Sulphoxide Substituted Pyridines as Phase-transfer Catalysts for Nucleophilic Displacements and Alkylations

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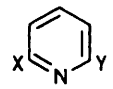
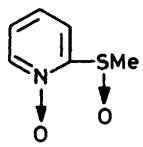
2-Methylsulphinyl-, 2-methylsulphinylmethyl-, 2,6-bis(methylsulphinyl)-, 2,6-bis(methylsulphinylmethyl)-pyridines, bis(2-pyridylmethyl) sulphoxide, and 2-methylsulphinylpyridine *N*-oxide have been prepared. These sulphoxides served as good phase-transfer catalysts which accelerate S_N2 type displacements of octyl bromide with various nucleophiles (thiolate, cyanide, thiocyanate, and phenoxide) in solid–liquid two-phase systems. Alkylations of phenylacetonitrile and benzyl methyl ketone with alkyl halides were also carried out in liquid–liquid two-phase systems in the presence of the above sulphoxides to afford the corresponding monoalkylated products in high yields. Pyridine derivatives bearing polysulphinyl groups were found to be even more effective catalysts for these two-phase alkylations. Neither 2-methylthio- nor 2-methylsulphonyl-pyridine catalysed S_N2 type displacement reactions effectively.

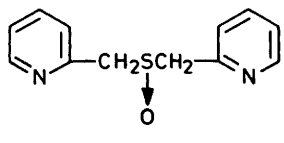
Phase-transfer catalysis (PTC) is an important synthetic technique,[1] and various catalysts such as onium salts (ammonium or phosphonium), crown ethers, and cryptands have been used for it. Neutral compounds such as tertiary amines[2] tertiary amine oxides,[3] and sulphoxides[4] have also been used as catalysts to promote alkylation and nucleophilic displacement reactions in the liquid–liquid or solid–liquid binary phase. Recently, we found that methyl 2-pyridyl sulphoxide (**1b**) is a good phase-transfer catalyst for S_N2 type reactions of various primary or secondary alkyl halides in a two-phase reaction system.[5] The activity of (**1b**) as a phase-transfer catalyst is considered to arise from the strong co-ordination of metal cations by both the pyridyl nitrogen and the sulphinyl oxygen atoms. Thus, the nucleophiles become highly nucleophilic 'naked anions'. Further, we have measured the pK_a values of several sulphoxide substituted pyridines to estimate their co-ordination ability.[6] The pK_a values of these sulphoxides have been found to be small (*ca.* 0 to *ca.* 3), suggesting that they should undergo only weak chelation with metal cations. However, when 2,6-bis(methylsulphinylmethyl)pyridine was used as a catalyst for ion-transfer experiments using alkali-metal picrates, the sulphoxide served as a mediator to transfer alkali-metal cations (Li^+, Na^+, and K^+) from the aqueous phase to organic phase.[7] In a search for better sulphoxide catalysts several others based on pyridine (**1**)—(**4**) together with their corresponding sulphides and sulphones have been synthesized and their catalytic activities examined both for simple displacements in a solid–liquid two-phase system and alkylations in a liquid–liquid two-phase system. This paper summarizes the results of these phase-transfer reactions.



(**1a**) X = H, Y = SMe
(**1b**) X = H, Y = S(O)Me
(**1c**) X = H, Y = $S(O)_2Me$
(**1d**) X = H, Y = $CH_2S(O)Me$
(**2a**) X = Y = S(O)Me
(**2b**) X = Y = $CH_2S(O)Me$
(**2c**) X = Y = $CH_2S(O)(CH_2)_3S(O)Me$
(**2d**) X = Y = $CH_2S(O)(CH_2)_3S(O)(CH_2)_3S(O)Me$



(**3**)



(**4**)

Scheme 1.

Results and Discussion

Pyridines carrying sulphide, sulphoxide, and sulphone groups were prepared by general methods,[8] and their catalytic activities tested (see Scheme 1).

Nucleophilic Substitution under PTC Conditions.—In order to test these sulphoxides as catalysts for nucleophilic substitution, octyl bromide was treated with various nucleophiles in xylene in the presence of the sulphoxides (**1**)—(**4**). Since a catalytic quantity of these sulphoxides (*e.g.* < 1.0 mol equiv.) gave only a low rate of reaction typically a 4.0 mol equiv. of sulphoxide was used, unless otherwise specified. In the absence of a catalyst, there was no reaction. The results are summarized in Tables 1—3.

Inspection of the data shown in Tables 1—3 reveals the following features characteristic of the reactions. The rate of displacement and the yield of product for the reaction of octyl bromide with potassium thiophenolate depends both on the nature of the catalyst and the amount used. From Table 1, (**1b**) is shown to be the most effective catalyst, the reaction finishing within 2 min at room temperature and affording octyl phenyl sulphide in quantitative yield.

The catalytic activity of (**1b**) is considered to arise from the strong co-ordination of the metal cation with both the sulphinyl oxygen and pyridine nitrogen. Thus, the 'naked anion' is sufficiently liberated in the organic phase to become a strong nucleophile. There is a possibility that the pyridyl nitrogen initially attacks the octyl bromide to form octyl-pyridinium salts which then undergo nucleophilic reaction, *i.e.* a Menshutkin-type reaction. This possibility is ruled out however by the results shown in Table 1, since the sulphide (**1a**) has a higher

Table 1. Solid–liquid two-phase reactions at room temperature catalysed by compounds (**1a**—**c**) and (**3**)

$$C_8H_{17}Br + PhSK \xrightarrow[Xylene]{Catalyst} C_8H_{17}SPh + KBr$$

Catalyst[a]	Time (min)	Yield (%)[b]
(**1a**)	1 440	8
(**1b**)	2	98
(**1c**)	360	65
(**3**)	30	85

[a] 4.0 Mol equiv. [b] By g.l.c. analysis.

Table 2. Solid–liquid two-phase reactions catalysed by methyl 2-pyridyl sulphoxide (**1b**)

$$C_8H_{17}Br + PhSK \xrightarrow[xylene]{(1b)} C_8H_{17}SPh + KBr$$

(**1b**) (equiv.)	Temp. (°C)	Time (h)	Yield[a] (%)
2.0	R.t.	1.0	98
1.0	R.t.	17.0	82
0.5	50	0.5	65
0.1	50	2.0	39
0.0	50	24.0	0

[a] By g.l.c. analysis.

pK_a value (pK_a = 3.64); it should therefore be a stronger nucleophile, and hence would be more reactive than the sulphoxide (**1b**) (pK_a = 0.17). In order to clarify the mechanism for typical nucleophilic displacement under two-phase reaction conditions, optically active octan-2-yl bromide (optical purity 94.8%) with potassium thiophenolate was carried out in the presence of the sulphoxide (**1b**).[8] The stereochemical result (see Scheme 2) reveals that the reaction proceeds with more than

$$\overset{*}{\text{2-Oct-Br}} + PhSK \xrightarrow[PhMe,\ Room\ temp.]{(1b)\ (4\ equiv.)} \overset{*}{\text{2-Oct-SPh}} \xrightarrow{H_2O_2} \overset{*}{\text{2-Oct-SO}_2\text{Ph}}$$

(*S*)-(+)
$[\alpha]_D^{21} = +39.9°$
(*c* 6.0, EtOH)
(Optical purity 94.8%)

2-Oct-SPh: 95.7% yield

2-Oct-SO_2Ph: (56.3% yield)
(*R*)-(+)
$[\alpha]_D^{17} = +11.4°$
(*c* 5.3, MeOH)
(Optical purity 91.2%; optical yield 96.2%)

Scheme 2. The stereochemical course for the reaction

96% net inversion, thus indicating that the mechanism is a typical S_N2 type substitution; this rules out the involvement of a Menshutkin-type reaction. From Table 2 it is seen that even with as little as 0.1 mol equiv. of the sulphoxide (**1b**), the reaction proceeds, although it requires a prolonged period of heating.

Several other sulphoxides (**1**)—(**4**) were also found to be efficient catalysts for the reactions of octyl bromide with nucleophiles (see Table 3); none of these reactions proceeded in the absence of sulphoxides.

The main factor for the phase-transfer catalytic activity of these sulphoxides is undoubtedly the specific affinity of the sulphoxides for alkali-metal cations, the gegen cations of nucleophiles. In the reactions of octyl bromide with nucleophiles (PhSK, KSCN, PhOK), the sulphoxides (**1b**), (**1d**), and (**4**) were shown to be good catalysts. Likewise with NaCN

Table 3. Solid–liquid two-phase reactions catalysed by sulphoxides

$$C_8H_{17}Br + MNu \xrightarrow[Xylene]{Catalyst} C_8H_{17}Nu + MBr$$

MNu	Catalyst[a]	Temp. (°C)	Time (h)	Yield (%)[b]
NaCN	(**1b**)	100	54	13
NaCN	(**1d**)	100	46	87
NaCN	(**2c**)	100	32	0
NaCN	(**2b**)	100	32	84
NaCN	(**4**)	100	50	64
KSCN	(**1b**)	100	40	96
KSCN	(**1d**)	100	27	96
KSCN	(**2a**)	100	40	20
KSCN	(**2b**)	100	40	23
KSCN	(**4**)	100	17	75
PhSK	(**1d**)	R.t.	0.5	91
PhSK	(**2a**)	R.t.	12	93
PhSK	(**2b**)	R.t.	12	88
PhSK	(**4**)	R.t.	0.5	90
PhOK	(**1b**)	70	36	93
PhOK	(**1d**)	70	36	93
PhOK	(**2a**)	70	40	33
PhOK	(**2b**)	70	40	88
PhOK	(**4**)	70	14	93

[a] 4.0 Mol equiv. [b] By g.l.c. analysis. [c] Decomposition of the sulphoxide was observed.

Table 4. Liquid–liquid two phase alkylations catalysed by some sulphoxides (10 mol%) bound to pyridine

$$PhCH_2CN + R\text{–}X \xrightarrow[50\%\ aq.\ NaOH,\ r.t.]{Catalyst} \underset{R}{PhCHCN} + NaX$$

RX	Catalyst	Time (h)	Product yield (%)[a] Mono	Di
MeI	(**1b**)	24	73	5
MeI	(**1d**)	24	79	13
MeI	(**2b**)	24	70	5
MeI	(**4**)	24	83	15
EtI	(**1b**)	24	85	0
EtI	(**1d**)	24	93	0
EtI	(**2b**)	24	73	0
EtI	(**4**)	24	90	0
BuI	(**1b**)	24	54	0
BuI	(**1d**)	24	88	0
BuI	(**2b**)	24	70	0
BuI	(**4**)	24	89	0

[a] By g.l.c. analysis: mono = monoalkylated product, di = dialkylated product.

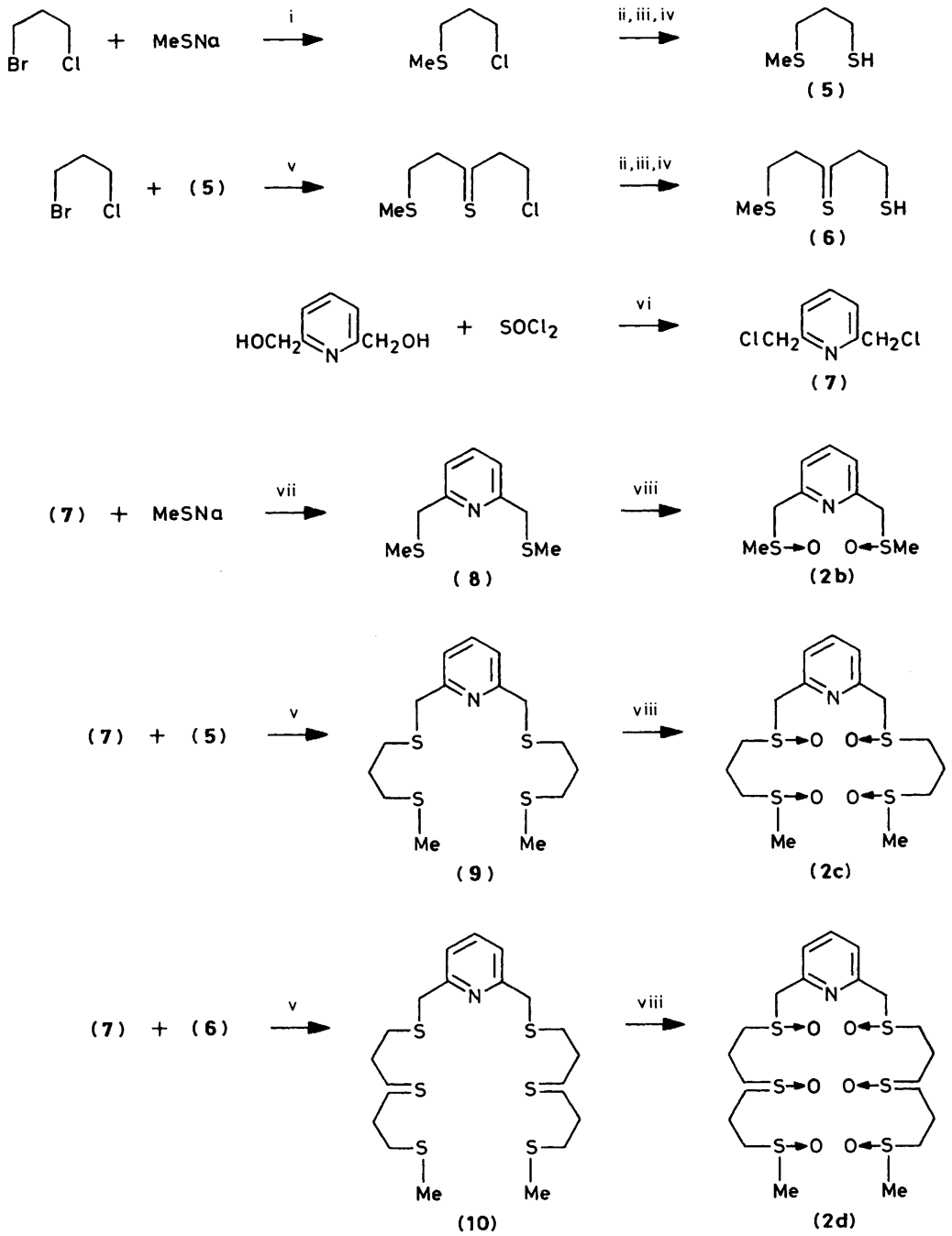
as a nucleophile, (**1d**) and (**2b**) were the most effective; generally, the sulphoxide (**2a**) was not a good catalyst. This seems to show that two sulphinyl groups attached directly to the 2,6-positions of the pyridine ring are too bulky for an alkali-metal cation to be inserted for chelation; this contrasts with the behaviour of other sulphoxides. Furthermore, the pK_a value of (**2a**) is too small to be measurable by the ordinary u.v. technique, thus demonstrating that the chelating ability of (**2a**) is remarkably diminished. A further interesting observation is that potassium phenoxide as the nucleophile gave, selectively, only the *O*-alkylated (no *C*-alkylated) product.[9]

Alkylation of Active Methylene Compounds under PTC Conditions.—Several sulphoxides have been reported to

catalyse two-phase alkylations.[4,5] In order to test our compounds as phase-transfer catalysts, under liquid–liquid two-phase conditions, compounds containing an active methylene group (*e.g.* $PhCH_2CN$ and $PhCH_2COMe$) and alkyl halides in 50% aqueous sodium hydroxide were allowed to react in the presence of the sulphoxide (**1b**), (**1d**), (**2b**), or (**4**). Inspection of the results obtained (see Tables 4 and 5) reveals the following features characteristic of the reactions. Although phenylacetonitrile reacts with methyl iodide in the absence of catalysts (12% yield after 24 h) the sulphoxides (**1b**), (**1d**), (**2b**), and (**4**) markedly improved the speed of the reaction and the yield of product. Further, several alkyl halides gave, selectively, only the monoalkylated products. In these reactions, the catalytic activities of (**1d**) and (**4**) are higher than those of (**1b**) and (**2b**).

Since it was expected that the chelating effect would be increased by increasing the number of sulphinyl groups (octopus effect),[10] pyridine derivatives having polysulphinyl groups at their 2,6-positions have been synthesized (see Scheme 3). Their catalytic activities have been tested by similar alkylation reactions to those described above and the results are summarized in Table 6.

As expected, the polysulphinyl-containing compounds have higher catalytic activities than (**1b**), (**1d**), (**2b**), and (**4**). The sulphoxide (**2c**), having four sulphinyl groups, accelerated the reaction, which was complete in 2 h at room temperature and afforded, selectively, the mono-ethylated product in quantitative yield. The sulphoxide (**2d**) having six sulphinyl groups, was the most effective catalyst, only 1.0 mol % affording selectively and quantitatively the monoethylated product in 4 h at room temperature.



Scheme 3. *Reagents:* i, EtOH; ii, $(NH_2)_2CS$–EtOH; iii, KOH–H_2O; iv, H_2SO_4; v, EtOH–EtONa; vi, Et_2O; vii, MeOH; viii, H_2O_2–AcOH

Table 5. Liquid–liquid two-phase alkylations catalysed by various sulphoxides (10 mol%)

$PhCH_2COCH_3 + RX \xrightarrow[50\%\ aq.\ NaOH,\ r.t.]{Catalyst} PhCH(R)COCH_3 + NaX$

RX	Catalyst[a]	Time (h)	Yield (%)[a]
MeI	(**1b**)	2	96
MeI	(**1d**)	2	96
MeI	(**2b**)	2	93
MeI	(**4**)	2	100
EtI	(**1b**)	3	83
EtI	(**1d**)	3	97
EtI	(**2b**)	3	75
EtI	(**4**)	3	95
BuI	(**1b**)	7	77
BuI	(**1d**)	7	89
BuI	(**2b**)	7	63
BuI	(**4**)	7	91

[a] By g.l.c. analysis.

Table 6. Comparison of the effect of the sulphinyl group number on two-phase alkylations

$PhCH_2COCH_3 + EtI \xrightarrow[50\%\ aq.\ NaOH,\ r.t.]{Catalyst\ (\mathbf{2c},\ \mathbf{d})} PhCH(R)COCH_3 + NaI$

Catalyst	(mol%)	Time (h)	Yield (%)[a]
(**2d**)	10.0	2.0	55
(**2c**)	5.0	2.0	92
(**2d**)	5.0	2.0	*ca.* 100
(**2d**)	1.0	4.0	92

[a] By g.l.c. analysis.

These sulphoxides described can be recovered very easily and quantitatively by shaking the reaction mother-liquor with any mineral acid; they are, therefore, useful catalysts of a new type.

Experimental

General.—All m.p.s taken on a Yanako micro melting point apparatus are uncorrected. I.r. spectra were obtained on JASCO A-3 spectrometer and the n.m.r. spectra were obtained on a Hitachi R-600 FT-NMR spectrometer or a JEOL JNH-MH-100 spectrometer in $CDCl_3$ or CCl_4 using $SiMe_4$ as an internal standard. All reactions were monitored by chromatography, namely, t.l.c. (Merck, Kieselgel 60-GF_{254}), g.l.p.c. (Hitachi 163, using a 5% silicon GE SE-30 on 60—80 mesh or 2% silicon OV-1 Chromosorb W on 80—100 mesh in column), LLC (JAI LC-09 or JASCO FAMILIC-100N). Mass spectra were taken with Hitachi RMU-6MG mass spectrometer. Elemental analyses were carried out by Chemical Analysis Center at this University.

Materials.—All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

Methyl 2-Pyridyl Sulphide (**1a**).—The sulphide (**1a**) was prepared from the pyridine-2-thiol with methyl iodide, according to the general method;[11] yield 74%, b.p. 60 °C/4 mmHg; $\nu_{max.}$(neat) 2 930, 1 580, 1 415, 1 125, and 755 cm^{-1}; $\delta(CDCl_3)$ 2.60 (3 H, s, CH_3), 6.84—7.62 (3 H, m, β,γ-pyrH), and 8.39—8.49 (1 H, m, α-pyrH).

Preparation of the Sulphoxides (**1b**), (**1d**), (**2a**), (**4**), *or the Sulphone* (**1c**).—The title compounds were prepared from the corresponding sulphides with *m*-chloroperbenzoic acid or hydrogen peroxide as oxidant, according to the general method.[12] (**1b**): yield 88%, b.p. 95—96 °C at 1.5 mmHg; $\nu_{max.}$(neat) 3 050, 1 570, 1 420, 1 055 (S→O), and 775 cm^{-1}; $\delta(CDCl_3)$ 2.83 (3 H, s, CH_3), 7.20—7.50 (1 H, m, γ-pyrH), 7.74—8.16 (2 H, m, β-pyrH), and 8.32—8.58 (1 H, m, α-pyrH).

(**1d**): yield 71%, b.p. 135 °C at 3 mmHg; $\nu_{max.}$(neat) 3 000, 1 585, 1 435, 1 045 (S→O), and 790 cm^{-1}; $\delta(CCl_4)$ 2.53 (3 H, s, CH_3), 4.15 (2 H, s, CH_2), 7.05—7.77 (2 H, m, β,γ-pyrH), and 8.46—8.57 (1 H, m, α-pyrH).

(**2a**): yield 70%, m.p. 109—114 °C; $\nu_{max.}$(KBr) 3 025, 1 565, 1 415, 1 050 (S→O), and 810 cm^{-1}; $\delta(CDCl_3)$ 2.93 (6 H, s, CH_3), and 8.10—8.23 (3 H, m, β-,γ-pyrH) (Found: C, 41.4; H, 4.4; N, 6.8. $C_7H_9NO_2S_2$ requires C, 41.4; H, 4.5; N, 6.9%).

(**3**): yield 67%, m.p. 122—123 °C; $\nu_{max.}$(KBr) 3 050, 1 430, 1 245, 1 035 (S→O), and 770 cm^{-1}; $\delta(CDCl_3)$ 3.10 (3 H, s, CH_3), 7.35—8.03 (3 H, m, β,γ-pyrH), and 8.19—8.35 (1 H, m, α-pyrH).

(**4**): yield 76%, m.p. 80—81 °C; $\nu_{max.}$(KBr) 2 990, 1 580, 1 470, 1 050 (S→O), and 750 cm^{-1}; $\delta(CDCl_3)$ 4.13 and 4.26 (2 H, J_{AB} 12 Hz, CH_2), 7.15—7.78 (6 H, m, β,γ-pyrH), and 8.59—8.69 (2 H, m, α-pyrH).

(**1c**): yield 93%, b.p. 136 °C (Kugelrohr); $\nu_{max.}$(neat) 2 940, 1 580, 1 430, 1 305 (SO_2), 1 165 (SO_2), 1 115, 960, and 765 cm^{-1}; $\delta(CDCl_3)$ 3.18 (3 H, s, CH_3), and 7.24—8.55 (4 H, m, α-,β,-γ-pyrH) (Found: C, 45.8; H, 4.5; N, 8.9. $C_6H_7NO_2S$ requires C, 45.8; H, 4.5; N, 8.9%).

4-*Thiapentane*-1-*thiol* (**5**).—A solution of 1-bromo-3-chloropropane (20 g, 0.127 mol) and sodium methanethiolate (*ca.* 15% in water, 71.2 g, 0.152 mol) in ethanol (300 ml) was stirred at room temperature for 4 h. Thiourea (11.6 g, 0.152 mol) was then added to the mixture and the whole heated for 24 h under reflux. After concentration of the solution, potassium hydroxide (50.4 g, 0.764 mol) in water (300 ml) was added to the residue. The mixture was refluxed for 5 h under N_2 atmosphere and then cooled in an ice–water bath; cooled aqueous sulphuric acid was then added dropwise until the mixture became acidic. After the addition of acid, the reaction mixture was extracted with chloroform (200 ml × 3) and the extract dried ($MgSO_4$). After removal of the solvent, the residue was distilled under reduced pressure to afford a colourless liquid; yield 9.8 g (60%), b.p. 64—65 °C at 6 mmHg, $\nu_{max.}$(neat) 2 900, 2 550 (SH), 1 430, 1 295, 1 255, 955, and 755 cm^{-1}; $\delta(CDCl_3)$ 1.41, (1 H, t, *J* 8 Hz, SH), 1.70—2.05 (2 H, m, CH_2C), 2.05 (3 H, s, CH_3), and 2.39—2.93 (4 H, m, CH_2S).

4,8-*Dithianonane*-1-*thiol* (**6**).—The title compound was synthesized by the same procedure as 4-thiapentane-1-thiol (**5**). 4,8-Dithianonane-1-thiol (**6**) was obtained by treating 1-bromo-3-chloropropane with the thiol (**5**), thiourea, KOH, and H_2SO_4, and was purified by silica-gel column chromatography using n-hexane–ethyl acetate (7:1) as eluant. A colourless liquid was obtained; yield 74%, $\nu_{max.}$(neat) 2 920, 2 550 (SH), 1 430, 1 295, 1 255, 960, and 685 cm^{-1}; $\delta(CDCl_3)$ 1.38 (1 H, t, *J* 8 Hz, SH), 1.65—2.02 (4 H, m, CH_2C), 2.06 (3H, s, CH_3) and 2.22—3.02 (8 H, m, CH_2S).

2,6-*Bis*(*chloromethyl*)*pyridine.*—A solution of 2,6-bis-(hydroxymethyl)pyridine (20 g, 0.144 mol) and thionyl chloride (37.6 g, 0.316 mol) in diethyl ether (200 ml) was stirred at room temperature for 6 h. The crude product was deposited and this was filtered off and dissolved in water. The solution was neutralized with dry NH_3 gas and extracted with methylene chloride (200 ml × 3). The organic layer was dried ($MgSO_4$), evaporated to dryness, and the residue recrystallized from n-hexane. White crystals were obtained (18.6 g, 73%), m.p.

75.0—75.5 °C, δ($CDCl_3$) 4.56 (4 H, s, CH_2) and 7.09—7.71 (3 H, m, β-,γ-pyrH).

2,6-*Bis*(*methylthiomethyl*)*pyridine* (**8**).—A solution of 2,6-bis(chloromethyl)pyridine (**7**) (14 g, 0.082 mol) and sodium methanethiolate (*ca.* 15% aqueous solution, 96.2 g, 0.206 mol) in methanol (500 ml) was stirred at room temperature for 12 h. After concentration of the solution, the residue was diluted with water and extracted with benzene (200 ml × 3). The organic layer was dried ($MgSO_4$) and concentrated and the resulting residue was purified by distillation under reduced pressure to give the colourless liquid (13.9 g, 81%), b.p. 125—126 °C at 1.5 mmHg; $\nu_{max.}$(neat) 2 920, 1 580, 1 430, 1 300, 1 160, 755, and 535 cm^{-1}; δ($CDCl_3$) 2.13 (6 H, s, CH_3), 3.83 (4 H, s, CH_2), and 7.14—7.82 (3 H, m, β-,γ-pyrH) (Found: C, 54.1; H, 6.6; N, 7.1. $C_9H_{13}NS_2$ requires C, 54.2; H, 6.6; N, 7.0%).

2,6-*Bis*(2,6-*dithiaheptyl*)*pyridine* (**9**).—A solution of 2,6-bis(chloromethyl)pyridine (**7**) (2 g, 0.011 mol), 4-thiapentane-1-thiol (**5**) (3.3 g, 0.027 mol), and sodium (0.78 g, 0.34 g-atom) in ethanol (50 ml) was stirred at room temperature for 4 h under N_2 atmosphere. The mixture was concentrated and water was added to the residue. The aqueous solution was extracted with dichloromethane (50 ml × 3) and the extract was dried ($MgSO_4$). After removal of the solvent the title compound was purified to afford a colourless liquid by silica-gel column chromatography with n-hexane–ethyl acetate (3:1) as eluant; yield 3.1 g (70%), $\nu_{max.}$(neat) 2 920, 1 590, 1 575, 1 455, 1 260, 815, and 750 cm^{-1}; δ($CDCl_3$) 1.66 (4 H, m, CH_2C), 2.03 (6 H, s, CH_3), 2.39—2.80 (8 H, m, CH_2S), 3.78 (4 H, s, CH_2pyr), and 7.12—7.80 (3 H, m, β-,γ-PyrH) (Found: C, 52.0; H, 7.3; N, 4.1. $C_{15}H_{25}NS_4$ requires C, 51.8; H, 7.2; N, 4.1%).

2,6-*Bis*(2,6,10-*trithiaundecyl*)*pyridine* (**10**).—A solution of 2,6-bis(chloromethyl)pyridine (**7**) (2 g, 0.011 mol), and 4,8-dithianonane-1-thiol (**6**) (5.4 g, 0.027 mol) and sodium (0.78 g, 0.034 g-atom) in ethanol (70 ml) was stirred at room temperature for 4 h under N_2 atmosphere. The mixture was concentrated and water was added to the residue. The mixture was extracted with dichloromethane (100 ml × 3) and the extract was dried ($MgSO_4$). After removal of the solvent the title compound was purified to afford a colourless liquid by silica-gel column chromatography using n-hexane–ethyl acetate (5:2) as eluant; yield 4.6 g (80%), $\nu_{max.}$(neat) 2 920, 1 590, 1 575, 1 450, 1 255, and 750 cm^{-1}; δ($CDCl_3$) 1.67—2.05 (8 H, m, CH_2C), 2.07 (6 H, s, CH_3), 2.38—2.87 (16 H, m, CH_2S), 3.80 (4 H, s, CH_2pyr), and 7.12—7.73 (3 H, m, β-,γ-pyrH) (Found: C, 50.7; H, 7.5; N, 2.9. $C_{21}H_{37}NS_6$ requires C, 50.9; H, 7.5; N, 2.8%).

Preparation of the Polysulphoxides (**2b**), (**2c**), *and* (**2d**).—The title compounds were prepared from the corresponding sulphide (**8**), (**9**), or (**10**) with hydrogen peroxide in acetic acid according to the general oxidation method.[12] The yields, spectral data and elemental analyses are shown as follows. (**2b**): yield 83%, m.p. 137—142 °C (white crystals), $\nu_{max.}$(KBr) 2 975, 1 580, 1 450, 1 030 (S→O), 820, and 750 cm^{-1}; δ($CDCl_3$) 2.66 (6 H, s, CH_3), 4.20 (4 H, s, CH_2), and 7.30—7.91 (3 H, m, β-,γ-pyrH) (Found: C, 46.7; H, 5.7; N, 6.0. $C_9H_{13}NO_2S_2$ requires C, 46.7; H, 5.7; N, 6.05%).

(**2c**): yield 85%, m.p. 130—140 °C (white crystals), $\nu_{max.}$(KBr) 3 000, 2 920, 1 590, 1 575, 1 043 (S→O), 1 000, 820, and 750 cm^{-1}; δ($CDCl_3$) 2.08—2.66 (4 H, m, CH_2C), 2.58 (6 H, s, CH_3), 2.68—3.10 (8 H, m, CH_2S), 4.08 and 4.19 (4 H, J_{AB} 12 Hz, CH_2pyr), 7.26 (2 H, d, *J* 8 Hz, β-pyrH), and 7.66 (1 H, t, *J* 8 Hz, γ-pyrH) (Found: C, 43.5; H, 6.1; N, 3.4. $C_{15}H_{25}NO_4S_4$ requires C, 43.8; H, 6.1; N, 3.4%).

(**2d**): yield 84%, m.p. 132—143 °C (white crystals); $\nu_{max.}$(KBr) 2 925, 1 590, 1 455, 1 425, 1 041 (S→O), 995, 830, and 755 cm^{-1}; δ($CDCl_3$) 2.08—2.66 (8 H, m, CH_2C), 2.58 (6 H, s, CH_3), 2.68—3.08 (16 H, m, CH_2S), 4.08 and 4.19 (4 H, J_{AB} 12 Hz, CH_2pyr), 7.26 (2 H, d, *J* 8 Hz, β-pyrH), and 7.66 (1 H, t, *J* 8 Hz, γ-pyrH) (Found: C, 42.4; H, 6.2; N, 2.3. $C_{21}H_{37}NO_6S_6$ requires C, 42.4; H, 6.3; N, 2.4%).

General Procedures for PTC Reactions.—Nucleophilic substitution reactions. The reactions were carried out in a two-necked reactor equipped with a condenser. A mixture of octyl bromide (1.0 mmol), nucleophile (*e.g.* NaCN, KSCN, PhOK, or PhSK; 5.0 mmol), and sulphoxide [*e.g.* (**1b**), (**1d**), (**2a**), (**2b**), (**3**), or (**4**); 0.1—4.0 mmol] in xylene (4 ml) was vigorously stirred at a specific temperature. Small samples of the reaction mixture were withdrawn with a microsyringe at intervals and monitored by gas chromatography. When the reaction was finished, the yield of product was determined by g.l.c. analysis.

Alkylation. The reactions were carried out in a two-necked reactor. To a mixture of phenylacetonitrile (or benzyl methyl ketone) (1.0 mmol), alkyl halide (*e.g.* methyl iodide, ethyl iodide, and n-butyl iodide; 1.2 mmol), and the sulphoxide [*e.g.* (**1b**), (**1d**), (**2b**), (**2c**), (**2d**), or (**4**); 0.01—0.1 mmol] was added 50% aqueous sodium hydroxide (5.0 mmol). The mixture was stirred vigorously at room temperature. Small samples of the reaction mixture were withdrawn with a microsyringe at intervals, quenched with dilute HCl, and extracted with dichloromethane; the extract was monitored by gas chromatography. When the reaction was finished, the yield of alkylated product was determined by g.l.c. analysis.

Reaction of Optically Active Octan-2-yl Bromide with Potassium Thiophenoxide in a Two-phase System.—Optically active (*S*)-(+)-octan-2-yl bromide (1.0 g, 5.18 mmol) {$[\alpha]_D^{21}$ +39.9° (*c* 6.0, EtOH), optical purity 94.8%}[13,14], prepared by a known method from commercially available optically active octan-2-ol and potassium thiophenoxide (0.92 g, 6.22 mmol) were mixed in toluene (10 ml). To this mixture, methyl 2-pyridyl sulphoxide (2.59 g, 20.7 mmol) was added and the solution was stirred for 15 h at room temperature. The mixture was filtered, the toluene removed by evaporation under reduced pressure, and the residue purified by column chromatography with n-hexane as an eluant to give optically active octan-2-yl phenyl sulphide (1.10 g, 95.7%), b.p. 78—80 °C at 20 mmHg.

The sulphide (0.5 g, 2.2 mmol) thus obtained was dissolved in acetic acid (50 ml) and oxidized with 30% hydrogen peroxide (0.8 g, 7.1 mmol) for 17 h at room temperature. The solution was extracted with n-hexane and the extract evaporated. The residue was chromatographed on silica gel with acetone as eluant; yield 0.33 g (56.3%), $[\alpha]_D^{17}$ +11.4° (*c* 5.3, MeOH), optical purity 91.2%, optical yield 96.2%.[15] The configuration of this sulphone was known to be *R*.

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Received 19*th October* 1983; *Paper* 3/1855