

## Asymmetric Induction in the Darzens Reaction by Means of Chiral Phase-transfer in a Two-phase System. The Effect of Binding the Catalyst to a Solid Polymeric Support

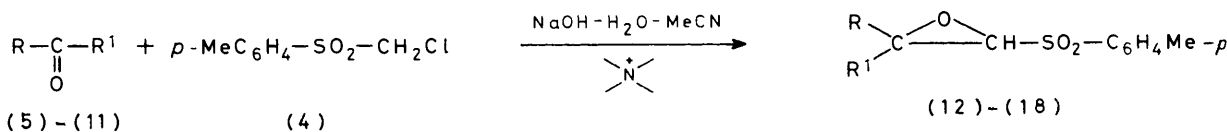
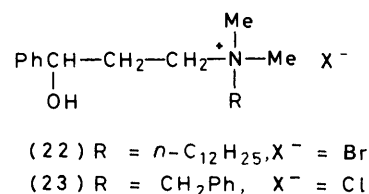
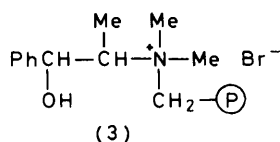
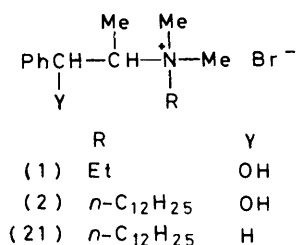
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Reaction of carbonyl compounds with chloromethyl *p*-tolyl sulphone or with chloro(phenyl)acetonitrile in a two-phase system, in the presence of chiral ammonium salts, affords the corresponding oxirans with 0–2.5% optical yields. The presence of a hydroxy-group  $\beta$  to the 'onium' function is essential to achieve asymmetric induction. Asymmetric induction is increased by binding of the catalyst to a polymeric matrix to give optical yields up to 23%.

ASYMMETRIC induction under phase-transfer conditions with optically active catalysts has recently been described.<sup>1</sup> Despite the claims of other workers that high optical yields can be obtained by the employment of chiral catalysts, this is generally not so. For instance the value of optical purity of 2-phenyloxiran (97%),<sup>1a</sup>

considered to be the only reaction thus studied yielding relatively high optical yields.

In this paper we report that the Darzens reaction<sup>2</sup> in an aqueous/organic two-phase system in the presence of chiral catalysts (–)-*N*-alkyl-*N*-methylephedrinium halides (1) and (2), supported or not on a polymeric



- (5), (12) R = H, R<sup>1</sup> = Me  
 (6), (13) R = H, R<sup>1</sup> = Ph  
 (7); (14) R = R<sup>1</sup> = Me  
 (8), (15) R = Me, R<sup>1</sup> = Et  
 (9), (16) R = Me, R<sup>1</sup> = Pr<sup>i</sup>  
 (10), (17) R = R<sup>1</sup> = Et  
 (11), (18) R = R<sup>1</sup> = Ph

reported by Nozaki and his co-workers was incorrect.<sup>1d</sup> The result obtained by Wynberg and his co-workers in the epoxidation of chalcones with hydrogen peroxide in the presence of a catalytic amount of benzyloquininium chloride yielding an enantiomeric excess of 25%<sup>1f,g</sup> is

<sup>1</sup> (a) T. Hijama, T. Mishima, H. Sawada, and H. Nozaki, *J. Amer. Chem. Soc.*, 1975, **97**, 1626; (b) T. Hijama, H. Sawada, M. Tsukanaka, and H. Nozaki, *Tetrahedron Letters*, 1975, 3013; (c) J. C. Fiaud, *ibid.*, p. 3495; (d) T. Hijama, T. Mishima, H. Sawada, and H. Nozaki, *J. Amer. Chem. Soc.*, 1976, **98**, 641; (e) J. Balcells, S. Colonna, and R. Fornasier, *Synthesis*, 1976, 266; (f) R. Helder, J. C. Hummelen, R. W. P. M. Laane, J. C. Wiering, and H. Wynberg, *Tetrahedron Letters*, 1976, 1831; (g) H. Wynberg, *Chimia*, 1976, **30**, 445.

matrix (3), affords optically active  $\alpha\beta$ -epoxy-sulphones and nitriles. The influence on asymmetric synthesis of both structural variations and binding of the ephedrinium catalysts to a polymeric matrix has also been examined.

The reaction of chloromethyl *p*-tolyl sulphone (4) with carbonyl compounds (5)–(11) was carried out at room temperature in 50% aqueous sodium hydroxide-acetonitrile in the presence of catalytic amounts of

<sup>2</sup> (a) P. Vogt and D. F. Tavares, *Canad. J. Chem.*, 1969, **47**, 2875; (b) A. Jonczyk, K. Banko, and M. Makosza, *J. Org. Chem.*, 1975, **40**, 266; A. Jonczyk, M. Fedorynski, and M. Makosza, *Tetrahedron Letters*, 1972, 2395.

compounds (1)–(3) (0.05 mole equiv.). In principle, enantiomerically enriched oxirans (diastereoisomeric mixtures or single compounds, respectively, for  $R \neq R^1$  or  $R = R^1$ ) could be obtained in this reaction.

The results reported in Table 1 indicate that the diastereoisomeric ratio of the products depends on the nature of the substrate. High stereoselectivity was

the diastereoisomers (15a) and (15b) respectively [(46% yield, relative ratio 37 : 63),  $[\alpha]_D^{20} +2.17$  (acetone)].

The degree of stereoselectivity of the condensation of carbonyl compounds with chloromethyl (4) and bromomethyl sulphone (20) reflects the differences in bulk between the substituents R and R'. The prevalence of the (*E*)-diastereoisomers in the epoxy-sulphones (12),

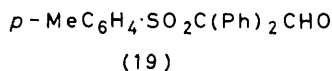
TABLE 1  
Reaction of the carbonyl compounds listed with the chlorosulphone (4) and chloromandelonitrile (24)

Substrate	Catalyst	Product	Yield %	$[\alpha]_D^{20}$ (Me <sub>2</sub> CO)	( <i>Z</i> )/( <i>E</i> ) ratio	Optical yield %
(5)	(2)	(12)	62	0.00	2 : 98	
(6)	(1)	(13)	96	0.00	0 : 100	
(7)	(1)	(14)	95	+1.22		2.5
(7)	(2)	(14)	94	+1.20		
(7)	(20)	(14)	96	0.00		
(7)	(3)	(14)	70	+2.90		
(7)	(22)	(14)	60	0.00		
(7)	(23)	(14)	60	0.00		
(8)	(2)	(15a)	98	+2.60	29 : 71	
		(15b)				
(8)	(21)	(15a)	80	0.00	30 : 70	
		(15b)				
(8)	(3)	(15a)	40	+6.25 <sup>a</sup>	32 : 68	23
		(15b)				20
(9)	(1)	(16a)	82	+0.92 <sup>a</sup>	31 : 69	
		(16b)				
(10)	(1)	(17)	90	+0.92 <sup>a</sup>		
(5)	(1)	(25)	71	-0.69 <sup>a</sup>	<i>b</i>	
(6)	(1)	(26)	100	-10.10 <sup>a</sup>	98 : 2	
(6)	(3)	(26)	60	-3.29 <sup>a</sup>	95 : 5	

<sup>a</sup> Values for the diastereomeric mixture. <sup>b</sup> The diastereoisomers, of unknown configuration, were in the ratio 98 : 2 (as indicated by <sup>1</sup>H n.m.r. spectroscopy).

observed starting from the aldehydes (5) and (6) which afforded practically only one of the two possible diastereoisomers, (12) and (13), respectively; unsymmetrically substituted ketones (8) and (9) gave mixtures of (*Z*)- and (*E*)-epoxides, (15a,b) and (16a,b), respectively. The optical yield ranged from 0 to 23%, depending on the starting carbonyl compound and on the catalyst used.

Di-isopropyl ketone did not react under our experimental conditions, as indicated by the quantitative recovery of the chlorosulphone (4) after a reaction time of 48 h. The sulphonyloxiran (18) could be isolated but rearranged easily at room temperature to give the  $\alpha$ -sulphonyl-aldehyde (19).\*

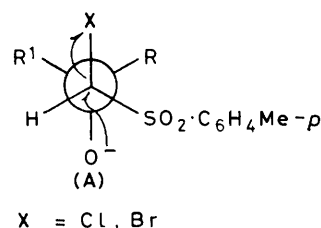


The configuration of the epoxides (12) and (13) was established by <sup>1</sup>H n.m.r. spectroscopy (see Experimental section). The (*Z*),(*E*)-configurations of compounds (15) and (16) were assigned by comparison of the chemical shifts of the methyl protons of (15) and (16), with those of (12) and (14) (see Table 2).

When bromomethyl *p*-tolyl sulphone (20) was used instead of (4) in the presence of the catalyst (2), reactions with acetone (7) and butan-2-one (8) afforded the optically inactive oxiran (14) (62% yield), and a mixture of

\* A similar rearrangement of sulphonyloxirans to  $\alpha$ -sulphonyl aldehydes has been observed by others.<sup>2a</sup>

(13), (15), (16) could be explained on the basis of a favoured transition-state of type (A) where R<sup>1</sup> is bulkier than R.



None of the products reported in Table 1 were known in optically active form prior to this work. The enantio-

TABLE 2  
Chemical shift of methyl protons of (12) and (14)–(16) in CDCl<sub>3</sub><sup>a</sup>

Compd.	$\delta$ CH <sub>3</sub>
(12)	1.37 <sup>b</sup>
(14)	1.37, 1.77
(15a)	1.35
(15b)	1.78
(16a)	1.27
(16b)	1.72

<sup>a</sup> Tetramethylsilane used as internal standard. <sup>b</sup> For the (*E*)-diastereoisomer.

meric compositions of 2-methyl-1-*p*-tolylsulphonyl-1,2-epoxybutane (14) and of (*Z*)-(15a) and (*E*)-(15b) oxirans were determined by using Eu(tfc)<sub>3</sub> as shift reagent.<sup>3</sup>

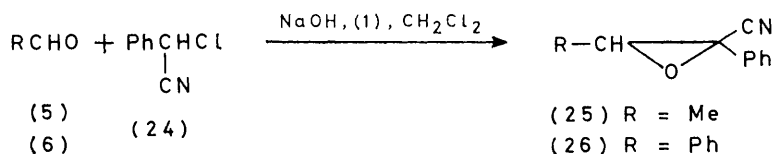
<sup>3</sup> H. L. Goering, J. N. Eikenberry, and G. S. Koerner, *J. Amer. Chem. Soc.*, 1971, **93**, 5913.

They were measured directly from relative peak areas of the epoxymethine proton, which was well split only on a 270 MHz  $^1\text{H}$  n.m.r. spectrometer. From the 270 MHz spectra, not only the enantiomeric purity of a single compound [oxiran (14)] could be established, but also the enantiomeric purities of diastereomeric mixtures [oxirans (15a,b)]. Unfortunately the epoxymethine proton was unsplit by  $\text{Eu}(\text{tfc})_3$  in the case of epoxy-sulphones (16) and (17), so that their optical purity could not be determined.

The enantiomeric excess of oxiran (14) was 2.5% when the soluble catalysts (1) and (2) were used. However a higher asymmetric induction (6%) was obtained by using the ephedrinium salt anchored on a polymeric matrix. A similar behaviour of (2), (3) was likely met with in the case of 2-methyl-1-*p*-tolylsulphonyl-1,2-epoxybutane, obtained as diastereomeric mixture (15a), (15b), in approximately the same ratio (3 : 7) both with catalyst (2) and (3), with optical rotation of +2.90 and +6.25°, respectively. In the latter case the enantiomeric excess of (15a) and (15b) was 23 and 20% respectively.

We have also examined the influence of structural variation within the soluble catalysts by testing 'onium' salts (21)–(23). The results in Table 1 show that the presence of a hydroxy-group  $\beta$  to the ammonium function is essential to achieve asymmetric induction. Indeed when (–)-(*R*)-*NN*-dimethyl-*N*-dodecylamphetaminium bromide (21) or  $\delta$ -hydroxy-derivatives (22) and (23) were used, the epoxides obtained were optically inactive. The dependence of such stereochemical results upon the position of the hydroxy-group is difficult to account for, although this behaviour is in accord with that previously found<sup>1e</sup> for the borohydride reduction of carbonyl compounds under phase-transfer conditions.

The Darzens condensation of aldehydes (5) and (6)



with chloro(phenyl)acetonitrile (24) in a two-phase system in the presence of soluble catalyst (1), was still highly stereoselective, with practically only one diastereoisomer formed, and afforded optically active oxirans (25) and (26),  $[\alpha]_D^{20}$  –0.6 and –10.1°, respectively.

The prevailing diastereoisomer of 2,3-diphenyl-2,3-epoxypropionitrile (26) had the (*Z*)-configuration.<sup>4</sup> Both the high stereoselectivity and the (*Z*)-configuration of (26) are in agreement with the results reported in the literature<sup>4</sup> for the same reaction using  $[\text{NBu}_4]\text{Br}$  as catalyst. Unfortunately, all attempts to estimate the enantiomeric excess of the epoxynitriles (25) and (26) with chiral shift reagents were unsuccessful. When benzaldehyde was condensed with (24) in the presence of

<sup>4</sup> E. D'Incan and J. Seyden-Penne, *Compt. rend.*, 1975, 1031.

<sup>5</sup> M. Cinquini, S. Colonna, H. Molinari, F. Montanari, and P. Tundo, *J.C.S. Chem. Comm.*, 1976, 394.

the polymer-supported catalyst (3), the oxiran (26) of the (*Z*)-configuration was formed almost exclusively ( $[\alpha]_D^{20}$  –3.29°). Although the stereoselectivity does not depend appreciably on the use of soluble or insoluble catalysts, the products from the supported catalyst (3) are of lower optical rotations than those from the soluble catalyst (1). Therefore the supported catalyst seems to be less efficient in promoting asymmetric induction in the synthesis of epoxynitriles. Although the effect on asymmetric induction of binding the catalyst to a solid polymeric matrix is difficult to account for, some general observations may be made. (i) Even if the use of the supported catalyst slows down the reaction,<sup>5</sup> the catalyst may be recovered and reused for other reactions. (ii) The chiral, polymer-supported catalyst may be completely removed from the reaction mixture, thus eliminating the possibility of optical contaminations of the reactions products. (iii) The catalytic efficiency of the supported catalyst is practically unchanged after being used several times: after three reactions of (3) the optical rotation +2.70° of the oxiran (14) was very similar to that (+2.90°) obtained using the new catalyst (3).

To the best of our knowledge the use of the ephedrinium salt (3) constitutes the first example of an asymmetric catalyst bound to a polymeric matrix in a two-phase aqueous organic system.

#### EXPERIMENTAL

$^1\text{H}$  N.m.r. spectra were recorded with a Varian A-60, an HA 100, and/or a Bruker HX 270 spectrometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter and are reported in Table 1.

*Optically Active Catalysts.*—*N*-Dodecyl-*N*-methyl-, *N*-ethyl-*N*-methyl-ephedrinium bromide (1), and *N*-dodecyl-*NN*-dimethylamphetaminium bromide (21) were prepared as previously described.<sup>1c</sup>

(+)-*N*-Dodecyl-3-hydroxy-*NN*-dimethyl-3-phenylpropylammonium bromide (22) and (+)-*N*-benzyl-3-hydroxy-*NN*-dimethyl-3-phenylpropylammonium chloride (23) were obtained by reaction of (+)-3-dimethylamino-1-phenylpropan-1-ol (27),  $[\alpha]_D^{27}$  +27.6° (*c* 1.5 in MeOH), lit.,<sup>6</sup>  $[\alpha]_D$  +27.6° (*c* 1.6 in MeOH), with dodecyl bromide or benzyl chloride (10% molar excess) in refluxing ethanol or benzene, respectively, for 24 h. After evaporation of the solvent under vacuum, compound (22) was obtained (60%), m.p. 104–105 °C (from ethyl acetate–hexane 1 : 10),  $[\alpha]_D^{25}$  +15.3° (*c* 7 in EtOH) (Found: C, 64.4; H, 9.8; N, 3.3.  $\text{C}_{23}\text{H}_{42}\text{BrNO}$  requires C, 64.5; H, 9.8; N, 3.3%),  $\delta$  for (22) ( $\text{CDCl}_3$ ) 7.20 (5 H, s, Ar), 4.80 (2 H, m, CH–OH), 3.45 (4 H, m, –CH<sub>2</sub>–N), 3.10 [6 H, s, –N(CH<sub>3</sub>)<sub>2</sub>], 2.20 (2 H, m, –CH–CH<sub>2</sub>–CH<sub>2</sub>–), and 1.24 (23 H). Compound (23) (80%), had m.p. 153–155 °C (from MeCN),  $[\alpha]_D^{25}$  +29° (*c* 3 in

<sup>6</sup> R. Andrisano, A. S. Angeloni, and S. Marzocchi, *Tetrahedron*, 1973, 29, 913.

EtOH) (Found: C, 70.4; H, 8.0; N, 4.5.  $C_{15}H_{24}ClNO$  requires C, 70.7; H, 7.8; N, 4.6%),  $\delta$  for (23) [(CD<sub>3</sub>)<sub>2</sub>SO] 7.15—7.25 (10 H, m, Ar), 4.56 (4 H, m, -CH-OH and -CH<sub>2</sub>Ph), 3.45 (2 H, m, -CH<sub>2</sub>-N), 2.96 [6 H, s, -N(CH<sub>3</sub>)<sub>2</sub>], and 2.20 (2 H, m, -CH-CH<sub>2</sub>-CH<sub>2</sub>).

*Polystyrene-Divinylbenzene-N-Methylephedrinium Chloride* (3).—Commercial strongly basic anion-exchange resin in the chloride form [Biobeads S-XI (Cl<sup>-</sup>); exchange capacity 1.29 mequiv. Cl/g], was heated with stirring at 60 °C for 90 h in the presence of a molar excess of *N*-methylephedrine. The resin was filtered off, washed with 95% ethanol, *n*-HCl, water, and absolute ethanol, and then dried *in vacuo* at 50 °C for 6 h. Its exchange capacity, determined by Volhard's method, was 0.9 mequiv. Cl/g.

*Optically Active  $\alpha\beta$ -Epoxy-sulphones*.—Chloromethyl *p*-tolyl sulphone (3) (1 mmol), carbonyl compound (1.1 mmol), 50% aqueous sodium hydroxide (1.5 ml), acetonitrile (0.1 ml), and catalyst (1) (0.05 mmol) were vigorously stirred at 20 °C for 2 h. In the case of the anchored catalyst (3) the reaction time was 24 h. The mixture was diluted with water and extracted with methylene chloride. The organic phase was concentrated on a rotatory evaporator, below 20 °C. The residue was chromatographed on silica with ether-light petroleum (1:1) as eluant. Physical and spectroscopic data are reported below, while optical rotations and purities are in Table 1.

(*E*)-1-*p*-Tolylsulphonyl-1,2-epoxypropane (12) had m.p. 82—83 °C (lit.<sup>20</sup> m.p. 83—84 °C). Its <sup>1</sup>H n.m.r. spectrum was identical to that described in the literature.<sup>2a</sup> When the reaction was repeated without catalyst, epoxide (12) was obtained in 30% yield, m.p. 81—83 °C.

(*E*)-2-Phenyl-1-*p*-tolylsulphonyl-1,2-epoxyethane (13) had m.p. 157—159 °C (lit.<sup>2a</sup> m.p. 157—159 °C); its <sup>1</sup>H n.m.r. spectrum was identical to that described in the literature.<sup>2a</sup> In a blank experiment without catalyst, epoxide (13) was obtained in 50% yield, m.p. 157—159 °C.

2-Methyl-1-*p*-tolylsulphonyl-1,2-epoxypropane (14) had m.p. 92—93 °C, independent of its enantiomeric purity (lit.<sup>2a</sup> m.p. 93.5—94 °C). Its <sup>1</sup>H n.m.r. spectrum was identical to that described in the literature.<sup>2a</sup>

2-Methyl-1-*p*-tolylsulphonyl-1,2-epoxybutane (15a, b) was obtained as an inseparable mixture of (*Z*)- and (*E*)-diastereoisomers. It had  $n_D^{22}$  1.5283 for a *Z/E* ratio 3:7 (Found: C, 59.9; H, 6.6.  $C_{12}H_{16}O_3S$  requires C, 60.0; H, 6.7%),  $\delta$  for (*E*)-(15b) (CDCl<sub>3</sub>) 7.35—7.80 (4 H, m, Ar), 3.60 (1 H, s, CH), 2.43 (3 H, s, *p*-CH<sub>3</sub>), 1.78 (3 H, s, CH<sub>3</sub>), 1.60 (2 H, m, CH<sub>2</sub>CH<sub>3</sub>), and 0.98 (3 H, t, CH<sub>2</sub>CH<sub>3</sub>),  $\delta$  for (*Z*)-(15a) (CDCl<sub>3</sub>) 7.35—7.80 (4 H, m, Ar), 3.60 (1 H, s, CH), 2.43 (3 H, s, *p*-CH<sub>3</sub>), 2.10 (2 H, m, CH<sub>2</sub>CH<sub>3</sub>), 1.35 (3 H, s, CH<sub>3</sub>), and 1.18 (3 H, t, CH<sub>2</sub>CH<sub>3</sub>).

2,3-Dimethyl-1-*p*-tolylsulphonyl-1,2-epoxybutane (16a, b) obtained as an oil, was an inseparable mixture of (*Z*)- and (*E*)-diastereoisomers,  $n_D^{22}$  1.5222 for a *Z/E* ratio 61:29. (Found: C, 61.3; H, 7.0.  $C_{13}H_{18}O_3S$  requires C, 61.4; H, 7.1%),  $\delta$  for (*E*)-(16b) (CCl<sub>4</sub>) 7.35—7.80 (4 H, m, Ar), 3.72 (1 H, s, CH-SO<sub>2</sub>), 2.43 (3 H, s, *p*-CH<sub>3</sub>), 1.68 (3 H, s, CH<sub>3</sub>), 1.10 [1 H, m, -CH(CH<sub>3</sub>)<sub>2</sub>], and 0.95 [6 H, d, -CH(CH<sub>3</sub>)<sub>2</sub>],  $\delta$  for (*Z*)-(16a) (CCl<sub>4</sub>) 7.35—7.80 (4 H, m, Ar), 3.72 (1 H, s, CHSO<sub>2</sub>), 2.43 (3 H, s, *p*-CH<sub>3</sub>), 1.50 [1 H, m, -CH(CH<sub>3</sub>)<sub>2</sub>], 1.20 (3 H, s, CH<sub>3</sub>), and 1.00 [6 H, d, CH(CH<sub>3</sub>)<sub>2</sub>].

2-Ethyl-1-*p*-tolylsulphonyl-1,2-epoxybutane (17) was an oil,  $n_D^{22}$  1.5258 (Found: C, 61.6; H, 6.9.  $C_{13}H_{18}O_3S$  requires C, 61.4; H, 7.1%),  $\delta$  for (17) (CCl<sub>4</sub>) 7.35—7.80 (4 H, m, Ar), 3.55 (1 H, s, CHSO<sub>2</sub>), 2.45 (3 H, s, *p*-CH<sub>3</sub>), 2.08 (2 H, q, CH<sub>2</sub>CH<sub>3</sub>), 1.60 (2 H, q, CH<sub>2</sub>CH<sub>3</sub>), 1.07 (3 H, t, CH<sub>2</sub>-CH<sub>3</sub>), and 0.85 (3 H, t, CH<sub>2</sub>CH<sub>3</sub>).

2,2-Diphenyl-2-*p*-tolylsulphonylethanal (19).—Reaction of benzophenone (11) with the chlorosulphone (4) afforded in 71% yield a mixture of 2,2-diphenyl-1-*p*-tolylsulphonyl-1,2-epoxyethane (18) and of the title compound (19). When set the reaction mixture was quantitatively converted into (19),  $[\alpha]_D^{20}$  0.0°, m.p. 107—109 °C (Found: C, 71.6; H, 5.2.  $C_{21}H_{18}O_3S$  requires C, 71.9; H, 5.2%),  $\delta$  for (19) (CDCl<sub>3</sub>) 9.70 (1 H, s), 7.73—6.90 (14 H, m, Ar), and 2.35 (3 H, s).

*Optically Active  $\alpha\beta$ -Epoxy-nitriles*.—Chloro(phenyl)acetonitrile (24) (10 mmol), aldehyde (10 mmol), 50% aqueous hydroxide (3 ml), ephedrinium salt (0.5 mmol), and methylene chloride were vigorously stirred at 20 °C for 2 h. Work-up of the reaction was similar to that described above.

1-Cyano-1-phenyl-1,2-epoxypropane (25) (71%), obtained as an oil, had  $n_D^{23}$  1.5171 and was *ca.* 98% diastereomerically pure as evidenced by <sup>1</sup>H n.m.r. spectroscopy (Found: C, 75.4; H, 5.7; N, 8.6.  $C_{10}H_9NO$  requires C, 75.5; H, 5.7; N, 8.8%),  $\delta$  (CDCl<sub>3</sub>) 7.25 (5 H, s, Ar), 3.18 (1 H, q, CHCH<sub>3</sub>), and 1.60 (3 H, d, *J* = 5 Hz, CHCH<sub>3</sub>). 2,3-Diphenyl-2,3-epoxypropionitrile (26) was obtained in 100% yield by reaction of benzaldehyde (6) with chloro(phenyl)acetonitrile (24) in the presence of catalyst (1), as a (*Z*)/(*E*)-diastereomeric mixture in a ratio 98:2 by <sup>1</sup>H n.m.r. spectroscopy.<sup>4</sup> It had m.p. 68—69 °C,  $[\alpha]_D^{20}$  -10.1° (*c* 3 in Me<sub>2</sub>CO), lit.<sup>7</sup> m.p. 70—70.5 °C for the (*Z*)-isomer. When the reaction was repeated at 20 °C for 24 h in the presence of the supported catalyst (3) under the conditions described above, 2,3-diphenyl-2,3-epoxypropionitrile (26) was obtained with a (*Z*)/(*E*) ratio 95:5, m.p. 61—66°,  $[\alpha]_D^{20}$  -3.29° (*c* 7 in Me<sub>2</sub>CO).

*Determination of Optical Purity in Oxirans* (14), (15a), and (15b).—The substrate was dissolved in CCl<sub>4</sub> (0.3 ml) in the presence of the shift reagent Eu(tfc)<sub>3</sub> in a <sup>1</sup>H n.m.r. tube. After a spectrum had been recorded on a Bruker HX 270 instrument, more Eu(tfc)<sub>3</sub> was added and the process repeated to get the best splitting for the epoxymethine proton. The optical yields were 6 ± 2% (average error) for oxiran (14),  $[\alpha]_D^{20}$  +2.90° (*c* 11 in Me<sub>2</sub>CO), 20 ± 2% (average error) for oxiran (15b), and 23 ± 4% (estimated value for the error due to a worse signal/noise ratio) for the oxiran (15a), the (*Z*)/(*E*) mixture (15a,b) having  $[\alpha]_D^{20}$  +6.25° (*c* 2 in Me<sub>2</sub>CO). The optical yield 2.5% for oxiran (14),  $[\alpha]_D^{20}$  +1.20° (*c* 11 in Me<sub>2</sub>CO), was evaluated by comparison with the value of optical rotation  $[\alpha]_D^{20}$  +2.90° of the same compound (see above).

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<sup>7</sup> R. N. McDonald and D. G. Hill, *J. Org. Chem.*, 1970, **35**, 2942.