CHEMISTRY LETTERS, pp. 1293-1296, 1981.

TETRAKIS-SULFOXIDES AS PHASE TRANSFER CATALYSTS

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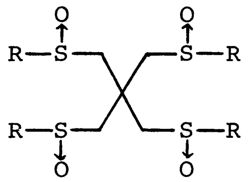
Tetrakis(alkyl-sulfinylmethyl)methanes serve as highly efficient phase transfer catalysts in S_N2 type displacement reactions of n-octyl bromide with a few nucleophiles.

Phase transfer properties of onium salts, crown ethers and cryptands have found a wide application in modern organic syntheses.$^{1)}$ However, only a few neutral open-chain compounds have been utilized as phase transfer catalysts. Instead of using expensive and toxic crown ethers, many armed neutral ligands-polypodants (octopus molecules) and open-chain polyethers have recently been advocated as excellent catalysts. The first compound described was hexakis(3,6,9-trioxatridecanethiomethyl)benzene which bears several donor-containing "tentacles" attached to a benzene ring by sulfide linkages.$^{2)}$ The compound exhibits a markedly strong coordination with alkali-metals. Similarly, 2,4,6-bis(3,6,9,12-tetraoxaeicocyl)amino-1,3,5-triazine, another polypode ligand has been shown to be a good phase transfer catalyst in nucleophilic substitutions, and borohydride reduction.$^{3)}$ Meanwhile, pentaerythritol derivatives having three polyoxyethylene are also known as effective phase transfer catalysts and their efficiency is also known to vary with the kind of reaction being catalyzed.$^{3)}$ Whereas α-phosphoryl sulfoxides have also been used as phase transfer catalysts in the alkylation of phenylacetone with alkyl halides and aqueous sodium hydroxide, they are considered to be inefficient catalysts for simple displacement reactions.$^{4)}$

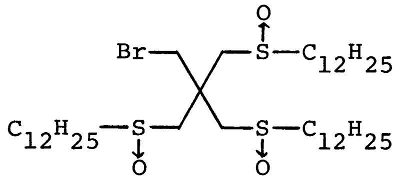
We now have found that tetrakis(alkyl-sulfinylmethyl)methanes, octopus molecules of a new type, are good phase transfer catalysts in S_N2 type nucleophilic substitution of organic halides. These phase transfer catalysts were prepared in the following manner. Tetrakis(alkyl- or phenylthiomethyl)methanes were prepared nearly quantitatively by treatment of several sodium thiolates with tetrakis(bromomethyl)methane obtained in the reaction of pentaerythritol with phosphorous tribromide. Then the sulfoxides (I̲a-e) and the sulfone (I̲I̲I̲) were obtained quantitatively by oxidation of the corresponding tetrakis(alkyl- or phenylthiomethyl)methanes with hydrogen peroxide in a mixture of acetic acid and benzene.$^{5)}$ 3,3-Bis(dodecylthiomethyl)thietane (I̲V̲)$^{6)}$ was allowed to react with dodecyl bromide in a good yield to give 3,3,3-tris(dodecylthiomethyl)-3-(bromomethyl)methane (V̲) which was then treated with H_2O_2 to afford I̲I̲ quantitatively.



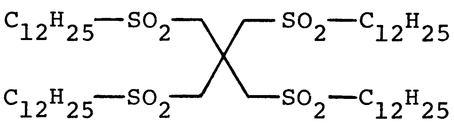
I

R = $-CH_3$(Ia), $-C_6H_{13}$(Ib), $-C_{12}H_{25}$(Ic),

$-C_{18}H_{37}$(Id), $-C_6H_5$(Ie)



II



III

The catalytic activity of compound Ib was tested with a few S_N2 type reactions of n-octyl bromide with various nucleophiles. All the reactions were carried out under solid-liquid biphase system. In a typical run, a mixture of n-octyl bromide (193 mg, 1 mmol), potassium thiophenoxide (148 mg, 1 mmol), xylene (1 ml), and Ib (60 mg, 0.1 mmol) was vigorously stirred at 20°C for 3 h, n-octyl phenyl sulfide was obtained in 95% yield. Meanwhile, the yield of n-octyl phenyl sulfide decreased in xylene-water solution (liquid-liquid phase). The results are shown in Table I. The reaction of n-octyl bromide with potassium thiophenoxide or thiocyanate in the presence of Ib in xylene solution, gave either the corresponding sulfide or thiocyanate, respectively, in nearly quantitative yield. Whereas, the reaction with either potassium cyanide or phenoxide was sluggish and afforded the corresponding product in a low yield. With no such catalyst, n-octyl bromide did not react at all with either potassium thiophenoxide or thiocyanate.

When a heterogeneous mixture of potassium thiocyanate, n-octyl bromide, xylene and the catalyst was heated at 100°C with vigorous stirring, n-octyl thiocyanate was obtained quantitatively, if the catalyst was either one of the three sulfoxides Ib, Ic, and Id. However, the sulfoxides Ia, and Ie were not effective in promoting the reaction, probably because alkyl chain in Ia i.e. methyl group is too short to be soluble in the reaction mixture while benzenesulfinyl group in Ie may not be as effective as long chain alkyl-sulfinyl group to chelate sufficiently the alkali metal cation due to the electron withdrowing phenyl groups. Whereas, unlike sulfoxides, the sulfone (III) did not serve as an effective catalyst. This weak catalytic activity of III is believed to be due to the weak affinity of the sulfonyl group to metal cation as compared to the sulfinyl function. These results are summarized in Table II. When compounds Ib, Ic, Id, II, and III, are used as catalysts, the order to catalytic activity of

Table I. Displacement of n-Octyl Bromide by Nucleophiles in the Presence of Ib.

Nu.	Cat.	n-Oct.Br/Nu/Cat.[a]	Xylene	Temp.(°C)	Time(h)	Yield(%)[b]	Product
KSCN	Ib	1/5/0.2	2 ml	100	35	90	n-$C_8H_{17}SCN$[8]
"	Ib	1/1/0.1	0.5 ml	100	5	100	"
"	Ib	1/1/0.1	---c	100	0.5	100	"
KCN	Ib	1/5/0.1	2 ml	100	40	5	n-$C_8H_{17}CN$
PhOK	Ib	1/5/0.2	2 ml	70	40	25	n-$C_8H_{17}OPh$
PhSK	Ib	1/1/0.1	1 ml	20	3	95	n-$C_8H_{17}SPh$[9]
"	Ib	4/4/0.04	1 ml	20	5	85	"
"	Ib	4/4/0.04	---c	20	4	95	"
"	Ib	4/4/0.04	---d	20	4	55	"

a) mmol. *b*) By g.l.c. analysis. *c*) no solvent. *d*) Added H_2O (0.5 ml), no solvent.

Table II. The Reaction of n-$C_8H_{17}Br$ with KSCN in the Presence of Various Catalysts.[a]

Catalyst	Time(h)	Yield(%)[b]
Ia	40	0
Ib	35	90
Ic	31	95
Id	28	91
Ie	40	0
II	40	76
III	40	20

a) n-$C_8H_{17}Br$ (1 mmol), KSCN (5 mmol), catalyst (0.2 mmol), xylene (2 ml), at 100°C. *b*) By g.l.c. analysis.

the compounds falls in the following, Ib, Ic, Id, > II > III. Namely the rates of nucleophilic substitutions greatly increase with Ib, Ic, and Id bearing tetrasulfinyl groups. These effects should be attributed to the cumulative chelation of the metal cation with the four sulfinyl groups.

Inspection of the results indicates that the simple tetrakis(sulfinylmethyl)methane can be used as a new type of phase transfer catalyst.

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7) See; H. Fujihara, K. Imaoka, N. Furukawa, and S. Oae, Heterocycles, in press.
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(Received June 29, 1981)