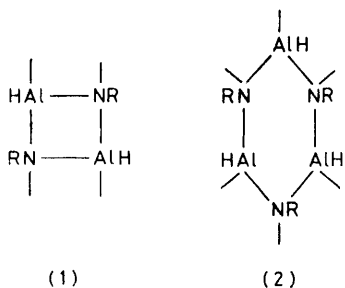


Kinetic Resolution of Sulphoxides by Chiral Poly(*N*-Alkyliminoalanes)

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Kinetic resolution of racemic sulphoxides by chiral poly[*N*-(1-phenylethyl)iminoalanes] (PIA-PHETs) from (+)- or (−)-1-phenylethylamine is described. For *p*-tolyl mesityl sulphoxide in the temperature range between −25 and +85 °C, optical yields increase with temperature to an upper limit of between 55 and 70 °C, with enantiomeric enrichments up to ca. 75%. It is shown that, among the three molecular species of PIA-PHET (closed-cage tetramer, closed-cage hexamer and open-cage tetramer), only the last is chemically active and capable of chiral recognition. Reactions follow second-order kinetics (first-order in sulphoxide, first-order in open PIA-PHET tetramer). The particular molecular structure of the latter probably accounts for the high degree of chiral recognition at high temperature.

POLY(*N*-ALKYLIMINOALANES) (PIAs), derived from substitution of two hydridic hydrogens of AlH_3 by NR groups of primary amines, can be obtained by various methods.¹ The structures of several PIAs from different amines have been characterized by X-ray analysis on single crystals,² as well as by ^1H n.m.r., ^{13}C , ^{27}Al , and ^{14}N n.m.r., and mass spectroscopy.^{3–5} They were found to be products of composition $(\text{HAINR})_n$, with n usually ranging from 4 to 10 and with closed molecular structures derived by the combination of four- and/or six-membered heterocyclic rings (1) and (2); or compounds having composition $[(\text{HAINR})_x(\text{H}_2\text{AlNHR})_y]$ derived from the formal hydrogenolysis of some imino-units $\text{HAl}-\text{NR}$ in $(\text{HAINR})_n$ or from the combination of some imino-units with amino-units $\text{H}_2\text{Al}-\text{NHR}$.



PIAs are highly soluble in aromatic and aliphatic hydrocarbons. Therefore, in addition to their use as active co-catalysts for polymerization of olefins and diolefins⁶ or of the catalytic reduction of unsaturated substrates,⁷ they also find use as reagents for organic stoichiometric reductions in non-polar non-protic solvents; thus $(\text{HAINPr})_6$ has been used for the reduction of carbonyl compounds⁸ and for the regioselective reduction of steroidal diketones.⁹ PIAs derived from optically active 1-phenylethylamine (PIA-PHETs) have been employed for asymmetric reductions of carbonyl derivatives¹⁰ and phosphinoides;¹¹ they were active also in the reduction of sulphur functionalities, such as sulphoxides, sulphilmines, and sulfoximides.¹²

We now describe the kinetic resolution of sulphoxides by chiral PIA-PHETs obtained from (−)-(S)- or (+)-(R)-1-phenylethylamine.

RESULTS

PIA-PHET Composition.—Optically active PIA-PHETs were prepared from (−)-(S) or (+)-(R)-1-phenylethylamine and equimolar amounts of $\text{AlH}_3 \cdot \text{NMe}_3$ in diethyl ether under nitrogen.¹¹ The results of several preparations are reported in Table 1: PIA-PHETs were usually a mixture of variable ratios of three different molecular species, *i.e.*, the closed-cage tetramer (3), the closed-cage hexamer (4), and the open-cage tetramer (5). The quantitative evaluation of percentages of species (3)–(5) was performed by ^1H n.m.r. spectroscopy.³ The closed hexamer (4) was isolated² from the crude mixture by fractional crystallization using *n*-hexane.

The optical rotation of a PIA-PHET was opposite in sign to that of the corresponding 1-phenylethylamine, and the absolute value depended on the PIA-PHET composition. Particular care was taken in the storage and withdrawal of samples of PIA-PHET under nitrogen to prevent decomposition.

Kinetic Resolution of Sulphoxides.—The sulphoxides studied were benzyl *p*-tolyl sulphoxide (6), 1-naphthyl *p*-tolyl sulphoxide (7), and mesityl *p*-tolyl sulphoxide (8).

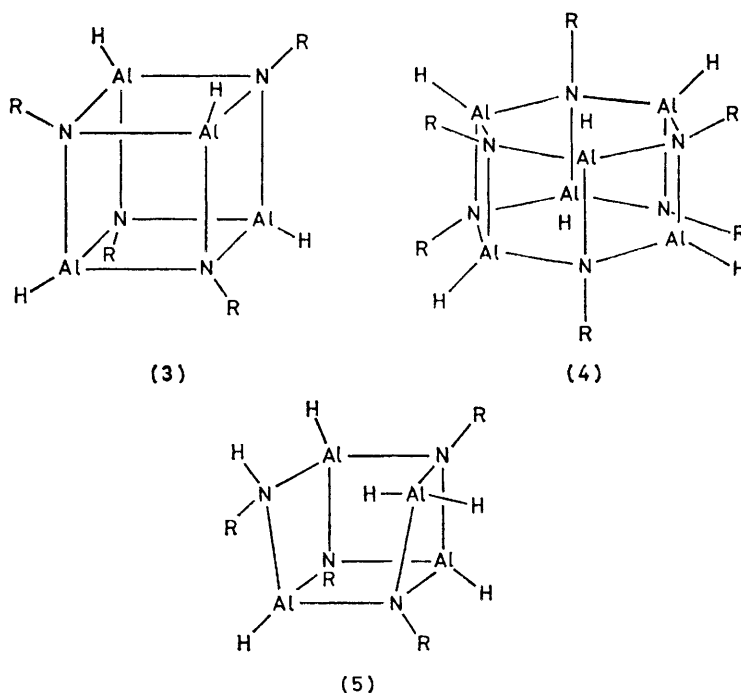
Reductions were carried out in anhydrous toluene, under nitrogen, with different PIA-PHET:substrate ratios, reaction times, and temperatures (Tables 2–5). Among the different PIA-PHET molecular species, only the tetramer (5) was chemically and stereochemically active (Table 2). Starting from racemic sulphoxide and PIA-PHET containing (5), and quenching the reaction before completion, a mixture of enantiomerically enriched sulphoxide and the corresponding sulphide was obtained. In contrast the closed cages (3) and (4) were completely inert under the reaction conditions, as shown by using the single poly(*N*-1-phenylethyliminoalanes) (10c) and (10g) (Table 2).

The highest optical yields were obtained for the sulphoxide (8) (Table 3), probably because of the significant difference in steric hindrance among the ligands at the sulphinyl group. In the case of the sulphoxide (6), reduction of the S=O group is accompanied by a noticeable amount of S–C (benzylic) bond breaking. This phenomenon was not observed in compounds (7) and (8), nor in the corresponding sulphides, even under drastic reaction conditions.

TABLE I
Poly[*N*-(1-phenylethyl)iminoalanes] (PIA-PHETs) ^a

AlH ₃ ·NMe ₃ (mmol)	1-Phenyl- ethylamine (+)-(R) ^f	Solvent (ml)	T/°C (h)	PIA-PHET	Nature ^e	Chemical composition ^d			¹ H N.m.r. analysis (mol %)			[α] _D ²⁵ (°) ^e (in benzene)
						Al (%)	N (%)	H _{act.} (mequiv. g ⁻¹)	(3)	(4)	(5)	
105	(+)-(R) ^f	Et ₂ O (150)	20 (2) reflux (4)	(10a)	C	17.3	9.6	7.40		25	75	−31
177	(−)-(S)	C ₆ H ₆ (80) Et ₂ O (300)	60 (2) 20 (24)	(10b)	C	16.8	10.1	7.00	11	11	78	+38
900	(−)-(S)	Et ₂ O (1 300)	20 (4) reflux (5)	(10c)	C	17.3	9.3	6.16	100			
165	(−)-(S)	C ₆ H ₆ (600) Et ₂ O (350)	55–60 (2) 20 (4)	(10d)	C	17.3	10.2	7.60	34	14	52	
250	(−)-(S)	Et ₂ O (350)	20 (8)	(10e)	C	16.2	8.1	7.44	17	16	67	
342	(−)-(S)	Et ₂ O (450)	20 (4)	(10f)	C	17.0	8.8	8.10	22	13	65	
282	(+)-(R)	Et ₂ O (380)	20 (1) reflux (2)	(10g)	I	18.1	9.4	6.88		100		−31
		C ₆ H ₆ (200)	55 (2)	(10g)	XX R	17.9 17.9	9.4 8.9	6.80 7.5	100 25		75	−20

^a Etheral solution of 1-phenylethylamine was added dropwise to equimolecular amounts of etheral solution of AlH₃·NMe₃ (ca. 1M) at 5–10 °C. Eventually benzene was added successively. ^b In every preparation the crude product was obtained in nearly quantitative yield, by removing solvents and NMe₃ *in vacuo* from the reaction solution. ^c C = crude product; I, XX, R indicate respectively insoluble crystalline fraction (15.5 g), separated crystals (4.0 g), and residue material (20 g) when the crude product (40 g) was refluxed with n-hexane (100 ml). ^d (C₆H₅NAlH)_n requires Al, 18.5; N, 9.6%; H_{act.}, 6.89 mequiv. g⁻¹. ^e PIA-PHETs have opposite sign with respect to starting amine. ^f Enantiomeric excess: 91.1%.



Other factors being equal, the enantiomeric enrichment of the sulphoxide depended on the conversion. It increased with the PIA-PHET : substrate molar ratio up to a value of

TABLE 2

Reduction of racemic sulphoxide (8) by PIAs (10a)–(10h) in toluene ^a

PIA-PHET	25 °C (1 h)		55 °C (10 min)	
	Conversion (%)	Optical purity (%) of recovered sulphoxide	Conversion (%)	Optical purity (%) of recovered sulphoxide
(10a) ^{a,b}	49	38.9	49	27.4
(10b) ^b	43	20.5	40	25
(10c) ^b	0	0		
(10d) ^b	33	10.7	30	8.8
(10e) ^{b,d}	81	45	84	72
(10f) ^{b,d}	70	77.5		
(10g) ^{a,b}	0	0		
(10h) ^a	51	27	64	44.7

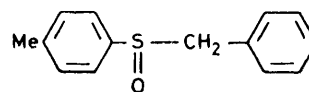
^a Hydridic hydrogens : sulphoxide ratio 2 : 1. ^b Composition reported in Table 1. ^c The highest optical purity (55.5%) was obtained when the reaction was carried out at 0 °C, with 53% conversion. ^d Hydridic hydrogens : sulphoxide ratio 4 : 1. ^e Prepared according to reference 11.

1 : 1 between the open tetramer (5) and the sulphoxide (8), then remained practically constant (Table 4).

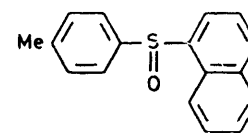
Optical yields were often increased by increasing the

PHET, maintained in every case the original optical purity.

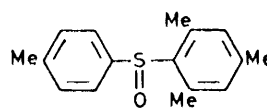
Kinetic Measurements.—Kinetic runs were performed in anhydrous toluene with equimolar amounts of the sulphoxide (8) and the open tetramer (5) at 55 °C. For both



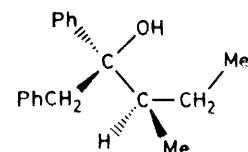
(6)



(7)



(8)



(9)

enantiomeric sulphoxides, the reactions followed second-order kinetics [first-order in (8) and first-order in (5)] up to at least 70% conversion (see Figure), with the sulphoxide : sulphide ratios determined by ¹H n.m.r. spectroscopy.

TABLE 3

Reduction of racemic sulphoxides (6)–(8) by PIA (9a)

Sulphoxide	Solvent	Conversion (%)	t/h	T/°C	Recovered sulphoxide	
					[α] _D ²⁵ (°)	Optical purity (%)
(6) ^b	Et ₂ O	54 ^c	1	+23	+3.5 ^d	3.3
(6) ^b	THF	52 ^e	24	–8	+4.2 ^d	3.9
(7) ^b	C ₆ H ₆	33	14	+21	–14.0 ^f	3.4
(7) ^b	THF	36	52	–8	–12.0 ^f	2.9
(8) ^g	PhMe	51	1	+25	+76.5 ^f	27.0
(8) ^g	PhMe	33	18	–22	+55.1 ^f	19.4

^a PIA-PHET (10h), prepared according to ref. 11. ^b Hydridic hydrogens : sulphoxide ratio 2 : 1. ^c Products are disulphide (36.5%) and sulphide (63.4%). ^d In chloroform. ^e Disulphide 58%, sulphide 42%. ^f In acetone. ^g Hydridic hydrogens : sulphoxide ratio 4 : 1.

temperature over a range which depended on the particular PIA-PHET sample: the upper limit was between 55 and 70 °C, and under these conditions the enantiomeric enrich-

TABLE 4

Influence of the amount of PIA-PHET ^a on the reduction of the racemic sulphoxide (8) in toluene

Open tetramer (5): sulphoxide molar ratio		T/°C	t/min	Conversion (%)	Optical purity (%) of recovered sulphoxide
0.5 : 1	25	60	33	10.7	
1 : 1	25	60	44	25	
1.2 : 1	25	60	47.4	23.5	
0.5 : 1	55	10	30	8.8	
1 : 1	55	10	63.2	34.3	
1.2 : 1	55	10	62	30	

^a PIA-PHET (10d); see Table 1.

ment of the recovered sulphoxide reached *ca.* 75% for 70–90% conversions (Table 5). However, in other instances the optimum temperature was noticeably lower, and is related to a lower chemical reactivity of the PIA-PHET (Table 2).

The 1-phenylethylamine recovered at the end of the reaction, after decomposition of the unchanged PIA-

The first-order kinetics in (5) supports the hypothesis that only two of the five hydridic hydrogens reacted with the sulphinyl group.

When the (+)-PIA-PHET, derived from (–)-1-phenylethylamine, was used, the observed rate constants *k* were

TABLE 5

Influence of temperature on the reduction of the racemic sulphoxide (8) by PIA-PHET ^a in toluene ^b

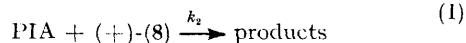
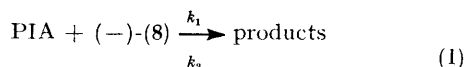
Conversion (%)	t	T/°C	Recovered sulphoxide	
			[α] _D ²⁵ (°) ^c	Optical purity (%)
33	18 h	–22	+55.1	19.4
47	11 h	0	+67.9	23.9
51	1 h	+25	+76.5	27.0
62	30 min	+40	+112.5	39.6
64	10 min	+55	+127.0	44.7
51	1 min	+70	+103.1	36.3
90	3 min	+70	+209.1	73.6
66	30 s	+85	+100.0	35.2

^a PIA-PHET (10h), prepared according to ref. 11.

^b Hydridic hydrogens : sulphoxide ratio 4 : 1. ^c In acetone.

0.84 and 0.12 for (+)-(8) and (–)-(8), respectively. On repeating the reaction with the racemic sulphoxide (8), the rate decreased with the steadily increasing excess of the less reactive enantiomer.

A kinetic analysis confirmed that reactions follow first-order kinetics in the open tetramer (5) and in the (+)- and (-)-sulphoxides (8) (Table 6). The reaction scheme (1) was interpreted by the kinetic equations (2) and (3), where



$$-dX = k_1 X^{n_1} Z^{n_1} \quad (2)$$

$$-dY = k_2 Y^{n_2} Z^{n_1} \quad (3)$$

k_1 and k_2 are the rate constants, measured separately for (+)- and (-)-(8), respectively, and n_1 and n_2 are the reaction orders for PIA-PHET [open tetramers (5)] and the

increases in the temperature range -25°C to an upper limit between 55 and 70°C : this can be attributed, in principle, to various effects. Among these the entropy factor is likely to play a dominant role, but the stereochemical outcome can also be due to a change in mechanism, in geometry, or in the degree of association of the reactants. A few examples of this behaviour have been reported in the literature.¹³⁻¹⁵ However, the extremely high degree of chiral recognition (up to *ca.* 75%) given by (5) in the range between 55 and 70°C , should be emphasized.

It is more difficult to rationalize the different reactivity and stereoselectivity of various samples of PIA-PHET,

TABLE 6

Simulation of reduction rate of racemic *p*-tolyl mesityl sulphoxide with PIA-PHET ^a at 55°C in toluene

Conversion		[[+)-(8)] $\times 10^{-2}$ ^b		[(-)-(8)] $\times 10^{-2}$ ^b		[[+)-(8) + (-)-(8)] $\times 10^{-2}$		Optical purity ^e
<i>t</i> /s	(%)					Calc. ^{c,d}	Found	
0	0	2.77	2.77	5.54	5.54	0	0	0
410	22.7	1.95	2.62	4.57	4.28	14.8	14.8	14.8
880	32.4	1.39	2.49	3.88	3.75	28.3	28.3	28.3
1 790	45.8	0.81	2.29	3.10	3.00	47.5	47.5	47.5
2 715	52.0	0.52	2.14	2.66	2.66	60.9	60.9	60.9
3 582	56.0	0.36	2.02	2.38	2.44	69.0	69.0	69.0
4 580	56.6	0.25	1.90	2.15	2.40	76.0	76.0	76.0

^a PIA-PHET (10e); see Table 1 [open tetramer (5): sulphoxide molar ratio equal to 1]. ^b Calculated from equation (5) for $n_1 = n_2 = 1$. ^c Sum of the values reported in columns 3 and 4. ^d Average difference $\{F = [(Calc. - Found)/Found] \times 100\} = 4.4\%$. ^e Calculated by $\{[(+)-(8)] - [(-)-(8)]\} / \{[(+)-(8)] + [(-)-(8)]\}$.

enantiomeric sulphoxides (8), respectively. X , Y , and Z are molar concentrations (mol l^{-1}). At each reaction time, Z was calculated from equation (4) where Z_i , X_i , and Y_i are

$$Z = Z_i - (X_i - X) - (Y_i - Y) \quad (4)$$

the initial concentrations of (5), (-)-(8), and (+)-(8), respectively. Equations (2) and (3) were integrated by the fourth-order Runge-Kutta method, and the kinetic orders n_1 and n_2 were adjusted in order to minimize the objective equation (5) where $(SO)_P$ is the experimental value

$$\phi = \sum_{P=1}^N [(X + Y)_P - (SO)_P]^2 \quad (5)$$

of the total sulphoxide concentration for the run P , and N is the total run number. The best fit to the experimental values (Table 6) was found for $n_1 = n_2 = 1$, up to *ca.* 60% conversion.

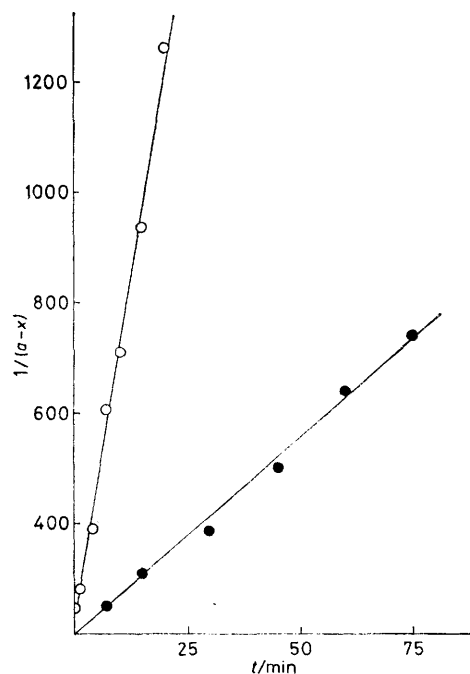
From the calculated amounts of the enantiomeric sulphoxides, a presumed optical purity of the recovered sulphoxide at various conversions could be determined. These values were in good agreement with those experimentally found in the kinetic resolutions.

DISCUSSION

The peculiar structure of the open tetramer (5) accounts well for its reactivity, compared to the inertness of the closed-cage structures (3) and (4). It seems likely that the high degree of asymmetric induction is related to the formation of an insertion complex of the sulphoxide corresponding to the open side of (5), where the chiral centre of phenylethylamine is responsible for the chiral recognition.

The optical purity of the recovered sulphoxide often

which cannot be simply due to different ratios of the three components (3)–(5), since (3) and (4) are completely inert under the reaction conditions. Indeed



Plots of second-order kinetics of the reduction of sulphoxides (+)-(R)-(8) (O) and (-)-(S)-(8) (●) at 55°C in toluene; for (+)-(R)-(8) $k = 0.84$; for (-)-(S)-(8) $k = 0.12$

some samples of PIA-PHET show the highest stereoselectivity at temperatures lower than 55°C [see for

example Table 2 (10a)]. This behaviour could be connected to an 'aging effect' of PIA-PHET. Variation of reactivity with 'age' has been reported by several authors for complex reducing agents derived from LiAlH_4 and alcohols or amines.¹⁶⁻¹⁸ In the case of chiral reducing agents a variation in chemical reactivity is often accompanied by variation in the stereoselectivity of the reaction, also as a function of the temperature. For example, with freshly prepared reagents derived from the alcohol (9) (Darvon alcohol) and LiAlH_4 the optical yield in the reduction of ketones increases as temperature is decreased; the opposite behaviour is seen with 'aged' reagent. In our case the 'aging' can be due to minor decomposition of the alane which is accompanied by a decrease in chemical reactivity, chiral recognition, and temperature of maximum stereoselectivity.

EXPERIMENTAL

Light petroleum had b.p. 40–60 °C. Extractions were performed with chloroform and extracts were dried over Na_2SO_4 . Toluene was distilled from CaH_2 . ^1H N.m.r. spectra were recorded with Varian A-60 and HA 100 instruments; i.r. spectra were run on a Perkin-Elmer 377 spectrometer. Optical rotations were measured with a Perkin-Elmer 141 polarimeter.

(+)-(R)-1-Phenylethylamine, $[\alpha]_D^{20} +40.1^\circ$ (neat), and (–)-(S)-1-phenylethylamine, $[\alpha]_D^{20} -40.1^\circ$ (neat), were commercial products and were purified by distillation *in vacuo*. Benzyl *p*-tolyl sulphide,¹⁹ 1-naphthyl *p*-tolyl sulphide,²⁰ and mesityl *p*-tolyl sulphide²¹ were obtained by literature methods. Racemic benzyl *p*-tolyl sulphoxide, m.p. 136–137 °C (lit.,²² 136–137 °C), 1-naphthyl *p*-tolyl sulphoxide, m.p. 107–108 °C (lit.,²³ 108 °C), and mesityl *p*-tolyl sulphoxide,²⁴ m.p. 84–85 °C, were prepared by periodate oxidation²⁵ of the corresponding sulphides. (+)-(R)-Benzyl *p*-tolyl sulphoxide, m.p. 169–170 °C, $[\alpha]_D^{20} +252^\circ$ (c, 1 in Me_2CO) {lit.,²⁶ m.p. 169–170 °C, $[\alpha]_D^{20} +252^\circ$ (c, 1 in Me_2CO)}; (–)-(S)-1-naphthyl *p*-tolyl sulphoxide, m.p. 137 °C, $[\alpha]_D^{25} -414^\circ$ (c, 2 in Me_2CO) {lit.,²⁷ m.p. 136–137 °C, $[\alpha]_D^{25} -414^\circ$ (c, 2 in Me_2CO)}; and (–)-(S)-mesityl *p*-tolyl sulphoxide, m.p. 106–107 °C, $[\alpha]_D^{25} -280^\circ$ (c, 1 in Me_2CO) (98% optically pure) {lit.,²⁴ m.p. 106–108 °C, $[\alpha]_D^{25} -286^\circ$ (c, 1 in Me_2CO)}, were prepared from (–)-menthyl (–)-toluene-*p*-sulphinate according to literature methods. (+)-(R)-Mesityl *p*-tolyl sulphoxide, m.p. 106–107 °C, $[\alpha]_D^{25} +270^\circ$ (c, 1 in Me_2CO) (94% optically pure), was similarly obtained *via* the Andersen synthesis²⁷ starting from (–)-menthyl (+)-toluene-*p*-sulphinate with $[\alpha]_D^{25} +23.6^\circ$ (c, 1 in Me_2CO) and $n_D^{28} 1.525$.

Poly[N-(1-phenylethyl)iminoalanes] (PIA-PHETs).—The PIA-PHETs (10) were obtained by reaction of $\text{AlH}_3 \cdot \text{NMe}_3$ and (–)-(S)- or (+)-(R)-1-phenylethylamine according to literature methods, with eventual minor changes (Table 1). Usually the product was a mixture of species (3), (4), and (5). The almost pure closed tetramer (3), PIA-PHET (10c) was sometimes obtained. In some cases [PIA-PHETs (10b) and (10d)] elemental analyses (N:Al ratio *ca.* 1.15) and ^1H n.m.r. spectra (singlet at δ 2.25) in benzene solution gave clear evidence for some NMe_3 complexation with PIA-PHET.

The closed and open tetramers (3) and (5) were amorphous to X-ray analysis and attempted crystallizations were

unsuccessful. In contrast, the closed hexamer (4), PIA-PHET (10g), was crystalline and was easily separated by crystallization of the crude reaction product from *n*-hexane; its crystal and molecular structures have been fully characterized by single-crystal X-ray analysis.²

Reduction of the Sulphoxides (6)–(8) by PIA-PHET (10a)–(10m). *General Procedure*.—The PIA-PHET [generally a mixture of (3), (4), and (5), containing 1 mmol of (5)] in the appropriate solvent (10 ml) was added quickly at the reaction temperature under nitrogen to a stirred solution of the sulphoxide (1 mmol) in the same solvent (20 ml). The mixture was stirred for the appropriate time, then poured into ice and 10% aqueous sulphuric acid, the aqueous layer was extracted twice with chloroform, and the combined layers dried and evaporated *in vacuo*. The crude material was separated by column chromatography [silica; diethyl ether–light petroleum (1:1)]. The products were identified by ^1H n.m.r. analysis; optical rotations and other pertinent results are reported in Tables 2–5.

Kinetics.—The kinetic runs were carried out at $\pm 55^\circ\text{C}$. Solutions of racemic (8), (+)-(R)-(8), and (–)-(S)-(8) were prepared by adding the sulphoxide (1 mmol) to 275 ml of anhydrous toluene. At zero time a solution of 1 mmol of (5) in 25 ml anhydrous toluene was added to the sulphoxide solution. Aliquots (50 ml) were withdrawn at various times, quenched, and worked up as described above. The sulphide:sulphoxide ratio was evaluated on the basis of the ^1H n.m.r. spectra in CDCl_3 . The following absorptions were taken into account: sulphide, δ 6.67–7.0 (6 H, m, aromatic); sulphoxide, δ 7.0–7.35 (4 H, AA'BB' system), δ 6.75br (2 H, s). The second-order rate constants were obtained, according to the equation $1/(a-x) - 1/a = kt$, by plotting $1/(a-x)$ vs. time t , where a is the initial concentration of both sulphoxide and (5).

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