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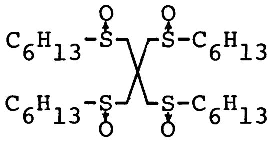
POLYSULFOXIDES AS NEW TYPE OF PHASE TRANSFER CATALYSTS IN TWO PHASE ALKYLATION

Naomichi FURUKAWA, Koji IMAOKA, Hisashi FUJIHARA, and Shigeru OAE*
Department of Chemistry, The University of Tsukuba, Sakura-mura,
Niihari-gun, Ibaraki 305

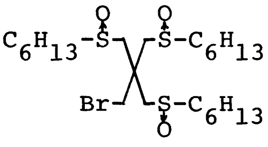
Tetrakis(hexylsulfinylmethyl)methane(I) and related compounds and polysulfoxides of crown thiaether(IV) were prepared and found to be used as effective catalysts in the binary phase alkylation of phenylacetonitrile(V) and phenylacetone(VI) with alkyl halides to afford selectively the corresponding monoalkylated products in high yields.

The phase transfer reaction is one of the most widely employed procedures for modern organic syntheses,1) and the catalysts used for these reactions are onium salts, crown ethers and cryptands.2) One interesting class of phase transfer catalysts is that of a few neutral open-chain compounds having polypode ligands, which are called as "octopus compounds".3) A few sulfoxides such as α-phosphoryl sulfoxides, have also been successfully used as effective phase transfer catalysts in the alkylation of phenylacetone4) with alkyl halides or in the Michael addition reaction.5) Howrver, these sulfoxides are usually incapable of promoting the ordinary displacement reaction. Recently, we have shown that tetrakis(alkylsulfinylmethyl)methane is a good phase transfer catalyst in the ordinary S_N2 type nucleophilic substitutions.6) Even such a simple sulfoxide as methyl 2-pyridyl sulfoxide markedly promotes the S_N2 type reaction.7) The catalytic activities of these sulfoxides can be attributed to the initial coordination of metal cation by the sulfinyl oxygen atom to result in the transfer of the nucleophile from aqueous phase to organic phase, since the displacement reactions of for example, 1-octyl bromide with nucleophiles either do not take place or are very sluggish in the presence of both sulfone and sulfide analogues. We now have prepared polysulfoxides of open chain molecules or crown thiaethers and tested their phase transfer catalytic activities. This paper describes that both tetrakis(hexylsulfinylmethyl)methane(I) and crown sulfoxide(IV) can be used as new types of phase transfer catalyst in the two-phase alkylation of phenylacetonitrile(V) and phenylacetone(VI) with alkyl halides in the presence of aqueous sodium hydroxide.

The sulfoxide(I) was prepared by treatment of tetrakis(hexylthiomethyl)-methane, obtained in the reaction of sodium hexane thiolate with tetrakis(bromomethyl)methane with hydrogen peroxide. Both the compounds (II) and (III) were also obtained by our previous method.8) The synthetic procedure of crown polysulfoxide (IV) used in the present investigation is shown in the following scheme which



I



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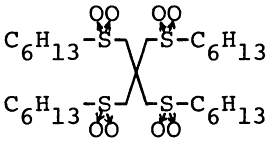

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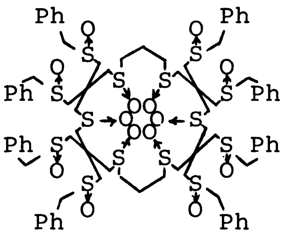
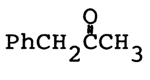


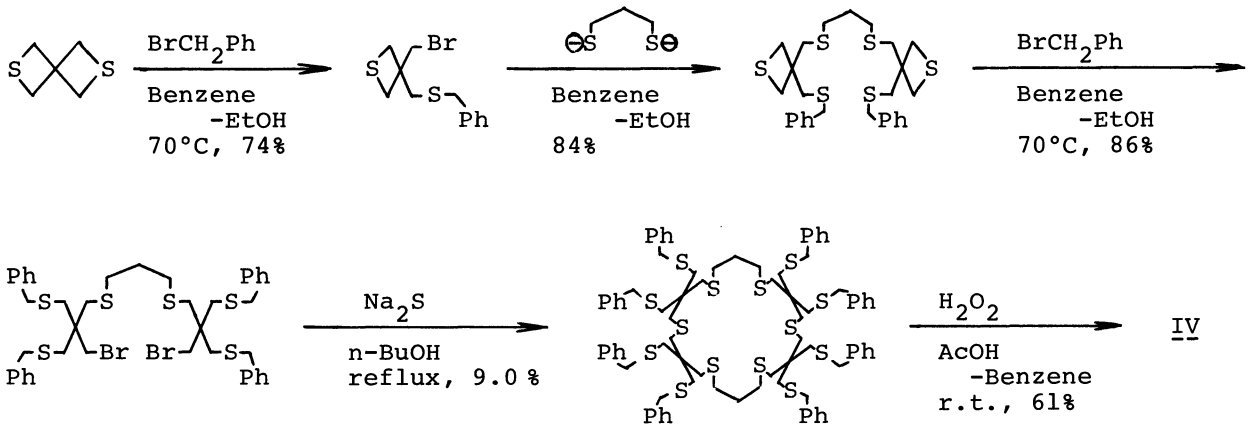
IV

PhCH$_2$CN V



$PhCH_2C(=O)CH_3$ VI

Scheme



VII

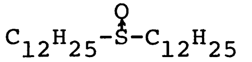
involves five steps, starting from 2,2'-dithiaspiro[3,3]hexane.

Oxidation of the sulfide (VII)[9] underwent smoothly under a normal procedure for oxidation of sulfides using 30% aqueous hydrogen peroxide in acetic acid. The oxidation did not proceed further to give the corresponding sulfone. The structure of sulfoxide(IV) was determined by ^{1}H-NMR (CDCl$_3$) : 2.20(m,4H -CH$_2$C$\underline{H}_2$CH$_2$-), 2.85(m,8H -C$\underline{H}_2$CH$_2$C$\underline{H}_2$-), 3.30(m,32H -C-C$\underline{H}_2$SO-), 3.95(s,16H -C$\underline{H}_2$-Ph), 7.20(s,40H -Ph), IR (KBr) : 1030cm^{-1} (S-O). The total yield of (IV) is 3.0%, M.p. 150-162°C. Elemental Analysis, Calculated for $C_{82}H_{100}O_{14}S_{14}$: C,56.04; H,5.69; S,25.51 : Found C,55.59; H,5.64; S,25.11,.[10]

In a typical run of the two-phase alkylation, a mixture of (VI)(2 mmol), methyl iodide (2.4 mmol) and catalyst(I) (0.02 mmol), was vigorously stirred with 50 % aqueous sodium hydroxide (liquid-liquid binary phase) at room temperature for 40-min, only mono-alkylated product was obtaind in 96% yield. Similarly, other compounds (V) and (VI) were successfully alkylated with alkyl halides as summarized in Table.

Table Two Phase Alkylation Reaction Catalyzed with (I)-(X)

Substrate	Halide	Catalyst (mol %)	Temp. (°C)	Time (h)	Products yield(%)[a] mono	di
(V)	CH_3I	none	r.t.	23	12	-
"	"	I (2.0)	"	20	87	3
"	"	I (2.0)	"	28	92	5
"	"	I (2.0)	"	24	58	4
"	C_2H_5Br	I (5.0)	"	17	91	1
"	C_2H_5I	"	"	13	92	-
"	i-C_3H_7Br	"	"	28	29	-
"	C_4H_9Br	"	"	28	84	-
(VI)	CH_3I	I (1.0)	"	0.65	96	-
"	C_2H_5I	IV (1.0)	"	0.9	92	-
"	"	I (1.0)	"	1.5	94	-
"	"	II (1.0)	"	2.0	91	-
"	"	III (1.0)	"	4.0	89	-
"	"	VIII[b] (1.0)	"	5.0	14	-
"	C_4H_9I	I (1.0)	"	4.0	92	-
"	C_4H_9Br	IX[c] (5.0)	80	1.5	93	-
"	"	X[d] (1.0)	20	4.0	65	-

a) By GLC analysis. b)

$C_{12}H_{25}-\overset{O}{S}-C_{12}H_{25}$ c) dicyclohexyl-18-crown-6[11)]
d) hexadecyltributylphosphonium bromide

Inspection of these results demonstrates the following characteristic features of the reaction. (1) The reaction of (V) with CH_3I proceeds without catalysts, resulting only in 12 % yield of the methylated product indicating that the sulfoxides are effective catalysts. (2) The reaction of (V) with methyl iodide in the presence of (I) gave monoalkylated product nearly exclusively. This result is in contrast to those of the reaction of (V) with methyl iodide using α-phosphoryl sulfoxides as catalysts in which a mixture of mono- and di-alkylated products are obtained in a 3:1 ratio.[4)] This selectivity for mono-alkylation would be quite important in the organic syntheses. (3) The catalytic activity of the sulfoxide(I) is far superior to those of the tri-sulfoxide(II) or sulfone(III). (4) All the sulfoxides used for these reactions are mixtures of diastereoisomeric sulfoxides as shown in the Table, and among these crown sulfoxide was the most effective catalyst. We believe that the sulfinyl groups in the crown ring and those of side chains function together jointly. Apparently, the fixed geometry of sulfinyl groups in (IV) is much more effective in trapping cations than that of the open chain analogs. Further detailed studies on the reaction between the structure of the sulfoxide and its catalytic activity is now underway in these laboratories.

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9) The structure of sulfide(VII) was determined by ^1H-NMR ($CDCl_3$) : 1.91(m,4H $-CH_2C\underline{H}_2CH_2-$), 2.59(m,40H $-C\underline{H}_2CH_2C\underline{H}_2-$ and $-\overset{|}{\underset{|}{C}}-C\underline{H}_2S-$), 3.70(s,16H $-C\underline{H}_2-Ph$), 7.22(s,40H -Ph). Elemental Analysis, Calculated for $C_{82}H_{100}S_{14}$: C,64.23; H,6.53, Found C,64.01; H,6.51,. The number-average moleculer weight ($\bar{M}n$) of the sulfide(VII) was determined by vapor pressure osmometry (VPO) CORONA-117 being 1507 ± 75 (calculated for $C_{82}H_{100}S_{14}$, M:1532), which can be distinguished clearly from other possible compounds e.g., monomer ; $C_{41}H_{50}S_7$ M:766, trimer ; $C_{123}H_{150}S_{21}$ M:2298,.
10) Sulfoxides used in this experiment are all mixtures of geometric isomers which were difficult to be separated. These polysulfoxides are generally highly soluble in water, therefore, in order to use for catalysts, such hydrophobic groups as hexyl or benzyl groups are necessary as tentaclus. The crown sulfoxides without tentaclus are also highly soluble in water. Therefore, we choose the sulfoxide (IV) which has eight rather hydrophobic benzyl sulfinyl groups.
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