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POLYPODE LIGANDS AS PHASE-TRANSFER CATALYSTS

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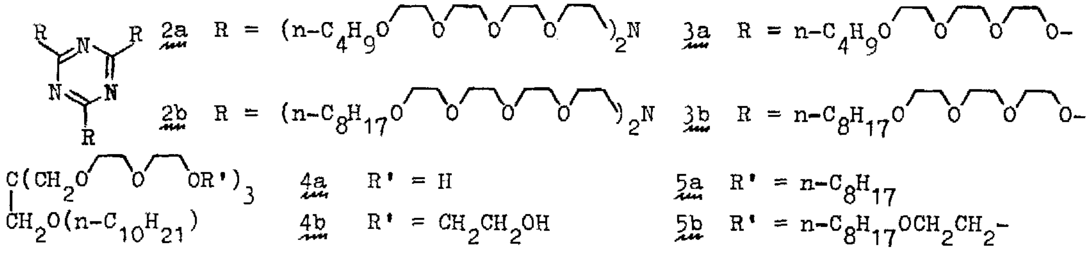
Several organic systems, such as onium salts,[1] crown ethers,[2] and aza-macrobicyclic polyethers,[3] are capable of activating anions, by transfering them from an aqueous or solid phase to an immiscible organic phase as a poorly solvated and associated ion pair. These therefore may be used as phase-transfer catalysts in anion promoted reactions. It has been shown[4] that "many armed" acyclic polyethers operate as polypode ligands with alkaline and alkaline-earth cations, extracting them from water as picrates soluble in an organic medium. In the case of the benzene hexakis(2-thia-5,8,11-trioxapentadecane) 1, the extractive effectiveness[4] is similar to that of aza-macrobicyclic polyethers [221] and [222] but, in contrast to the latter, 1 is a very poor catalyst, at least in solid-liquid phase-transfer reactions.[5]

We have found that other polypode ligands show good phase-transfer catalytic activity. The systems examined belong to classes 2a,b,3a,b, and 4a,b,5a,b,derived from 1,3,5-triazine and pentaerythritol, respectively. Compounds 2a,b were prepared by condensation of *sym*-trichlorotriazine with bis (3,6,9,12-tetraoxahexadecyl) and bis (3,6,9,12-tetraoxaeicosyl)amine[6] (benzene, Et_3N; 2h at 25°-45°, followed by 12h at 80°); and compounds 3a,b by condensation of trichlorotriazine with monobutyl and monooctyl triethyleneglycol[7] (toluene, t-BuOK; 2h at 25°-45°, followed by 12h at 110°). Compound 4a was obtained by condensation of mono-n-decylpentaerythritol with $ClCH_2COOH$, reduction with $LiAlH_4$ and subsequent repetition of the two reactions. Compound 4b was prepared from 4a by the same sequence of reactions. Alkylation of 4a and with n-octyl bromide afforded ethers **5a** and **5b**, respectively.[8]



Some examples of catalytic activity of compounds **2**-**5** in phase-transfer reactions are reported in the Table. In the triazine series the activity is maximum for compound **2b** with six polyoxyethylene branches, and diminishes when the terminal alkyl group is shortened (**2a**) or the number of branches is reduced to three (**3a**, **3b**). The efficiency of **2b** is similar to that of a typical phase-transfer catalyst, hexadecyl tributyl phosphonium bromide **6**, and close to that[3] of the alkyl-substituted aza-macrobicyclic polyethers, which probably represent the best type of catalyst.

In the case of **2b** the catalytic activity is high for all the reactions examined, but for other compounds it is noticeably dependent on the reaction. This fact is particularly true for the pentaerythritol derivatives: compounds **4** are fairly efficient in the nucleophilic substitution of bromide with I^- and PhS^- in 1-bromooctane and in the reduction of ketones to alcohols with BH_4^-, but they are completely inactive in the formation (and alkylation) of carbanions. Catalysts **5a**,**b** are ineffective not only in the formation of carbanions, but also in Br/I exchange, although they show some activity in the formation of thioethers and in the reduction of ketones. Compounds **2a**,**b** and **3a**,**b** are very good catalysts in the oxidation of alkenes with aqueous $KMnO_4$ (quantitative conversion of 1-octane to heptanoic acid in 30-60 min. at 25°).

Insertion of aliphatic chains provides a degree of organophilic character to compounds **2**-**5**. It is possible that in some cases (see **2a** and **2b**) associative apolar interactions among the terminal alkyl groups lead to a relatively stable cavity inside the polyoxymethylene chains and favour, therefore, the chelation of the metallic cation. A similar effect may be caused by intramolecular hydrogen bonds among the terminal OH in **4a** and **4b**. These effects should balance in part the unfavourable role that enthalphy and entropy factors (especially the latter) play in polypode systems,[9] in comparison with multidentate polycyclic ligands such as [222] cryptates.

Table

Substrate [a]	Reagent	Catalyst [f]	T/°C	Time/h	Yield% [g]	Product [h]
n-$C_8H_{17}Br$	KI [b]	**2a**	60	72	82	n-$C_8H_{17}I$
"	"	**2b**	60	3	85	"
"	"	**3a**	60	3	45	"
"	"	**3b**	60	3	42	"
"	"	**4a**	60	24 (72)	45 (86)	"
"	"	**4b**	60	24 (72)	51 (87)	"
"	"	**5a**	80	10	< 1	"
"	"	**5b**	80	10	< 1	"
"	"	**6**	60	3	72	"
"	KCN [b]	**2b**	80	5	48	n-$C_8H_{17}CN$
"	"	**6**	80	5	100	"
"	PhSNa [c]	**2b**	20	5	70	n-$C_8H_{17}SPh$
"	"	**3b**	20	5	44	"
"	"	**4b**	20	5	80	"
"	"	**5b**	20	5	30	"
"	"	**6**	20	0.15	100	"
$PhCH_2COMe$	n-C_4H_9Br [d]	**2b**	20	4	78	PhCH(n-C_4H_9)COMe
"	"	**3b**	20	4	50	"
"	"	**4b**	20	4	–	"
"	"	**5b**	20	4	–	"
"	"	**6**	20	4	65	"
n-$C_6H_{13}COMe$	$NaBH_4$ [e]	**2b**	20	3	97	PhCH(OH)Me
"	"	**3a**	20	3	25	"
"	"	**4b**	20	3	42	"
"	"	**5b**	20	3	18	"
"	"	**6**	20	3 (9)	35 (60)	"

[a] The reactions were carried out with a saturated aqueous solution of the reagent; no solvent was used for the substrate, except for benzene in the borohydride reduction. [b] 5 Mol. equiv. [c] 1 Mol. equiv. [d] 1.2 Mol. equiv. in 50% aq. NaOH. [e] 1.5 Mol. equiv. [f] 0.01 Mol. equiv. [g] By g.l.c. analysis. [h] The products were characterized by g.l.c. retention time and by comparison (i.r. and ^1H n.m.r. spectra) with authentic samples.

References and Notes

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[6] From N-tritylditosyldiethanolamine, triethyleneglycol monoalkyl ether and t-BuOK in DMSO for 48h at 100°, and successive detritylation with HCl-H_2O-MeOH for 30 min. at r.t.

[7] From triethyleneglycol monotetrahydropyranyl ether, n-alkyl bromide and t-BuOK in anhydrous THF for 12h at reflux, and successive depyranylation with HCl-H_2O-MeOH for 30 min. at r.t.

[8] Compounds **2-5** are viscous oils, purified by column chromatography. Elemental analyses, i.r. and ^{1}H n.m.r. data are in agreement with the assigned structures.

[9] J.M. Lehn, *Structure and Bonding*, Vol. 16, Springer-Verlag, Berlin, 1973, p. 1.