then decanted and the solid dried in vacuo, giving 0.43 g (35%) of **7** as yellow crystals: mp 142.5–143 °C; ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 5 H, Cp), 3.89 (s, 10 H, CH_2), 6.63–6.92 (m, 25 H, Ph); ^{13}C NMR ($CDCl_3$) δ 33.29 (CH_2), 72.11 (C_5H_5), 85.62 (C_5Bz_5), 125.4, 127.8, 128.6, 140.9 (Ph). Anal. Calcd for $C_{45}H_{40}Fe$: C, 84.90; H, 6.33. Found: C, 84.64; H, 6.51.

X-ray Data Collection, Structure Determination, and Refinement. Single crystals of the title complexes were mounted on pins and transferred to the goniometer. The crystal of **5** was cooled to −150 °C during data collection, using a stream of cold nitrogen gas. The space groups were uniquely determined from the systematic absences. A summary of data collection parameters is given in Table III.

The geometrically constrained hydrogen atoms in **3** were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R found in Table III. The final values of the positional parameters are given in Tables IV (**3**) and V (**5**).

Acknowledgment is made to the donors to the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this research to M.D.R. The National Science Foundation Chemical Instrumentation Program provided funds used to purchase the diffractometer (N.I.U.).

Registry No. **3**, 118631-25-7; **4**, 118631-26-8; **5**, 118631-28-0; **6**, 118631-29-1; **7**, 118631-30-4; pentabenzylcyclopentadiene, 67209-29-4.

Supplementary Material Available: Full tables of bond distances and angles, H-atom coordinates, thermal parameters, and least-squares plane results (21 pages); listings of structure factors (17 pages). Ordering information is given on any current masthead page.

Asymmetric Catalysis. 44.[1] Enantioselective Monophenylation of Diols with $Cu(OAc)_2$/Pyridinyloxazoline Catalysts

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Received September 9, 1988

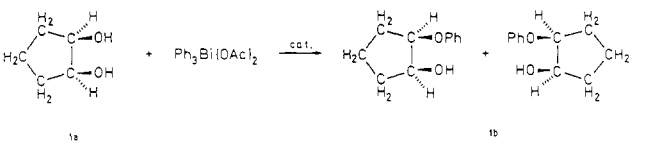
The $Cu(OAc)_2$-catalyzed monophenylation of meso diols with $Ph_3Bi(OAc)_2$ was rendered enantioselective by using optically active pyridinyloxazoline ligands as cocatalysts. Screening of 12 meso diols and 14 optically active pyridinyloxazolines gave enantioselectivities in the middle range up to 50.4% ee. *trans*-Cyclohexane-1,2-diol was submitted to a kinetic resolution.

Introduction

For several years organobismuth compounds[2-4] have been increasingly used in organic synthesis. Bi(V) compounds are reagents for the oxidation of alcohols, thiols, and hydrazones, and the cleavage of 1,2-diols under mild conditions.[5] Arylated Bi(V) reagents may transfer the aryl group to organic substrates such as phenols[6] or ketones.[7] Alcohols can be phenylated with triphenylbismuth diacetate in a copper-catalyzed reaction without oxidation.[8]

A special case is the monophenylation of diols with triphenylbismuth diacetate. In refluxing CH_2Cl_2, 1,n-diols (n = 2–6) are converted into the corresponding monophenyl ethers in good yields.[9-11] The chemoselectivity of this reaction is very high. Diphenylated byproducts have never been observed. Typical for this reaction is an induction period of about 2 h and a remarkable solvent dependence. In solvents other than CH_2Cl_2 the yield drops drastically.[12] Recently, Barton et al. discovered that the monophenylation of diols is catalyzed by copper(II) acetate.[12] In the presence of small amounts of $Cu(OAc)_2$ there is no induction period, the reaction now proceeds at room temperature, and the yields are higher than in the uncatalyzed reaction. Additionally, the Cu-catalyzed reaction is not confined to CH_2Cl_2 as a solvent.[12]

Scheme I



With the use of prochiral substrates and optically active copper catalysts, we tried to make this monophenylation reaction enantioselective. A typical example is the monophenylation of *meso*-cyclopentane-1,2-diol (**1a**) with $Ph_3Bi(OAc)_2$ to give the two enantiomers of 1-phenoxy-2-hydroxycyclopentane (**1b**) (Scheme I). A short account of part of this work has already been published.[13] In this paper we describe our results on the enantioselective monophenylation of diols **1a**–**13a** with $Ph_3Bi(OAc)_2$, ex-

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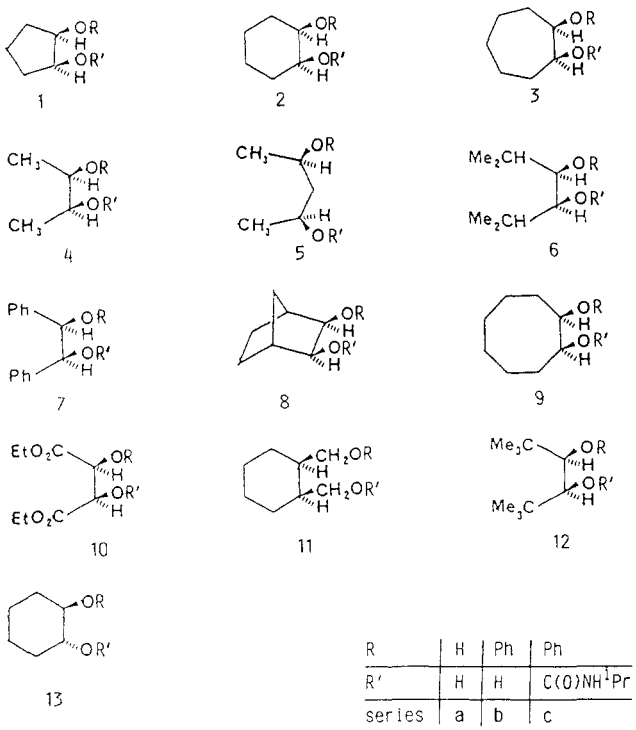
Chart I



R	H	Ph	Ph
R'	H	H	C(O)NH^{i}Pr
series	a	b	c

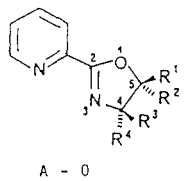
tending the concept of enantioselective catalysis with transition-metal complexes[14-16] to a new reaction type.

Synthesis of Monophenyl Ethers 1b–11b from Meso Diols 1a–11a. Appropriate prochiral substrates are meso 1,*n*-diols, which contain a plane of symmetry (**a** series in Chart I). The monophenylation removes the symmetry plane, rendering the monophenyl ethers chiral (**b** series in Chart I). The two asymmetric centers of opposite configuration lead to the two enantiomers 1*R*,*nS* and 1*S*,*nR*, only the first of which is depicted in Chart I, except for **5b**, **10b**, and **13b** which have the configurations 1*R*,3*S*, 1*S*,2*R*, and 1*R*,2*R*, respectively.

Details on the synthesis of diols **1a–12a** and a large-scale preparation of $Ph_3Bi(OAc)_2$ are given in the Experimental Section. The racemic phenyl ethers **1b–11b** were prepared from equimolar amounts of diol, $Ph_3Bi(OAc)_2$, and 3 mol % $Cu(OAc)_2$ in CH_2Cl_2 at room temperature.[17] Workup was carried out by chromatography. Ph_3Bi was eluted with the first fraction of 100 mL of CH_2Cl_2. The second fraction of 300 mL of CH_2Cl_2 contained the monophenyl ethers **1b–11b** in yields between 45 and 91%. With CH_2Cl_2 the Cu catalyst and unreacted diols were eluted so slowly that they remained on the column. Phenyl ethers **1b–11b** were purified by vacuum distillation. The chemical yields were determined after distillation. Diol **12a** could not be converted into its monophenyl ether, presumably due to steric reasons.[17]

The phenyl ethers **1b–11b** were characterized by elemental analysis, mass spectrometry, and ^1H NMR spectroscopy. **1b–11b** showed similar fragmentation patterns in the 70-eV EI mass spectrum. The molecular ion, which was found with low intensity for all compounds **1b–11b**, was followed by an intense peak at *m/e* 94, usually the base peak of the spectrum. This peak was due to the $PhOH^+$ ion which was eliminated from the molecular ion. A peak at M – 94 was not observed. The ^1H NMR spectrum of compounds **1b–11b** are given in the Experimental Section and are shown in ref 17. The chemical shifts of the H atoms of the C*H*(OH)–C*H*(OPh) moiety were found between δ 3.64 and δ 5.16 ppm, with the C*H*(OPh) signal shifted low field by 0.1–0.6 ppm with respect to the C*H*(OH) signal. Because of additional coupling with the H atom of the OH group the C*H*(OH) signal was broader and more complex than the signal of the C*H*(OPh) group. The Ph absorptions showed two multiplets at about 6.9 and 7.3 ppm in a ratio of 2:3.

Chart II



	R^1	R^2	R^3	R^4
A	H	H	H	S-CHMeEt
B	H	H	H	$CHMe_2$
C	H	H	Et	H
D	H	H	H	Et
E	H	H	H	Me
F	H	H	H	CH_2CH_2SMe
G	H	H	Ph	H
H	H	H	H	CH_2Ph
I	H	H	H	CH_2CHMe_2
K	H	H	H	CMe_3
L	Ph	H	H	CH_2OMe
M	Ph	H	H	Me
N	Ph	H	Me	H
O	H	Ph	H	Me

Enantioselective Monophenylation of Meso Diols with $Ph_3Bi(OAc)_2$. The chiral catalysts were prepared in situ from the procatalyst $Cu(OAc)_2$ and the pyridinyloxazolines A–O as optically active cocatalysts (Chart II). The pyridinyloxazoline ligands were synthesized by reacting methyl 2-pyridinecarboximidate with optically active 1,2-amino alcohols either commercially available or accessible by $LiAlH_4$ reduction of amino acids.[18] Eleven of the ligands, most of them derived from natural amino acids, have the *S* configuration at C4, and three have the *R* configuration at C4. C and D are enantiomers, C having the lower optical purity. In ligands L–O, C5 carries a phenyl substituent, making also C5 an asymmetric center. The enantiomers N and O are diastereomers with respect to M.

The asymmetric phenylations were carried out at a 3-mmol scale with 3 mol % $Cu(OAc)_2$ and a copper/ligand ratio of 1:3. The reactions were started by dissolving the components in 50 mL of dichloromethane, the standard reaction time being 15 h at room temperature. The phenoxy alcohols were isolated by SiO_2 column chromatography and distillation as described above.

The optical yields were determined by GC analysis after the phenoxy alcohols were transformed into the corresponding urethanes by reaction with isocyanates. For phenoxy alcohols **1b**, **3b–6b**, and **8b** the isopropylurethanes (c series in Chart I) and for **2b** the ethyl- or methylurethanes gave a base-line separation of the enantiomers on an optically active 50-m chirasil-L-val capillary column.[19] The retention times are given in the Experimental Section. It was not possible to obtain a base-line separation for the enantiomers of the urethanes of **7b** and **9b–11b** by this GC procedure.

On a chirasil-L-val column the urethanes of (*S*)-alcohols have longer retention times than those of (*R*)-alcohols.[19]

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Table I. Monophenylation of Diols 1a and 2a (3 mmol) with $Ph_3Bi(OAc)_2$ (3 mmol) in 50 mL of CH_2Cl_2[a]

	diol **1a**			diol **2a**		
ligand	no. of runs	% ee (config)[b]	yield,[c] %	no. of runs	% ee (config)[b]	yield,[c] %
A	5	49.3–48.5 (1*R*,2*S*)	56	3	31.9–29.0 (1*R*,2*S*)	43
B	2	50.4; 49.6 (1*R*,2*S*)	56	4	27.4–26.0 (1*R*,2*S*)	35
C	2	41.6; 40.9 (1*S*,2*R*)	54	3	19.2–17.9 (1*S*,2*R*)	42
D	2	47.1; 46.5 (1*R*,2*S*)	50	2	21.5; 21.0 (1*R*,2*S*)	42
E	2	41.8; 39.6 (1*R*,2*S*)	48	2	15.3; 14.3 (1*R*,2*S*)	45
F	3	31.5–31.3 (1*R*,2*S*)	50	2	13.5; 12.4 (1*R*,2*S*)	35
G	2	36.3; 35.9 (1*S*,2*R*)	50	2	15.0; 14.1 (1*S*,2*R*)	49
H	2	43.7; 43.1 (1*R*,2*S*)	59	3	16.9–16.6 (1*R*,2*S*)	36
I	2	44.9; 44.3 (1*R*,2*S*)	54	2	14.3; 12.3 (1*R*,2*S*)	38
K	3	23.6–20.6 (1*R*,2*S*)	39			
L	2	22.7; 22.6 (1*R*,2*S*)	50			
M	2	22.6; 22.1 (1*S*,2*R*)	50	2	11.7; 10.9 (1*R*,2*S*)	42
N	2	42.2; 41.6 (1*S*,2*R*)	53	2	17.1; 16.1 (1*S*,2*R*)	40
O	2	42.7; 42.6 (1*R*,2*S*)	53	2	20.3; 19.4 (1*R*,2*S*)	38

[a] Catalyst: 3 mol % $Cu(OAc)_2$ and ligands A–O (9 mol %). Reaction time = 15 h; T = 22 °C. [b] The carbon atom bearing the OPh group is defined as C1. [c] Average.

The configurations of the alcohols **1b–6b** and **8b**, obtained in the monophenylation, were assigned tentatively on this basis. So, the (1*R*,*nS*)-phenoxy alcohols **1b–6b** and **8b**, having the *S* configuration at the asymmetric center bearing the OH group, are assumed to have longer retention times than the (1*S*,*nR*)-isomers.

The ee of **7b** was determined by HPLC, using a chiral hypersil-Pirkle-I column.[20] Elution of a THF solution of **7b** with hexane/2-propanol (99:1) allowed a base-line separation of the enantiomers. At this stationary phase, (*R*)-alcohols have longer retention times than (*S*)-alcohols,[21] so the (1*S*,2*R*)-isomer of **7b** should be eluted after the (1*R*,2*S*)-isomers.

The results of the monophenylation of diols **1a** and **2a** are summarized in Table I. Each experiment was carried out several times (at least twice). The chemical yields were in the range from 35 to 59%, significantly lower than those obtained with $Cu(OAc)_2$ catalysts unmodified with further ligands, which for comparison are given in the Experimental Section. The best optical yields were obtained with the cocatalysts A and B, A giving also the highest enantiomeric excess with other diols. In the monophenylation of cyclopentane-1,2-diol (**1a**) with $Ph_3Bi(OAc)_2$ (Scheme I) up to 50.4% ee was achieved.

There is a correlation between the configuration at C4 of the pyridinyloxazoline ligand and the product configuration. The *S* configuration at C4 of the ligand induces the 1*R*,*nS* configuration in the phenyl ethers, and the *R* configuration at C4 induces the 1*S*,*nR* product configuration. An exception is ligand M. Having the *S* configuration at C4 and at C5, it gives surprisingly (1*S*,2*R*)-**1b** and expectedly (1*R*,2*S*)-**2b** in the phenylation of **1a** and **2a**, respectively.

There is no clear trend between the nature of the substituents and the substitution patterns of the oxazoline ring on the one hand and the enantiomeric excess of the product on the other hand. In the monophenylation of diol **1a** with pyridinyloxazoline ligands, large substituents at C4 such as CHMeEt, $CHMe_2$, or CH_2CHMe_2 in A, B, and I with 44–50% induced a higher enantiomeric excess than ligands with smaller substituents at C4 (Table I). However, the *tert*-butyl-substituted ligand K gave a drastically reduced enantiomeric excess of 22% ee, contrary to the assumption that the bulk of the C4 substituent is the most significant factor for high enantiomeric excess.

Although the pyridinyloxazoline ligands are assumed to coordinate via pyridine N and oxazoline N, substitution at C5 of the oxazoline ring has an influence on the enantioselectivity. Phenylation of **1a** with the enantiomers N and O gave nearly the same optical yield of 42% ee with the opposite product configuration (Table I). On the other hand, with M, the diastereomer to N and O, the optical induction dropped to about 22% ee. Ligand E, with only H substituents at C5, gave an optical yield of about 41% ee, lying in the range of Ligands N and O. So, it is the trans phenyl substituent in M which caused the decrease in enantioselectivity. The same trends were observed in the phenylation of cyclohexane-1,2-diol (**2a**) (Table I).

Table II. Monophenylation of Diols 3a–7a (3 mmol) with $Ph_3Bi(OAc)_2$ (3 mmol) in 50 mL of CH_2Cl_2[a]

diol	ligand	no. of runs	% ee (config)[b]	yield,[c] %
3a	A	2	38.7; 36.3 (1*R*,2*S*)	58
	B	2	37.3; 34.3 (1*R*,2*S*)	51
	C	2	28.8; 28.0 (1*S*,2*R*)	63
4a	A	2	33.7; 29.0 (1*R*,2*S*)	44
	B	2	24.5; 24.2 (1*R*,2*S*)	40
	C	2	17.0; 15.7 (1*S*,2*R*)	42
5a	A	2	38.1; 37.5 (1*R*,3*S*)	42
	B	2	30.4; 30.3 (1*R*,3*S*)	42
	C	2	30.8; 29.8 (1*S*,3*R*)	44
6a	A	2	37.1; 36.8 (1*S*,2*R*)	36
	B	2	28.8; 28.7 (1*S*,2*R*)	36
	C	2	24.6; 23.4 (1*R*,2*S*)	38
7a	A	2	20.0; 15.3 (1*S*,2*R*)	28
	B	2	18.5; 18.9 (1*S*,2*R*)	28
	C	2	14.6; 8.8 (1*R*,2*S*)	30

[a] Catalyst: 3 mol % $Cu(OAc)_2$ and ligands A–C (9 mol %). Reaction time = 15 h; T = 22 °C. [b] The carbon atom bearing the OPh group is defined as C1. [c] Average.

Also, in the monophenylation of meso diols, optically active ligands were used which were not of the pyridinyloxazoline type, such as (*R*,*R*)-(−)-diop[22] (83% of racemic **2b** from **2a**; two runs), the Schiff base of salicylaldehyde and (*R*)-(+)-1-phenylethylamine[23] (83% of racemic **2b** from

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2a; five runs), the Schiff base of salicylaldehyde and (S)-(−)-phenylalanine[23] (81% of racemic 2b from 2a; two runs), the Schiff base of 2-pyridinealdehyde and (R,R,-R,R)-(−)-aminomethylpinane[24] (56% of 3.4% ee 1S,2R of 1b from 1a; two runs), commercial (−)-spartein (65% of racemic 1b from 1a; two runs), (R)-(−)-benzylethylenediamine[25] (67% of racemic 1b from 1a; two runs), (4R)-(−)-2-pyridyl-4-carbethoxy-1,3-thiazolidine[26] (57% of 2.8% ee (1R,2S)-2b from 2a, four runs), and (R,R,R,R)-(+)-N-(3-methylpinanyl)-2-(2-pyridyl)-thiazolidine-4-one[27] (65% of racemic 1b from 1a; two runs). It is particularly interesting to note that (−)-diop, the most widely used ligand in transition-metal-catalyzed enantioselective synthesis,[14-16] in the monophenylation of diols gives racemic products. The reason for this probably is that the Bi(V) reagent,[5] present in a high concentration, oxidizes the phosphorus(III) species such as (−)-diop, present in only low concentration, to phosphine oxides, which no longer are good ligands. Oxazolines, however, are known to be remarkably stable against oxidizing agents.[28] Therefore, pyridinyloxazolines are appropriate ligands for the enantioselective monophenylation of diols with $Ph_3Bi(OAc)_2$ under oxidizing conditions.

An undesired side effect in the catalytic asymmetric phenylation is the drop in the chemical yield compared to the reaction catalyzed by $Cu(OAc)_2$ only. Therefore, detailed investigations were carried out with diols 1a and 2a, varying the usual workup of the reaction mixtures. In a first variant, the chromatography of the reaction mixture was carried out as described before, eluting the first two fractions with 100 and 300 mL CH_2Cl_2. Then, elution was continued with acetone, eluting $Ph_3Bi(OAc)_2$ and diol, from which the diol could be isolated by vacuum distillation. In a second variant, the reaction mixture was distilled without chromatography giving unreacted diol and monophenyl ether as volatile products. Both variants showed that after stoichiometric amounts of $Ph_3Bi(OAc)_2$ and diols 1a or 2a were reacted under standard conditions, 1a and 2a were present in the reaction mixture in amounts corresponding to the difference of diol minus monophenyl ether. Therefore, the low yields in the enantioselective monophenylation are not caused by side reactions consuming the diol but by an inhibition of the reaction, with the diol still being present in the reaction mixture. This is supported by the fact that an increase of the reaction time from 15 to 120 h does not increase the yield because the reaction has come to a stop prior to a reaction time of 15 h. The deactivation must involve $Ph_3Bi(OAc)_2$, $Cu(OAc)_2$, and the pyridinyloxazoline ligand, as after these components in CH_2Cl_2 are stirred for 1 h at room temperature, there was no reaction on the addition of the diol, which could be isolated in nearly quantitative yield. However, if a mixture of the diol, $Cu(OAc)_2$, and the pyridinyloxazoline ligand was treated with $Ph_3Bi(OAc)_2$ after an aging period of 1 h, the reaction proceeded as usual.

The attempted enantioselective phenylation of the bicyclic diol 8a gave an unexpected result. Whereas the racemic phenyl ether 8b could be obtained with a $Cu(OAc)_2$ catalyst in 49% yield, in the presence of a $Cu(OAc)_2$ catalyst modified with a pyridinyloxazoline ligand no phenyl ether 8b was detected in the reaction product. A cleavage of the central C–C bond had occurred resulting in the formation of *cis*-cyclopentane-1,3-dicarbaldehyde, which was characterized by its spectroscopic and analytical data.[29,30]

Table III. Monophenylation of Diol 2a (3 mmol) with $Ph_3Bi(OAc)_2$ (3 mmol) in 50 mL of CH_2Cl_2[a]

$Cu(OAc)_2$:2a	no. of runs	% ee	yield,[b] %
1:10000	2	14.7; 13.7	57
1:1000	2	18.3; 16.9	49
1:100	2	31.4; 30.8	47
1:33	3	31.9–29.0	43
1:10	2	25.0; 24.8	40

[a] Variation of the catalyst concentration (catalyst: $Cu(OAc)_2$:A = 1:3). Reaction time = 15 h; T = 22 °C. [b] Average.

To find optimized conditions for the standard procedure of the monophenylation reaction, a couple of parameters was varied by using as substrates diol 2a, which is most easily accessible, and 1a, which gives the best optical yields. Variation of the $Cu(OAc)_2$/ligand ratio did not change the optical yields significantly. With 48–49% ee for 1b, the enantiomeric excess was constant for $Cu(OAc)_2$/A ratios from 1:3 to 1:7; it dropped slightly to 45% ee for the ratios 1:1 and 1:10. The same trend was observed for 2b by using $Cu(OAc)_2$/B catalysts.[17]

The results obtained by variation of the $Cu(OAc)_2$/diol ratio are summarized in Table III for 2a, showing that ratios of 1:33 to 1:100 were best. The decrease of the enantioselectivity at $Cu(OAc)_2$/2a ratios of 1:10 probably was due to the fact that the reaction mixtures at such high catalyst concentrations were heterogeneous, whereas the decrease at $Cu(OAc)_2$/2a ratios of 1:1000 and 1:10000 could be due to a rate increase of the uncatalyzed reaction of 2a with $Ph_3Bi(OAc)_2$.

Lowering the reaction temperature to 0 °C did not increase the optical induction. At −10 °C the reaction rate became too slow for practical application.[17] With substoichiometric amounts of $Ph_3Bi(OAc)_2$ a small increase of the optical induction was observed. In the phenylation of 1a with 0.5 mol equiv of $Ph_3Bi(OAc)_2$ and A as the cocatalyst, the average ee rose from 48.7 to 50.7%.

The investigations of Barton et al.[12] had shown that a series of solvents was suitable for the Cu-catalyzed monophenylation reaction. Surprisingly, this was no longer true for the enantioselective variant in the presence of pyridinyloxazoline cocatalysts. Whereas racemic 1b was obtained in about 65–75% yield from 1a, $Ph_3Bi(OAc)_2$, and $Cu(OAc)_2$ in the solvents C_6H_6, $CHCl_3$, CH_2Cl_2, and THF, on the addition of an oxazoline ligand 1b was formed only in the solvent CH_2Cl_2. Also, there was no product formation on carrying out the monophenylation in air, while the racemic synthesis was hardly influenced by access of air.[17]

Kinetic Resolution of *trans*-Cyclohexane-1,2-diol (13a). The monophenylation of diols with $Ph_3Bi(OAc)_2$ in the presence of chiral copper catalysts was also applied to the kinetic resolution of *trans*-cyclohexane-1,2-diol (13a). Reaction of a racemic mixture of *trans*-cyclohexane-1,2-diol (13a) with less than 1 equiv of $Ph_3Bi(OAc)_2$ in the presence of an optically active $Cu(OAc)_2$/pyridinyloxazoline catalyst resulted in the formation of the enantiomeric phenyl ethers 13b[11,31] in a ratio different from

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Table IV. Kinetic Resolution in the Monophenylation of Diol 13a (4 mmol) with $Ph_3Bi(OAc)_2$ in 50 mL of CH_2Cl_2. Chemical and Optical Yields of 13a and 13b[a]

				13b		13a	
13a:(Bi)	time, h	*T*, °C	no. of runs	% ee[b]	yield,[d,f] %	% ee[c]	yield,[e,f] %
1:0.1	95	0	2	50.9; 49.1	78	8.5; 3.9	93
1:0.3	94	0	2	44.9; 44.5	74	21.1; 18.7	77
1:0.5	17	22	3	37.1–34.8	71	17.7–16.5	56
1:0.5	90	0	2	39.7; 39.1	78	39.2; 37.4	54
1:0.7	97	0	2	24.5; 24.1	52	44.4; 44.0	47
1:0.9	94	0	4	7.2–5.6	51	65.5–59.4	26

[a] (Bi) = $Ph_3Bi(OAc)_2$. [b] Predominant configuration 1R,2R. [c] Predominant configuration 1S,2S. [d] Based on the amount $Ph_3Bi(OAc)_2$ used. [e] Based on the amount **13a** used. [f] Average.

1:1, the unreacted diol **13a** being also enriched in one enantiomer. As cocatalyst the pyridinyloxazoline A was used, the best ligand in the monophenylation of the meso diols.

The reaction was carried out with a $Cu(OAc)_2$/A ratio of 1:3 as described above for the meso diols, except that reaction times were 90–97 h at 0 °C. The monophenyl ether **13b** was isolated by silica gel column chromatography with CH_2Cl_2; then acetone eluted the unreacted cyclohexane-1,2-diol (**13a**). Both products were purified by vacuum sublimation.

The optical yields were determined by GC of the isopropylurethane **13c** and the diisopropylurethane of **13a**, respectively, on a 50-m chirasil-L-val column. The configuration of the products in this case could easily be determined by polarimetry because the optical rotation of (+)- and (−)-cyclohexane-1,2-diol (**13a**) is known.[32]

The results of the kinetic resolution are summarized in Table IV. It is obvious that with an increase of the $Ph_3Bi(OAc)_2$/**13a** ratio the optical yield of the product **13b** decreases whereas that of the cyclohexanediol **13a** increases. The best enantioselectivity obtained for cyclohexane-1,2-diol (**13a**) was 65.5% ee in a chemical yield of 26%. On the other hand, the highest optical yield for the phenyl ether **13b**, isolated in 8% yield based on **13a**, was 50.9% ee. The ratio of the rate constants of the two enantiomers of **36a** is estimated to be approximately 4:1.[17]

Unlike the phenylation of the meso diols, the ee of the kinetic resolution of the trans diol **13a** is temperature-dependent. For **13a**/$Ph_3Bi(OAc)_2$ = 1:0.5, lowering the temperature from 22 to 0 °C, the ee of **13a** increases from 17.1 to 38.3% and the ee of **13b** from 35.2 to 39.4% (runs 3 and 4, Table IV). Therefore, all the other experiments were carried out at 0 °C.

The chemical yields of unreacted **13a** in the kinetic resolution (Table IV) again demonstrate the inhibition of the reaction before completion, discussed above. In all the experiments more unreacted **13a** was isolated as expected on the basis of the quantities of $Ph_3Bi(OAc)_2$ used.

Experimental Section

Synthesis of Diols 1a–13a. *meso*-1,2-Diphenylethane-1,2-diol (**7a**), *meso*-pentane-2,4-diol (**5a**), *cis*-1,2-bis(hydroxymethyl)-cyclohexane (**11a**), and *trans*-cyclohexane-1,2-diol (**13a**) were commercial products. *cis*-Cyclohexane-1,2-diol (**2a**),[33] *cis*-cycloheptane-1,2-diol (**3a**),[33] *cis*-cyclooctane-1,2-diol (**9a**),[33] and *exo-cis*-bicyclo[2.2.1]heptane-2,3-diol (**8a**)[30] were synthesized by $KMnO_4$ oxidation of the corresponding *cis*-alkenes. *meso*-Butane-2,3-diol (**4a**)[34] and *cis*-cyclopentane-1,2-diol (**1a**)[35,36] were prepared by cis-hydroxylation of *cis*-2-butene and cyclopentene, respectively, with iodine and silver acetate in aqueous acetic acid. *meso*-Diethyl tartrate **10a** was obtained by esterification of *meso*-tartaric acid.[37] *meso*-2,5-Dimethylhexane-3,4-diol (**6a**)[38] and *meso*-2,2,5,5-tetramethylhexane-3,4-diol (**12a**) were synthesized by $LiAlH_4$ reduction of the commercial racemic ketones 2,5-dimethyl-4-hydroxy-3-hexanone and 4-hydroxy-2,2,5,5-tetramethyl-3-hexanone.[38]

Synthesis of Triphenylbismuth Diacetate. The synthesis of $Ph_3Bi(OAc)_2$ was carried out according to a modified literature procedure.[39] In a 5-L beaker, AgOAc (25.0 g, 0.150 mol) was dissolved in 3.5 L of water. After the addition of a solution of 38.5 g (0.075 mol) of Ph_3BiCl_2,[40] obtained from triphenylbismuth,[41] in 1 L of CH_2Cl_2, the solution was stirred for 5 h. The AgCl precipitate was filtered off and washed with CH_2Cl_2. The organic phase was separated and dried over $MgSO_4$. After evaporation of the solvent the yellow-brown residue was dissolved in 1.5 L of boiling toluene. Petroleum ether (2 L) was added. After crystallization at −30 °C colorless crystals were obtained that were washed with petroleum ether and dried: yield 35.2 g (84%); mp 169–173 °C.

General Procedure for the Synthesis of Monophenyl Ethers 1a–11a. $Ph_3Bi(OAc)_2$ (1.68 g, 3.00 mmol), one of the diols **1a–11a** (3 mmol), and $Cu(OAc)_2$ (16.3 mg, 0.09 mmol) were dissolved in 50 mL of CH_2Cl_2 and stirred for 5 h at room temperature. Subsequently, the mixture was chromatographed on a 14 × 2 cm silica column with CH_2Cl_2. The first 100-mL eluent was discarded. The next 300-mL eluent contained the phenyl ethers **1b–11b** as yellow oils. High vacuum Kugelrohr distillation afforded **1b–11b** as colorless liquids. The chemical yield was determined by weight after distillation.

1b:[11] colorless oil; yield 69%; bp 110 °C (0.1 Torr); ^1H NMR (250 MHz, internal TMS, $CDCl_3$) δ 1.50–2.13 (m, 6 H), 2.41 (s, br, 1 H), 4.24 (m, 1 H), 4.55 (m, 1 H), 6.88, 7.27 (2 m, 5 H); MS (70 eV) *m/e* 178 (M^+, 25), 138 (3), 94 (100). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; M_r, 178.23. Found: C, 73.95; H, 7.80.

2b:[11] colorless oil; yield 87%; bp 60 °C (10^{-3} Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 1.31, 1.67, 1.87 (3m, 8 H), 2.14 (d, 1 H), 3.94 (m, 1 H), 4.31 (m, 1 H), 6.94, 7.29 (2m, 5 H); MS (70 eV) *m/e* 192 (M^+, 100), 94 (76). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39; M_r, 192.26. Found: C, 74.96; H, 8.51.

3b: colorless oil; yield 76%; bp 70 °C (10^{-3} Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 1.35–2.15 (m, 10 H), 2.41 (s, br, 1 H), 4.10 (m, 1 H), 4.32 (dt, 1 H), 6.91, 7.28 (2m, 5 H); MS (70 eV) *m/e* 206 (M^+, 10), 94 (100). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80; M_r, 206.29. Found: C, 75.06; H, 8.55.

4b: colorless oil; yield 84%; bp 90 °C (0.1 Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 1.25, 1.28 (2d, 6 H), 2.05 (d, 1 H), 4.03 (m, 1 H), 4.34 (dq, 1 H), 6.93, 7.27 (2m, 5 H); MS (70 eV) *m/e* 166 (M^+, 27), 121 (27), 94 (100). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49; M_r, 166.22. Found: C, 72.07; H, 8.48.

5b: colorless oil; yield 87%; bp 105 °C (0.1 Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 1.23, 1.31 (2d, 6 H), 1.70, 1.96 (2m, 2 H), 2.63 (s, br, 1 H), 4.05 (m, 1 H), 4.59 (m, 1 H), 6.96, 7.28 (2m, 5 H); MS

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Table V. GC Parameter for the Urethanes 1c–6c and 13c[a]

urethane	p, bar	T, °C (column)	retentn time, min
1c	2.0	135	31.6 (1S,2R), 33.2 (1R,2S)
2[b]	2.0	135	42.5 (1S,2R), 44.0 (1R,2S)
2[c]	2.0	135	36.0 (1S,2R), 36.9 (1R,2S)
3c	2.0	150	43.2 (1S,2R), 44.1 (1R,2S)
4c	1.7	110	44.3 (1S,2R), 45.4 (1R,2S)
5c	2.0	115	48.9 (1S,3R), 50.5 (1R,3S)
6c	2.0	140	20.3 (1S,2R), 21.2 (1R,2S)
13c	2.0	140	50.4 (1R,2R), 51.5 (1S,2S)
13[d]	2.0	135	12.3 (1S,2S), 13.1 (1R,2R)

[a] 50-m chirasil-L-val capillary column; H_2 gas; injector temperature 260 °C. [b] Methylurethane. [c] Ethylurethane. [d] diisopropylurethane of **13a**.

(70 eV) *m/e* 180 (M^+, 26), 121 (5), 94 (100), 45 (14). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; M_r, 180.25. Found: C, 71.31; H, 8.80.

6b: colorless oil; yield 82%; bp 85 °C (10^{-3} Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 0.90, 0.99, 1.02, 1.07 (4d, 12 H), 1.68 (d, 1 H), 1.95, 2.19 (2m, 2 H), 3.64 (m, 1 H), 4.20 (dd, 1 H), 6.95, 7.26 (2m, 5 H); MS (70 eV) *m/e* 222 (M^+, 10), 149 (25), 107 (17), 94 (100). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97; M_r, 222.33. Found: C, 75.13; H, 9.82.

7b:[11] colorless oil; yield 45%; bp 150 °C (10^{-3} Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 2.38 (d, 1 H), 5.08 (dd, 1 H), 5.16 (d, 1 H), 6.74–7.43 (m, 15 H); MS (70 eV) *m/e* 290 (M^+, 1), 184 (70), 183 (100), 94 (23). Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25; M_r, 290.37. Found: C, 82.42; H, 6.31.

8b: colorless liquid; yield 49%; bp 85 °C (10^{-3} Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 1.16, 1.55, 1.91, 2.35 (4m, 8 H), 2.96 (s, br, 1 H), 3.89 (dd, br, 1 H), 4.13 (dd, 1 H), 6.94, 7.29 (2m, 5 H); MS (70 eV) *m/e* 204 (M^+, 29), 120 (7), 111 (9), 94 (100), 77 (18). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; M_r, 204.27. Found: C, 76.61; H, 7.95.

9b: colorless liquid; yield 91%; bp 90 °C (10^{-3} Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 1.39–2.26 (m, 12 H), 2.54 (d, br, 1 H), 4.07 (m, 1 H), 4.47 (m, 1 H), 6.90, 7.28 (2 m, 5 H); MS (70 eV) *m/e* 220 (M^+, 8), 94 (100). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15; M_r, 220.31. Found: C, 76.21; H, 8.75.

10b: colorless liquid; yield 50%; bp 120 °C (10^{-3} Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 1.29, 1.34 (2t, 6 H), 3.32 (d, 1 H), 4.15–4.44 (m, 4 H), 4.77 (dd, 1 H), 5.02 (d, 1 H), 6.97, 7.29 (2 m, 5 H); MS (70 eV) *m/e* 282 (M^+, 70), 191 (26), 180 (44), 179 (33), 147 (10), 143 (34), 133 (44), 123 (20), 119 (43), 115 (18), 107 (93), 94 (100), 77 (48). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43; M_r, 282.30. Found: C, 59.20; H, 6.46.

11b: colorless liquid; yield 91%; bp 100 °C (10^{-3} Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 1.31–1.85 (m, 8 H), 1.99, 2.17, 2.34 (3 m, 3 H), 3.59 (m, 2 H), 3.91, 4.12 (2dd, 2 H), 6.91, 7.27 (2 m, 5 H); MS (70 eV) *m/e* 220 (M^+, 5), 127 (2), 109 (11), 94 (100). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15; M_r, 220.31. Found: C, 75.71; H, 9.07.

Pyridinyloxazoline Ligands A–O. The synthesis of the pyridinyloxazoline ligands A–O is described in ref 18.

Enantioselective Monophenylation of Meso 1,*n*-Diols. The enantioselective phenylation of 1,*n*-diols with $Ph_3Bi(OAc)_2$ followed the general procedure given above with degassed CH_2Cl_2 under the exclusion of air. The standard procedure was carried out with 3 mol % $Cu(OAc)_2$ (16.3 mg, 0.09 mmol) and 9 mol % ligands A–O (0.27 mmol), respectively.

Determination of the Enantiomeric Purity of Monophenyl Ethers 1b–8b. In a 3-mL reacti-vial, the distilled alcohol (0.1 mL) and isopropyl isocyanate (0.4 mL) were kept 15 h at 70 °C. After the solution was cooled to room temperature, the excess of isopropyl isocyanate was removed. The urethane left behind was dissolved in 1 mL of CH_2Cl_2. This solution was used for a GC analysis with a 50-m chirasil-L-val glass capillary.[19] Table V contains the GC parameters and the retention times. For phenyl ether **2b**, ethyl isocyanate at 70 °C or methyl isocyanate at room temperature is to be preferred. Their derivatives give better base-line separation than the isopropylurethane. The enantiomers of **7b**, dissolved in THF, were separated by HPLC on a 500 × 46 mm hypersil-Pirkle-I column[20] with hexane/propan-2-ol (99:1). The enantiomers gave base-line separation with retention times of 16.6 and 17.4 min (flux 2 mL/min; 190 bar).

***cis*-Cyclopentane-1,3-dicarbaldehyde.** Following the general monophenylation procedure with *exo-cis*-bicyclo[2.2.1]heptane-2,3-diol (**8a**) after column chromatography, a yellow oil was obtained which on Kugelrohr distillation at 50 °C, (10^{-3} Torr) gave 79% of a colorless liquid of *cis*-cyclopentane-1,3-dicarbaldehyde:[29,42,43] colorless liquid; yield 79%; bp 50 °C (10^{-3} Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 1.89–2.35 (m, 6 H), 2.89 (m, 2 H), 9.64 (d, *I* = 2.8 Hz, 2 H); MS (12 eV) *m/e* 126 (M^+, 4) 98 (100), 57 (38); IR (film): 2722, 1726 cm^{-1} (lit.[43] 2720, 1720 cm^{-1}). Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99; M_r, 126.16. Found: C, 64.98; H, 7.62. Bis((2,4-dinitrophenyl)hydrazone): mp 223–225 °C (lit.[29] mp 225–226 °C).

***trans*-1-Phenoxy-2-hydroxycyclohexane (13b).**[11,31] The synthesis of **13b** was carried out following the general procedure given for **2b**. **13b**: colorless crystals; yield 87%; mp 80–82 °C; sublimation 60 °C (10^{-3} Torr); ^1H NMR (250 MHz, $CDCl_3$) δ 1.34, 1.76, 2.14 (3 m, 8 H), 2.64 (s, br, 1 H), 3.72 (m, 1 H), 4.00 (m, 1 H), 6.95, 7.27 (2 m, 5 H); MS (70 eV) *m/e* 192 (M^+, 11), 94 (100). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39; M_r, 192.26. Found: C, 74.33; H, 8.34.

Kinetic Resolution of *trans*-Cyclohexane-1,2-diol (13a). *trans*-Cyclohexane-1,2-diol (**13a**) (0.47 g, 4.00 mmol), $Cu(OAc)_2$ (10.9 mg, 0.06 mmol), pyridinyloxazoline A (36.8 mg, 0.18 mmol), and $Ph_3Bi(OAc)_2$ were dissolved in 50 mL of CH_2Cl_2 under the conditions indicated in Table IV. Subsequently, the products were isolated by chromatography on a 14 × 2 cm silica gel column. The first fraction of 100 mL of CH_2Cl_2 was discarded. The second fraction of 300 mL of CH_2Cl_2 contained the crude phenyl ether **13b**. Further elution with acetone (150 mL) gave the crude *trans*-cyclohexane-1,2-diol (**13a**). Both products were purified by vacuum sublimation at 10^{-3} Torr: **13a**, 40 °C; **13b**, 60 °C.

The optical purity of **13a** and **13b** was determined by GC analysis after transformation into the corresponding isopropylurethanes as described before (Table V).

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG for support of this work. P.W. thanks the Stiftung Volkswagenwerk for a Kekulé-Stipendium.

Registry No. **1a**, 5057-98-7; **1b**, 118599-88-5; (1*R*,2*S*)-**1b**, 118711-13-0; (1*S*,2*R*)-**1b**, 118711-14-1; (1*S*,2*R*)-**1c**, 118599-89-6; (1*R*,2*S*)-**1c**, 118711-15-2; **2a**, 1792-81-0; **2b**, 118599-90-9; (1*R*,2*S*)-**2b**, 118711-16-3; (1*S*,2*R*)-**2b**, 118711-17-4; (1*S*,2*R*)-**2c** (methylurethane deriv.), 118599-91-0; (1*R*,2*S*)-**2c** (methylurethane deriv.), 118711-18-5; (1*S*,2*R*)-2c (ethylurethane deriv.), 118599-92-1; (1*R*,2*S*)-**2c** (ethylurethane deriv.), 118711-19-6; **3a**, 42114-72-7; **3b**, 118599-93-2; (1*R*,2*S*)-**3b**, 118711-20-9; (1*S*,2*R*)-**3b**, 118711-21-0; (1*S*,2*R*)-**3c**, 118599-94-3; (1*R*,2*S*)-**3c**, 118711-22-1; **4a**, 5341-95-7; **4b**, 118599-95-4; (1*R*,2*S*)-**4b**, 118711-23-2; (1*S*,2*R*)-**4b**, 118711-24-3; (1*S*,2*R*)-**4c**, 118599-96-5; (1*R*,2*S*)-**4c**, 118599-97-6; **5a**, 3950-21-8; **5b**, 118599-98-7; (1*R*,3*S*)-**5b**, 118711-25-4; (1*S*,3*R*)-**5b**, 118711-26-5; (1*S*,3*R*)-**5c**, 118599-99-8; (1*R*,3*S*)-**5c**, 118600-00-3; **6a**, 22520-38-3; **6b**, 118600-01-4; (1*S*,2*R*)-**6b**, 118711-27-6; (1*R*,2*S*)-**6b**, 118711-28-7; (1*S*,2*R*)-**6c**, 118600-02-5; (1*R*,2*S*)-**6c**, 118600-03-6; **7a**, 579-43-1; **7b**, 118600-04-7; (1*S*,2*R*)-**7b**, 118711-29-8; (1*R*,2*S*)-**7b**, 118711-30-1; **8a**, 16329-23-0; **8b**, 118600-05-8; **9a**, 27607-33-6; **9b**, 118600-06-9; **10a**, 21066-72-8; **10b**, 118600-07-0; **11a**, 15753-50-1; **11b**, 118600-08-1; **12a**, 118600-09-2; **13a**, 54383-22-1; (1*S*,2*S*)-**13a**, 57794-08-8; **13b**, 118600-10-5; (1*R*,2*R*)-**13b**, 118711-31-2; (1*R*,2*R*)-**13c**, 118600-11-6; (1*S*,2*S*)-**13c**, 118711-32-3; (1*S*,2*S*)-**13c** (diisopropylurethane deriv.), 118600-12-7; (1*R*,2*R*)-**13c** (diisopropyluretane deriv.), 118711-33-4; A, 118600-13-8; B, 108915-04-4; C, 117408-95-4; D, 108915-06-6; E, 108915-05-5; F, 108915-09-9; G, 117408-99-8; H, 108915-08-8; I, 108915-07-7; K, 117408-98-7; L, 117409-06-0; M, 118600-14-9; N, 118600-15-0; O, 108915-10-2; $Ph_3Bi(OAc)_2$, 7239-60-3; AgOAc, 563-63-3; Ph_3BiCl_2, 594-30-9; $Cu(OAc)_2$, 142-71-2; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; bicyclo[2.2.1]hept-2-ene, 498-66-8; *cis*-2-butene, 590-18-1; cyclopentene, 142-29-0; *cis*-cyclopentasne-1,3-dicarbaldehyde, 10283-91-7.

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