all reactions except for the SCN^-, where dodecane was employed The reactions under LL-PTC conditions were carried out by heating, under stirring, an aqueous solution (5 mL) of MY (25 mmol) with a chlorobenzene solution (5 mL) of the same reagents (see above) In all cases the mass balance was $\geq$ 95%

In kinetic measurements under SL-PTC conditions a standardized chlorobenzene solution (2 mL) of methanesulphonate (1M) and tetradecane (0 5M) was added, in a flask thermostatted at 60$\pm$0 1°C, to a standardized solution (8 mL) of ligand (**1b, 1c, 2** or **3**) (0 025 M) which had previously been stirred over solid NaI (20 mmol) for 1h, to obtain the complex formation Timing and stirring were started Aliquots of the organic phase were withdrawn

after stopping the stirring, for 30-60 s, to allow adequate separation The aliquots were quenched by cooling and, after centrifugation and separation from any eventual solid precipitate they were analyzed by GLC (see General Methods) The rates were measured by following the disappearance and/or appearance of substrate and reaction product, respectively The pseudo-first order rate constants (k_{obsd}) were computer generated by plotting log[substrate] vs time and determining the slope of the straight lines.

Stability of polypodands 1b,c. A C_6D_6 solution (3 mL) of ligand **1b** (or **1c**) (0.1 mmol) was stirred with an aqueous NaOH 50% solution (2 mL) or ground solid NaOH (40 mmol) at 60°C for three days. TLC (eluant CH_2Cl_2 MeOH = 10 1), ^1H and ^{31}P NMR analyses of the organic phase were identical to those of authentic samples of **1b** and **1c**.

1b ^1H NMR (C_6D_6) δ 0 80-1 80 (m, 138 H), 3 30-4 40 (m, 108 H), ^{31}P NMR[16,17] (C_6D_6) δ 19 45 [s,$P(OR)_2$]

1c ^1H NMR (C_6D_6) δ 0.65-1.80 (m, 102 H), 3 30-4 40 (m, 120 H), 6.80-7.30 (m, 24 H), ^{31}P NMR[16,17] (C_6D_6) δ 19 48 [s,$P(OR)_2$]

A chlorobenzene solution (3 mL) of ligand **1b** (or **1c**) (0 1 mmol) was refluxed for 2 days and no changes were observed by TLC and ^1H, ^{31}P NMR analyses. Heating **1b** or **1c**, without solvent, at 110°C for 2 days gave the same results On the contrary the above analyses of these ligands indicated the presence of undefined tars together with the undecomposed product ($\geqslant$ 40%) when the ligands were heated for 2 days at 160-170°C, as such or in o-dichlorobenzene solutions

2-Octanol. A benzene solution (10 mL) of 2-octanone (1 28 g, 10 mmol), catalyst **1a, 1b, 1c** or **3** (0 5 mmol) and solid $NaBH_4$ (0 757 g, 20 mmol) was stirred at r t for 3-38 h. The organic layer was filtered off, washed with diluted aqueous HCl, dried and distilled to give 2-octanol (1 14 g, 88%), bp 188-190°C, n_D^{20} 1 4297 [lit[18], bp 195°C, n_D^{20} 1 4291], ^1H NMR ($CDCl_3$) δ 0 50-1 10 (m, 6H), 1 10-1 80 (m, 10H), 1.80-2 00 (s, 1H), 3 50-4 00 (m, 1H).

n-Heptanoic acid. A benzene solution (5 mL) of oct-1-ene (1 12 g, 10 mmol), catalyst **1b** or **1c** (0 5 mmol) was stirred at r t with a saturated aqueous solution (30 mL) of $KMnO_4$ (6 3 g, 40 mmol) for 1 h The excess of permanganate was reduced with Na_2SO_3, the precipitated MnO_2 was filtered through celite and the acidified solution was extracted with benzene The combined benzene layers were dried and evaporated and the residue distilled to afford n-heptanoic acid (1 05 g, 82%), bp 119-121°C, (10 mm), n_D^{20} 1 4234 [lit[19] bp 92-93°C (4 mm), n_D^{20} 1.4236], ^1H NMR ($CDCl_3$) δ 0 70-2 00 (m, 11H), 2.20-2 60 (t, 2H), 11 40-11 60 (s, 1H).

3-Phenyl-2-Heptanone. A chlorobenzene solution (10 mL) of benzyl methyl ketone (1 34 g, 10 mmol), 1-bromobutane (1 75 g, 15 mmol), catalyst **1b, 1c** or **3** (0 5 mmol) and 50%

aqueous NaOH (10 mL) was stirred at r.t. for 4 5-8 h Work-up of the reaction mixture afforded 3-phenyl-2-heptanone (1 84 g, 85%), bp 94-97°C, (2 mm), n_D^{25} 1 4993 [lit[20] bp= 92-94°C (1 8 mm), n_D^{25} 1.4997], ^{1}H NMR ($CDCl_3$) δ 0.75-1.80 (m, 9H), 1 95 (s, 3H), 3.25 (t, 1H) and 7 16 (s, 5H).

Acknowledgment. This work was supported in part by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica, MURST (Rome).

References and Notes.

1) a) Università di Milano, b) Università di Cagliari.
2) a) Vogtle, F., Weber, E Angew. Chem. Int. Ed. Engl. **1979**, 18, 753, and references therein, b) Weber, F., Vogtle, F. Top. Curr Chem. **1981**, 98, 1, c) Montanari, F ; Landini, D.; Rolla, F. Top Curr. Chem. **1982**, 101, 147, d) Gokel, G.W., Korzeniowski, S.H. Macrocyclic Polyether Syntheses in "Reactivity and Structure Concepts in Organic Chemistry", Springer-Verlag, Berlin (1982) vol. 13, chp. 7, e) Menger, F.M. Top. Curr. Chem. **1986**, 136, 1, f) Kron, T.E , Tsvetkov, E N. Russian Chemical Reviews **1990**, 59, 283, and references therein
3) a) Corda, L., Anchisi, C , Podda, G , Traldi, P., Gleria, M Heterocycles **1986**, 24, 2821, b) Podda G. Gazz. Chim. Ital. **1988**, 118, 397
4) Landini, D , Maia, A , Corda, L , Maccioni, A , Podda, G Tetrahedron Lett **1989**, 30, 5781
5) Soula, G J. Org. Chem **1985**, 50, 3717
6) Even$_4$ higher stoichiometries were found in complexes of polypodands **1b** and **1c** with LiI
7) a) Arrad, O ,Sasson, Y. J Am. Chem. Soc. **1988**, 110, 185, and references therein, b) Dehmlow, E.V., Raths H J. Chem Res (S), **1988**, 384, J. Cnem Res. (M), **1988**, 2901, and references therein, c) Albanese, D., Landini, D , Penso, M Synthesis **1990**, 333
8) As previously found under these conditions the concomitant reduction of reactivity, due to the hydration of the anion, must be taken into account[2e,9-13] Such an effect is more relevant for Br^- than for I^- or SCN^-
9) a) Starks, C M., Liotta, C L Phase-Transfer Catalysis Principles and Techniques, Academic New York, 1978, b) Dehmlow, E V., Dehmlow, S.S. Phase-Transfer Catalysis, 2nd Ed., Verlag-Chemie Weinheim, West Germany, 1983.
10) Landini, D , Maia, A., Montanari, F Isr J Chem **1985**, 26, 263, and references therein.
11) Landini, D.,Maia, A. Chim Ind (Milano) **1987**, 69, 94 and references therein.
12) Landini, D , Maia, A J. Chem Soc , Chem Commun **1984**, 1041.
13) Landini, D , Maia, A , Rampoldi, A J Org Chem **1989**, 54, 328
14) The different reactivity measured in these systems can be due in part to a different cation-anion interaction in the ion pair A more detailed kinetic study of the anion activation in nucleophilic aliphatic substitution reactions is in progress
15) Williams, H R., Mosher, H.S J Am Chem Soc. **1954**, 76, 2984
16) Alkubaisi, A.H , Parkes, H G , Shaw, R.A Heterocycles **1989**, 28, 347
17) Cheng, T.C , Mochel, V D , Adams, H E , Longo, T F Macromol **1980**, 13, 158
18) Dreisbach, R R., Martin, R A Ind Eng. Chem. **1949**, 41, 2876.
19) Paul, R , Tchelitcheff, S. Bull. Soc Chim France **1948**, 1199
20) Mislow, K , Hamermesh, H.H J Am Chem Soc. **1955**, 77, 1590.