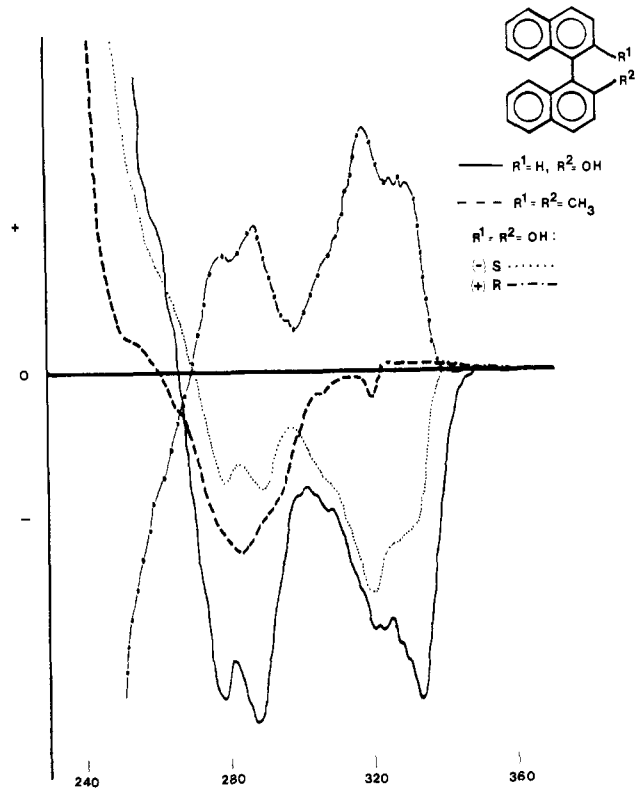

Figure 2. CD spectra in dioxane.

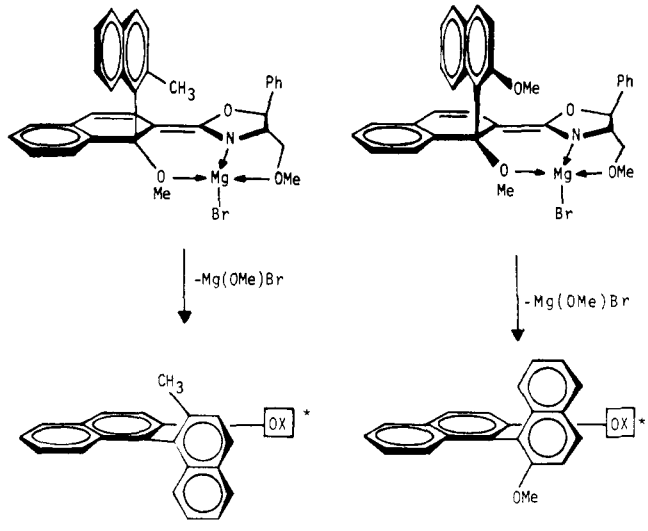

Figure 3.

MeOH) to the hydroxy ether **16**.[17] Cleavage, using boron tribromide (−78 °C, CH_2Cl_2), gave the (*R*)(+)-diol **17** which exhibited virtually mirror image Cotton curves with the (*S*)(−) enantiomer (Figure 2). The optical rotation of (+)-**17**, when compared to the known rotation of (−)-**17**, indicated ~100% ee, once again the result of enantiomeric enrichment in going from **5** (R = MeO) to **7** (R = MeO) (Table I). The absolute configurations of **7** (R = H, Me, MeO) and **13** were further substantiated from their CD spectra (Figure 1).

A preliminary rationalization of the sense of asymmetric coupling (**4** → **5**) can be advanced by examining the initially formed adducts (Figure 3), which after loss of Mg(OMe)Br leads to the observed chiral binaphthyls **5**. For the H and Me substituted systems, the approach of the naphthalene Grignard reagent will be most accessible with the unsubstituted ring at the maximum distance from the 5-phenyl substituent in the oxazoline. For the methoxy-substituted naphthalene, chelation with the magnesium appears to override the steric effect and leads to the observed opposite configuration. Further experiments will need to be performed in order to gain additional insight into this process.

Acknowledgment. Financial assistance by the Army Research Office and the National Science Foundation is gratefully acknowledged.

Registry No. 1, 883-21-6; **2**, 80409-51-4; **3**, 80409-53-6; **4**, 80409-54-7; **5** (R = H) isomer 1, 80409-55-8; **5** (R = H) isomer 2, 80409-56-9; **5** (R = Me) isomer 1, 80409-57-0; **5** (R = Me) isomer 2, 80409-58-1; **5** (R = MeO) isomer 1, 80409-59-2; **5** (R = MeO) isomer 2, 80409-60-5; **6** (R = H) isomer 1, 80409-61-6; **6** (R =H) isomer 2, 80446-25-9; **6** (R = Me) isomer 1, 80409-62-7; **6** (R = Me) isomer 2, 80446-26-0; **6** (R = MeO) isomer 1, 80409-63-8; **6** (R = MeO) isomer 2, 80446-27-1; **7** (R = H), 80409-64-9; **7** (R = Me), 80409-65-0; **7** (R = MeO), 80409-66-1; **8**, 80409-67-2; **9**, 80409-68-3; **10**, 35216-79-6; **11**, 80317-68-6; **12**, 80409-69-4; **13**, 32587-64-7; **14**, 80409-70-7; **15**, 80409-71-8; **16**, 79547-82-3; **17**, 18531-94-7; (+)-1-methoxy-2-amino-3-phenyl-3-hydroxypropane, 51594-34-4.

Chiral Leaving Groups Induce Asymmetry in Syntheses of Binaphthyls in Nucleophilic Aromatic Substitution Reactions[1]

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The binaphthyl unit has enjoyed extensive use in the design and syntheses of chiral hosts for resolving amino acids by complexation[2], of chiral catalysts for organic carbon–carbon[3] or carbon–hydrogen[4] bond-making reactions, and of chiral reagents for reducing ketones to optically active alcohols.[5] The degrees of chiral recognition, induction, and transfer observed for these binaphthyl compounds have been among the highest reported and have been attributed to the rigidity and freedom from conformational ambiguity in the complexes or transition states involved.[2-5] In some cases, the direction of the configurational bias has been rationalizable on stereoelectronic grounds.[2-5] These facts stimulated our search for methods of synthesizing optically active substituted binaphthyl compounds that avoid classical resolution methods. We report here the syntheses of substituted binaphthyl compounds in high to medium optical yields through nucleophilic aromatic substitution reactions in which the leaving groups are asymmetric alkoxy moieties derived from naturally occurring alcohols. The results provide the first examples of asymmetric induction by chiral leaving groups in nucleophilic substitution reactions at carbon.[6]

The 4,4-dimethyl-Δ^2-oxazoline (a masked carboxyl group that Meyers has developed so successfully)[7] was selected as the ac-

(17) Jacques and Fouquey, (Jacques, J.; Fouquey, C. *Tetrahedron Lett.* **1971**, 4617) report that (−)-**16** possesses the *S* configuration.

(1) (a) This paper is dedicated to the memory of Professor F. Sörme for his contributions and devotion to chemical science. (b) The authors warmly thank the National Science Foundation for Grant NSF 80-00044, which supported this research.

(2) (a) Peacock, S. C.; Walba, D. M.; Gaeta, F. C. A.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 2043–2052. (b) Lingenfelter, D. S.; Helgeson, R. C.; Cram, D. J. *J. Org. Chem.* **1981**, *46*, 393–406.

(3) (a) Cram, D. J.; Sogah, G. D. Y. *J. Chem. Soc., Chem. Commun.* **1981**, 625–628. (b) Mazaleyrat, J.-P.; Cram, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 4585–4586.

(4) (a) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932–7934. (b) Miyano, S.; Nawa, M.; Hashimoto, H. *Chem. Lett.* **1980**, 729–730.

(5) Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3129–3133.

(6) Asymmetric induction by chiral leaving groups in nucleophilic substitution reactions at elements other than carbon have been reported. For example, for nucleophilic substitution reactions on tin, see: (a) Folli, U.; Iarossi, D.; Taddei, F. *J. Chem. Soc., Perkin Trans. 2* **1973**, 638–642. (b) Lequan, R. M.; Lequan, M. *Tetrahedron Lett.* **1981**, 1323–1326.

(7) (a) Meyers, A. I.; Gable, R.; Mihelich, E. D. *J. Org. Chem.* **1978**, *43*, 1372–1379. (b) Meyers, A. I.; Williams, B. E. *Tetrahedron Lett.* **1978**, 223–226.

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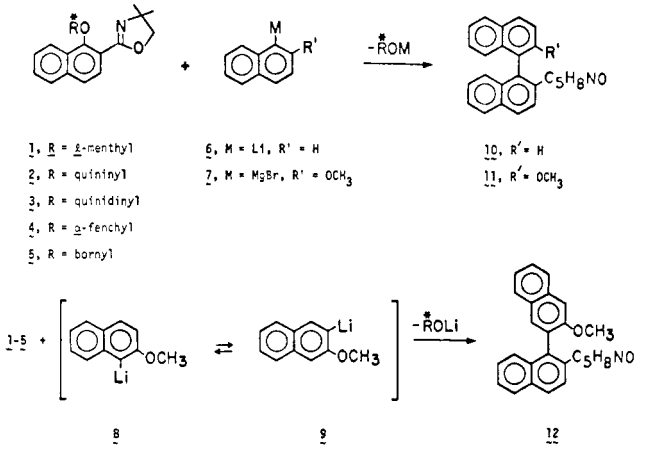
Scheme I



tivating substituent for the nucleophilic aromatic substitution reaction formulated. The *l*-menthoxy in **1**,[8,9] quininoxy in **2**,[8,9] quinindinoxy in **3**,[8,9] α-fenchoxy in **4**,[8,9] and bornoxy in **5**[8,9] served as leaving groups. Ethers **1** and **4** were produced in 70% and 88% respective yields by heating α-methoxy-β-oxazolinonaphthalene[8-10] in *l*-menthol–sodium *l*-menthoxide (90 °C, 3.5 h) or in α-fenchol–sodium α-fenchoxide (90 °C, 6 h), respectively. Ethers **1–5**[11] were synthesized from α-bromo-β-oxazolinonaphthalene and the corresponding sodium alkoxide (NaH + ROH) in DMF at 50 °C in 87% (5 h), 67% (20 h), 45% (15 h), 83% (15 h), and 73% (3 h) yields, respectively. The nucleophiles that gave normal products were α-naphthyllithium (**6**) and β-methoxy-α-naphthylmagnesium bromide (**7**). The normal products were binaphthyl compounds **10** and **11**, respectively. The reactions to give **10**[8,9,12] were run in $(CH_2)_4O$ at −42 °C, the chemical yields were 83–12%, and the optical yields were 80–10% ee. The reactions to give **11**[8,9,13] were run at 80 °C in C_6H_6, the chemical yields were 65–7%, and the optical yields were 94–48% ee. Table I summarizes the results.

When **1–5** were treated with **8** at −20 °C in $(CH_2)_4O$, only rearranged product **12**[8,9,14] was produced in chemical yields of 67–20% and optical yields of ≥95% to 8% ee (see Table I).[15] Treatment of **1** with **9**[16] under the same conditions gave **12** in 92% chemical and 92% optical yields. Possibly **8** and **9** equilibrate through successive metalation reactions through traces of protonated materials.[17] Since **9** is the less hindered, it reacts faster with **1–5** than does **8**. When α-bromo-β-methoxynaphthalene[18] was metalated in $(CH_2)_4O$ at −30 °C and the product was carbonated, a 6:1 ratio of γ-methoxy-β-naphthoic to β-methoxy-α-naphthoic acid was produced (78%).

The absolute configurations of binaphthyl compounds **10** and **11** were determined by the conversions of optically active samples to products **14**, **17**, and **19** of established absolute configurations[19] by the sequences formulated.[20] Unexpectedly, (*R*)-**17** changes its sign of rotation at λ = 589 nm when the solvent is changed from $(CH_2)_4O$ to CH_3OH. Our series of interconverions, as well as those of Meyers and Lutomski,[21] confirm the Yamaguchi[19b] observation that the Yamada[19a] and Berson[22] configurational assignment of **17** is incorrect.

The direction of the configurational bias was probably governed by steric differences in the diastereomeric σ complexes that intervene as intermediates in these reactions. Interestingly, with

(8) These new compounds gave C + H (and N where applicable) elementary analyses within 0.30 of theory and the expected ^1H NMR spectra (200-MHz Bruker instrument).

(9) These compounds gave the expected molecular ions in their mass spectra.

(10) Conversion of α-bromo-β-naphthalenecarboxylic acid [Newman, M. S.; Dhawan, B.; Tuncay, A. *J. Org. Chem.* **1976**, *41*, 3924–3925. Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1955**, 1242–1251] to α-bromo-β-oxazolinonaphthalene (mp 102–106 °C) by the Meyers method[7] was achieved in 74% yield.

(11) Ether **1** gave mp 71–73 °C, $[\alpha]^{25}_{578}$ −66.8° (*c* 5.0, $CHCl_3$); **2** gave mp 97–100 °C, $[\alpha]^{25}_{578}$ 50.5° (*c* 5.01, $(CH_2)_4O$) (this sample contains 1 equiv of acetone of crystallization); **3** gave mp 135–137 °C, $[\alpha]^{25}_{578}$ −97.2° (*c* 5.2, $(CH_2)_4O$); **4** gave mp 80–83 °C, $[\alpha]^{25}_{578}$ 38.6° (*c* 5.1, $(CH_2)_4O$); **5** gave mp 99–102 °C, $[\alpha]^{25}_{578}$ −48.0° (*c* 4.9, $(CH_2)_4O$).

(12) The reaction of **1** with **6** exemplifies the procedure. To a solution at −78 °C of 0.75 mL of α-bromonaphthalene (see: Jones, M.; Capworth, A. *J. Chem. Soc.* **1914**, *105*, 1804–1809, for purification) in 12 mL of $(CH_2)_4O$ was added 5.00 mmol of *sec*-butyllithium. After standing at −78 °C, the mixture was warmed to −42 °C. A 2 mL $(CH_2)_4O$ solution of 0.40 g of **1** was added, and the resulting solution was stirred at −42 °C for 1 h. The mixture was quenched at −42 °C with 5 mL of saturated aqueous NH_4Cl solution. The usual isolation by extraction–evaporation gave a yellow oil, which when submitted to medium-pressure chromatography (SiO_2, CH_2Cl_2) gave **10** (0.29 g). An analytical sample was prepared by submitting this material to additional thick layer chromatography (Al_2O_3, 1:1 (v/v) toluene/hexane).

(13) The reaction of **1** with **7** illustrates the procedure. A solution of α-bromo-β-methoxynaphthalene (8.0 g) in 30 mL of benzene was added to 1.0 g of magnesium turnings just covered with ether under N_2. The mixture was refluxed for 3 h, the ether evaporated, and the Grignard reagent was added through a fritted funnel to a refluxing solution of **1** in 6 mL of dry benzene. The solution was refluxed for 2 h, cooled, and mixed with 50 mL of a saturated aqueous NH_4Cl solution. Crude product was isolated by the usual extraction–evaporation procedure. The resulting brown oil was chromatographed on 100 g of SiO_2 with gradient elution [100% $(CH_2)_6$ to 100% CH_2Cl_2, to 100% Et_2O] and gave 1.08 g of **11** and 0.50 g of β-oxazolino-α-naphthol. An analytical sample of **11** was prepared by thick layer chromatography (Al_2O_3, CH_2Cl_2).

(14) The reaction of **1** with **8** illustrates the procedure. To a solution of 0.011 mol of α-bromo-β-methoxynaphthalene in 10 mL of $(CH_2)_4O$ at −78 °C was added 0.010 mol of *sec*-butyllithium. The mixture was stirred at −78 °C for 1.5 h and warmed to −20 °C. A solution of 2.11 mmol of **1** in 4.5 mL of $(CH_2)_4O$ was added, and the resulting mixture was stirred at −20 °C for 9.5 h. The product was isolated in the usual way and chromatographed (Al_2O_3, CH_2Cl_2) to give 0.23 g of recovered **1** and 0.39 g of **12**. An analytical sample of **12** was prepared by thick layer chromatography (SiO_2, 5% Et_2O in CH_2Cl_2).

(15) The maximum rotations for (*R*)- and (*S*)-**10**, (*R*)- and (*S*)-**11**, and (*R*)- and (*S*)-**12** were calculated from shift reagent data (footnote *e*, Table I). To check that of **11**, a 1.7-g sample of **11**, 82% enantiomerically enriched in the *R* isomer, was hydrolyzed under basic conditions[7a] to 84% of methoxy acid **15**, $[\alpha]^{25}_{578}$ −23.0° (*c* 1.2, $(CH_2)_4O$), mp 150–180° (whole sample). This material was brought to 94% ee by crystallization from benzene and then brought to maximum rotation by three recrystallizations of its quinidine salt to give (*R*)-**15**,[8] $[\alpha]^{25}_{578}$ −28.3° (*c* 1.2, $(CH_2)_4O$), mp 190–193 °C. Calculation of the maximum rotation of **11** from these data provides $[\alpha]^{25}_{578}$ −123.8° (*c* 2.0, $(CH_2)_4O$), close to that of −124° calculated from shift reagent data.

(16) Lithiation of β-methoxynaphthalene [Fowler, R. G.; Caswell, L. R.; Sue, L. I. *J. Heterocycl. Chem.* **1973**, *10*, 405–406] followed by treatment of the resulting organometallic with 1.0 equiv of Br produced a 5:1 mixture (^1H NMR analysis) of β-methoxynaphthalene and β-methoxy-α-bromonaphthalene. Crystallization of the latter from hexane followed by reworking the filtrates gave β-methoxy-α-bromonaphthalene (15%), mp 71–73 °C (see: Clemo, G. R.; Spence, R. *J. Chem. Soc.* **1928**, 2811–2819). Treatment of this material in $(CH_2)_4O$ at −78 °C with 0.99 equiv of *sec*-butyllithium gave **9**.

(17) The arrangement probably is a simple acid–base reaction of **8** to give the more stable **9** in the presence of a small amount of unreacted starting material or β-methoxynaphthalene. For similar rearrangements, see: Wittig, G.; Benz, E. *Chem. Ber.* **1959**, *92*, 1999–2103. Barnes, R. A.; Bush, W. M. *J. Am. Chem. Soc.* **1959**, *81*, 4705.

(18) Fuson, R. C.; Chadwick, D. H. *J. Org. Chem.* **1948**, *13*, 484–488.

(19) (a) Akimoto, H.; Yamada, S. *Tetrahedron* **1971**, *27*, 5999–6009. (b) Kabuto, K.; Yasuhara, F.; Yamaguchi, S. *Tetrahedron Lett.* **1981**, *22*, 659–662 and ref 8 in this article.

(20) Product **10**, 0.80 g, $[\alpha]^{25}_{578}$ +31.8° (*c* 3.4, $(CH_2)_4O$) was hydrolyzed under basic conditions[7a] to give **13**, 0.45 g, $[\alpha]^{25}_{578}$ −11.76° (*c* 2.8, C_6H_6), mp 174–181 °C. A 0.40-g sample of **13** was refluxed with $SOCl_2$ and a trace of DMF, and the resulting acid chloride was rearranged to amine **14** by the procedure applied to rearrange 2,2′-carboxy-1,1′-binaphthyl chloride to its corresponding diamine. Crude **14** was purified by thick layer chromatography on alumina (toluene) and was decolorized by a charcoal treatment. The resulting white solid was crystallized to give **14** (0.19 g, mp 187–189 °C, $[\alpha]^{25}_{578}$ +13.70° (*c* 1.1, $(CH_2)_4O$), see ref 19). A sample of **11** (1.15 g, $[\alpha]^{25}_{578}$ −84.7° (*c* 2.3, $(CH_2)_4O$)) was hydrolyzed under basic conditions[7a] to give **15** (0.84 g, mp 188–235 °C, $[\alpha]^{25}_{578}$ −19.6°, *c* 1.2, $(CH_2)_4O$). On twice the scale used for conversion of **13** to **14** and by the same procedure (see above), **15** was converted to its corresponding amine. This compound was diazotized wiht $NaNO_2$ in 5 N hydrochloric acid. The red diazonium salt was reduced by treatment with H_3PO_2[19] at 4 °C to give an orange oil, which was thick layer chromatographed (SiO_2, 5% CH_2Cl_2 in petroleum ether (V)) to give **16** as a white foam, 0.50 g, $[\alpha]^{25}_{578}$ −33.24° (*c* 2.1, $(CH_2)_4O$). Treatment of a CH_2Cl_2 solution of **16** with 12 equiv of BBr_3 gave 0.42 g of an oil which was purified by thick layer chromatography (SiO_2–CH_2Cl_2) followed by crystallization (CH_3OH) to give **17**, 0.32 g, mp 121–145 °C, $[\alpha]^{25}_{578}$ +6.7° (*c* 1.0, $(CH_2)_4O$), $[\alpha]^{25}_{578}$ −0.95° (*c* 2.0, CH_3OH) (see ref **21** for procedure for conversion of **15** to **19**).

(21) A. I. Meyers; K. Lutomski, private communication. We thank these authors for the procedure of converting (−)(*S*)-**15** to (−)(*S*)-**19**.

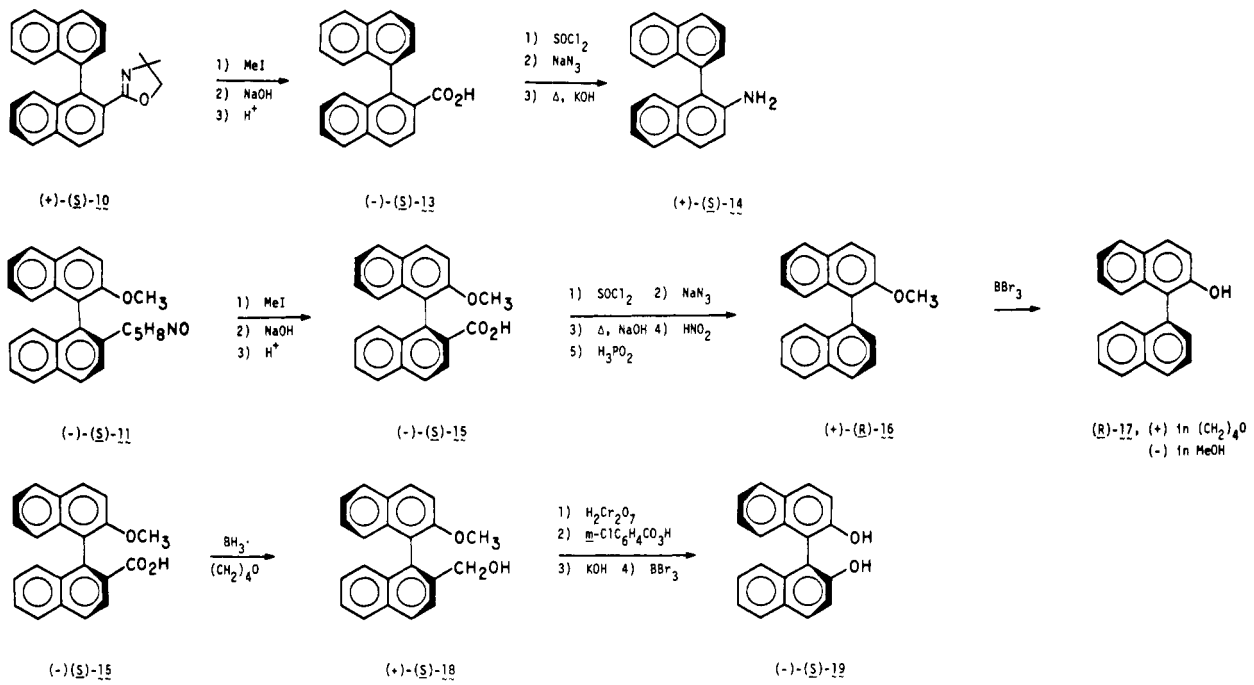
(22) Berson, J. A.; Greenbaum, M. A. *J. Am. Chem. Soc.* **1958**, *80*, 653–656.

Table I. Asymmetric Induction by Chiral Leaving Groups in Aromatic Nucleophilic Substitutions

run no.	substrate[a] compd	substrate[a] leaving group	nucleophile[b]	reaction conditions[c] solvent	temp, °C	time, h	product[d] struct	% yld	% opt yld[e]	config[f]	$\Delta(\Delta G^{\ddagger})$,[g] kcal mol^{-1}
1	1	*l*-menthoxy	6	$(CH_2)_4O$	−42	1	10	80	67	*S*	0.7
2	2	quininoxy	6	$(CH_2)_4O$	−42	1	10	12	80	*S*	1.0
3	3	quinidinoxy	6	$(CH_2)_4O$	−42	0.75	10	15	81	*R*	1.0
4	4	α-fenchoxy	6	$(CH_2)_4O$	−42	5	10	78	45	*S*	0.4
5	5	bornoxy	6	$(CH_2)_4O$	−42	1	10	83	10	*R*	0.09
6[h]	1	*l*-menthoxy	7	C_6H_6	80	2	11	53	78	*S*	1.5
7	2	quininoxy	7	C_6H_6	80	0.8	11	7	94	*R*	2.4
8	3	quinidinoxy	7	C_6H_6	80	0.8	11	27	84	*S*	1.7
9	4	α-fenchoxy	7	C_6H_6	80	9	11	65	48	*S*	0.8
10	1	*l*-menthoxy	8	$(CH_2)_4O$	−20	9.5	12	68	≥95	(+)	>1.8
11	2	quininoxy	8	$(CH_2)_4O$	−20	4	12	20	87	(+)	1.3
12	3	quinidinoxy	8	$(CH_2)_4O$	−20	1.25	12	22	84	(−)	1.2
13	4	α-fenchoxy	8	$(CH_2)_4O$	−20	9.5	12	88	77	(+)	1.0
14	5	bornoxy	8	$(CH_2)_4O$	−20	10	12	67	8	(+)	0.08

[a] See ref 11. [b] Treatment of α-bromonaphthalene in $(CH_2)_4O$ at −78 °C with 0.93 equiv of BuLi in hexane gave **6**. Treatment of α-bromo-β-methoxynaphthalene in ether with 1.26 equiv of Mg gave **7**. The ether was displaced with C_6H_6 by distillation-addition procedure. Treatment of α-bromo-β-methoxynaphthalene in $(CH_2)_4O$ with 0.91 equiv of BuLi in hexane gave **8**, which in turn produced **8** $\rightleftarrows$ **9**. [c] Solvents were purified and dried, and reactions carried out in a N_2 atmosphere. In runs 6–9, β-oxazolino-α-naphthol was isolated as byproduct. [d] Yields were not maximized. Products were isolated by chromatography on silica gel and alumina, care being taken not to optically fractionate. [e] Optical purities given as % ee were determined with Eu(tfc)$_3$ shift reagent in $(CD_2)_6$ for runs 6–9 and in $CDCl_3$ for runs 1–5 and 10–14 by ^1H NMR spectral methods with a Bruker 200-MHz instrument on analytically pure samples. Extrapolated maximum rotations in $(CH_2)_4O$ as $[\alpha]^{25}_{578}$ values are calculated to be the following: for **10** at *c* 2.6, ±118.5 (±3.4°) excluding the least accurate run 5 values; for **11** at *c* 2.0, ±124 (±0.8°); for **12** at *c* 3.2, ±36.1 (±0.5°). [f] For those of **10** and **11**, see text. That of **12** was not determined. [g] The differences in diastereomeric transition-state free energies. [h] When run for 1 day at 25 °C and 2 days at reflux in 1:1 (v/v) ether-benzene, a 33% yield of **11** of 87% optical purity was obtained.

Scheme II



(+)-(S)-10 (-)-(S)-13 (+)-(S)-14

(-)-(S)-11 (-)-(S)-15 (+)-(R)-16 (R)-17, (+) in $(CH_2)_4O$ (-) in MeOH

(-)(S)-15 (+)-(S)-18 (-)-(S)-19

l-menthoxy and α-fenchoxy leaving groups, the direction of the configurational bias changed when a β-methoxy group was substituted for a hydrogen in the α-naphthyl nucleophile (compare run 1 with 6 and 4 with 9). However, with quininoxy and quinidinoxy leaving groups, the direction of the conformational bias was independent of whether the β-methoxy group was present in the nucleophile (compare run 2 with 7 and 3 with 8). Since quininoxy and quinidinoxy have opposite configurations at the two asymmetric centers closest to the seat of reaction, it was not surprising that they produced opposite directions of configurational bias which were of about the same magnitude (compare run 2 with 7, 7 with 8 and 11 with 12). Examination of CPK molecular models of diasetereomeric σ complexes with various leaving groups and nucleophiles provided too many conformational alternatives for meaningful correlations to be made between structure and direction of configurational bias.

The *l*-menthoxy leaving group provided the maximum chiral reaction efficiency, which we define by eq 1. Thus, in runs 1, 6, and 10, the chiral reaction efficiencies were 54%, 41%, and 65%, respectively. The least hindered nucleophile, β-methoxy-γ-naphthyllithium, reacting with **1** (run 10) gave the highest optical yield (≥95% ee) and the highest $\Delta(\Delta G^{\ddagger})$ value (≥1.8 kcal mol^{-1}). In general, the more spherical and least dissymmetric α-fenchoxy and bornoxy groups gave the lowest optical yields. The α-fenchoxy ether required the longest reaction times, a fact that correlates with its forming the most hindered σ complexes in molecular models. Although the leaving groups based on the alkaloids were

$$\text{chiral reaction efficiency} = \frac{(\%\ \text{chemical yield} \times \%\ \text{optical yield})}{100\%} \quad (1)$$

the most consistent in giving high optical yields, they also consistently gave the lowest chemical yields, probably due to side reactions. It is likely that leaving groups could be designed to give substantially higher chiral reaction efficiencies than those reported here.

Registry No. 1, 80317-59-5; **2**, 80325-17-3; **3**, 80373-29-1; **4**, 80317-60-8; **5**, 80317-61-9; **6**, 14474-59-0; **7**, 36321-90-1; **9**, 43029-67-0; **10***S*, 80317-62-0; **10***R*, 80317-63-1; **11***S*, 80317-64-2; **11***R*, 80317-65-3; **12**(+), 80317-66-4; **12**(−), 80317-67-5; **13***S*, 80317-68-6; **14***S*, 18531-97-0; **15***S*, 80317-69-7; **15***R*, 80317-70-0; **16***R*, 80317-71-1; **17***R*(+), 35216-79-6; **17***R*(−), 35216-79-6; α-methoxy-β-(4,4-dimethyl)oxazolinonaphthalene, 78265-10-8; α-bromonaphthalene, 90-11-9; α-bromo-β-methoxynaphthalene, 3401-47-6.

A New, General Route to η^5-Vinylcyclopentadienyl Organometallic Monomers

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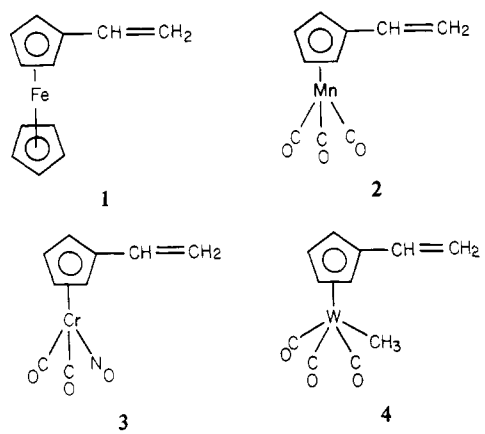
Organometallic polymers are useful in a variety of applications such as catalysts, UV absorbers, semiconductors, and antifouling agents.[1-3] In spite of these potential applications, very few η^5-vinylcyclopentadienyl organometallic monomers are known. Indeed, only vinylferrocene (**1**),[4] vinylcymantrene (**2**),[5,6] vinylcynichrodene (**3**),[7,8] and (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten (**4**)[9,10] have been studied in detail under homo- and copolymerization conditions. The paucity of η^5-vinylcyclopentadienyl monomers stems in part from a lack of suitable synthetic methods, which, in turn, is due to the failure of most η^5-cyclopentadienylmetal compounds to undergo aromatic-type ring substitution reactions. We have recently overcome part of this problem with the development of a new method for the formation of various functionally substituted η^5-cyclopentadienylmetal compounds.[11]

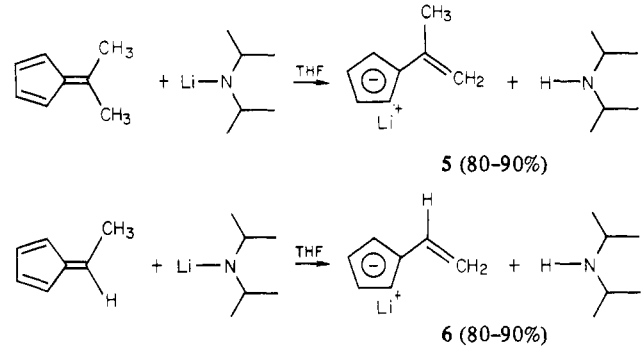
We now report the development of a new and apparently general route for the synthesis of a wide variety of η^5-vinylcyclopentadienyl organometallic monomers. This method provides a convenient means of introducing vinyl substituents directly onto η^5-cyclopentadienyl rings in systems which are incapable of undergoing electrophilic aromatic substitution.

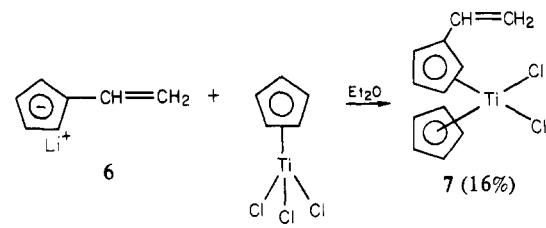
6,6-Dimethylfulvene and 6-methylfulvene react with lithium diisopropylamide in THF at 25 °C to produce isopropenylcyclopentadienyllithium (**5**) and vinylcyclopentadienyllithium (**6**), respectively, in yields of 80–90%. The solid products are air sensitive, as is cyclopentadienyllithium itself. The ^{1}H NMR spectrum of **5**[12] is in agreement with a recent report by Schore et al.[13] The ^{1}H NMR spectrum of the previously unknown compound **6** exhibits two apparent triplets due to the cyclopentadienyl protons as well as the typical ABX pattern for a terminal vinyl group (Figure 1).

The reaction between organolithium reagent **6** and η^5-cyclopentadienyltrichlorotitanium in ethyl ether produces (η^5-vinylcyclopentadienyl)η^5-cyclopentadienyldichlorotitanium (**7**) (mp 154–157 °C, 16%).[14] Polymers of **7** after reduction could function as hydrogenation catalysts similarly to polystyrene-bound titanocene dichloride.[15] Further investigations into the synthesis of other titanocene-type monomers are in progress.[16]

Organolithium reagents **5** and **6** react with molybdenum hexacarbonyl and with tris(dimethylformamide)tricarbonyltungsten in refluxing THF to give η^5-vinylcyclopentadienyl monomers of these metals. Nitrosylation of the intermediate metal carbonyl anions with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide has afforded monomers **8** (liquid, 58%), **9** (mp 27–29 °C, 93%), **10** (mp 22–23 °C, 36%), and **11** (mp 38–40 °C, 24%). This completes the series







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(12) ^{1}H NMR spectral data for **5** (THF-d_8): δ 2.08 (s, 3 H, CH_3), 4.34 (m, 1 H, vinyl), 4.90 (m, 1 H, vinyl), 5.64 (t, 2 H, $H_{3,4}$), 5.92 (t, 2 H, $H_{2,5}$).
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(14) ^{1}H NMR spectral data for **7** ($CDCl_3$): δ 5.32–5.82 (m, 2 H, C=CH_2), 6.38–6.66 (m, 10 H, CH=C and Cp H_{2-5} and C_5H_5). Elemental analyses and spectroscopic data (^{1}H NMR, IR, MS) were consistent with the proposed structures of all η^5-cyclopentadienylmetal compounds.
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(16) For example, treatment of **7** with Al/$HgCl_2$ in the presence of carbon monoxide has afforded (η^5-vinylcyclopentadienyl)η^5-cyclopentadienyldicarbonyltitanium [(η^5-CH_2=CHC_5H_4)η^5-$C_5H_5Ti(CO)_2$]: ν_{CO} 1980, 1910 cm^{-1} (recorded in benzene).

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