

the Soret band of the isolated MgTPP molecule, together with the previous data¹⁷ on the Soret band of zinc tetrabenzoporphine in solid Ar, strongly indicates that the almost universal extensive broadening reported for the Soret band of porphyrins¹⁵ originates from thermal inhomogeneous broadening effects rather than from lifetime broadening. This conclusion is pertinent for the understanding of the quantitative aspects of intramolecular interstate radiationless processes in the photosynthetic pigments.

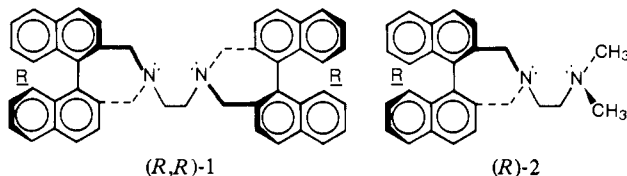
Chiral Catalysis of Additions of Alkylolithiums to Aldehydes¹

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Received February 12, 1981

The well-known activation of organolithium reagents by complexation with tetramethylethylenediamine² suggested that derivatives **1** and **2** might serve as chiral catalysts for asymmetric induction in reactions of organometallic reagents. Hosts **1** and **2** were chosen for the following reasons. (1) Molecular models (CPK) of organometallic complexes of **1** and **2** indicate that the rigid naphthalene rings, coupled with the spirane structures, provide a high degree of "sidedness" to carbonyl groups ligated to complexed organometallics and that high asymmetric induction should result. (2) Both hosts contain C₂ axes, which reduces the number of possible conformations for diastereomeric transition states. Less averaging of host-guest interactions that favor opposite enantiomeric products should result. (3) The key intermediate in the synthesis of **1** and **2** is 2,2'-bis(bromomethyl)-1,1'-binaphthyl (**3**). The maximum rotations³ and absolute configurations⁴ of the enantiomers of **3** have been established and provide a convenient means of determining these properties for the enantiomers of **1** and **2**. We report here studies of chiral catalysis using (R,R)-**1**^{5,6} and (R)-**2**^{5,6} in the additions of alkylolithiums to aldehydes to give alcohols.



Exploratory additions of CH₃(CH₂)₃Li to C₆H₅CHO with (R)-**2** as catalyst established the following facts. (1) Without the

catalyst, the reaction takes place with 81% yield at -120 °C in Et₂O. (2) Under the same conditions with molar ratios of catalyst to RLi that varied between 1.1 and 1.4, (R)-C₆H₅CH(OH)-(CH₂)₃CH₃ was produced with 57% enantiomeric excess (ee). With a ratio of 0.0077, only 7% ee of (R)-alcohol was produced. Thus the catalyzed addition rate exceeds the noncatalyzed rate by orders of magnitude but by a factor too small to provide useful catalyst turnover. Ratios of 1.2 ± 0.2 were used in subsequent *stoichiometric catalysis* experiments. (3) Optical yields increased sequentially from 4 to 58% (ee) as the solvent was changed from THF (-100 °C) to C₆H₅CH₃ (-80 °C) to CH₃(CH₂)₃CH₃-Et₂O (30:1, v/v, -120 °C) to (CH₃O)₂CH₂-(CH₃)₂O (1:1, v/v, -120 °C) to (CH₃O)₂CH₂-Et₂O (1:1, v/v, -120 °C) to Et₂O at -120 °C. Variation in the volume of Et₂O by a factor of 10 provided the same results. Those reported here were obtained at the dilute end of the scale for convenience only. The reactions in Et₂O of methyl-, ethyl-, propyl-, and butyllithium with benzaldehyde complexed with (R,R)-**1** or (R)-**2** (molar ratios of 1.2 ± 0.2) and that of phenyllithium with pentanal were studied at -120 °C. The absolute configurations of the four product alcohols have been determined,⁸ and maximum rotations have been reported.⁹ We determined the dominant configurations and optical purities of our products from their optical rotations. The optical purities were also determined from the 200-MHz ¹H NMR spectra of their (+)-α-methoxy-α-[(trifluoromethyl)phenyl]acetic esters by Dale's method.¹⁰ Table I records the results.

Chiral catalysis occurred in runs 1-9 to give optical yields of 92-22% ee.¹¹ The differences in free energies of the diastereomeric transition states leading ultimately to the two enantiomeric alcohols varied from 1 to 0.1 kcal mol⁻¹. The higher values are associated with three structural features: (1) the reactants with the higher steric requirements, (2) the more highly shaped and sterically confining catalyst, and (3) the use of benzaldehyde rather

(8) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice Hall; Englewood Cliffs, NJ, 1971; pp 415-419.

(9) The maximum rotations used here for C₆H₅CH(OH)R are as follows. R = CH₃, [α]_D²⁰ 43.1° (c 7.2, cyclopentane); Yamaguchi, S.; Mosher, H. S. *J. Org. Chem.* **1973**, *38*, 1870-1877. R = CH₂CH₃, [α]_D 45.45° (c 5.15, CHCl₃); Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1914**, 1115-1131. R = CH₂CH₂CH₃, [α]_D²⁷ 45.9° (c 6.1, C₆H₆); Mislou, K.; Hamermesh, C. L. *J. Am. Chem. Soc.* **1955**, *77*, 1590-1594. R = (CH₂)₃CH₃, [α]_D 37.6° (c 3, C₆H₆); Horeau, A.; Guetté, J. P.; Weidmann, R. *Bull. Soc. Chim. Fr.* **1966**, 3513-3515. Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3129-3131. P. A. Levene and R. E. Marker [*J. Biol. Chem.* **1932**, *97*, 379-391] reported [α]_D²⁴ 31.3° (c 3, C₆H₆) for C₆H₅CH(OH)(CH₂)₃CH₃, but Horeau et al. (see above) showed this value to represent only 83.3% optically pure material, and Noyori et al. (see above) confirmed this latter value by NMR spectra of diastereomeric esters.

(10) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543-2549.

(11) Ether and toluene were distilled from lithium aluminum hydride and THF from sodium benzophenone ketyl. Reactions were conducted under dry N₂. Reagent solutions were added by syringe. Commercial CH₃Li, LiBr, CH₃(CH₂)₃Li, and C₆H₅Li were used directly, and CH₃CH₂Li and CH₃(C-H₂)₂Li were prepared [Meyers, A. I.; Smith, R. K.; Whitten, C. E. *J. Org. Chem.* **1979**, *44*, 2250-2256]. The procedure for run 1 is illustrated. A solution of 3.12 g of (R,R)-**1** of maximum rotation in 150 mL of Et₂O was cooled to -50 °C, and 2 mL of a 2.2 M solution of CH₃(CH₂)₃Li in hexane was added. The solution was stirred for 1.3 h at -50 °C, and cooled to -120 °C. A solution of 0.133 g of freshly distilled C₆H₅CHO in 1 mL of Et₂O was added dropwise with stirring. The mixture was stirred for 1 h at -120 °C and rapidly quenched with 100 mL of 1 N aqueous HCl and allowed to come to 25 °C. The white precipitate of (R,R)-1·2HCl was filtered, thoroughly washed with water and ether, dried, and converted with KOH back to unaltered (R,R)-**1**, 3.09 g (99%), [α]_D²⁵ -256° (c 1, CHCl₃). The ether layer of the original filtrate was washed with three 200 mL portions of H₂O, dried, filtered and evaporated. The residue was chromatographed on a preparative TLC plate (SiO₂, CH₂Cl₂), and the desired C₆H₅CH(OH)(CH₂)₃CH₃ was collected in ether. The ether was evaporated, and the residue dried under vacuum for 30 min at 25 °C to give 0.150 g (73%) pure by TLC and ¹H NMR, [α]_D²⁵ 36.1° (c 3, C₆H₆). After submission to a second preparative TLC and a preparative gas chromatogram (5% SE 30 on firebrick at 150 °C), the sample gave [α]_D²⁵ 35.7° (c 3, C₆H₆), 95% ee of (R)-C₆H₅CH(OH)-(CH₂)₃CH₃, mp ca. 30 °C. At 22 °C, [α]_D was 35.8°, and at 18 °C was 36.0°. The original sample was esterified with excess (+)-α-methoxy-α-[(trifluoromethyl)phenyl]acetyl chloride,⁹ and the ester was chromatographed on a preparative TLC plate (SiO₂, CH₂Cl₂). The ¹H NMR (200 MHz) spectrum gave the major CH₃O singlet at 3.447 ppm and the minor at 3.538 ppm, whose integration indicated an 89% ee of one enantiomer of the original alcohol.

[†]C.N.R.S. Postdoctoral Fellow, 1978.

(1) This work was supported by the U.S. Public Health Service, Grant GM-12640 from the Department of Health, Education and Welfare.

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(3) Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1955**, 1242-1251.

(4) Harata, K.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2747-2751.

(5) All new compounds prepared here gave C and H analyses within 0.30% of theory and the expected ¹H NMR (200 MHz) and mass spectra.

(6) Treatment of **3** with 0.5 mol equiv. of H₂NCH₂CH₂NH₂ in C₆H₆-Et₃N (reflux 65 h) gave **1** (79%). Racemic **3** gave a 1.2 ratio of meso⁵ to racemic, **1**,⁵ the latter of which was easily resolved with (-)-dibenzoyltartaric acid in 95% EtOH to give 41% of (S,S)-**1**,⁵ [α]_D²⁵ +256° (c 1.1, CHCl₃), and 31% of (R,R)-**1**,⁵ [α]_D²⁵ -251° (c 1.1, CHCl₃). From (R)-**3** of [α]_D²⁵ +197° (c 1, C₆H₆) was similarly produced 85% of (R,R)-**1** of [α]_D²⁵ -255° (c 1, CHCl₃). Racemic **3** with 2 mol equiv of (CH₃)₂NCH₂CH₂NH₂ gave 88% of racemic **2**,⁵ which was resolved with (-)-dibenzoyltartaric acid in 95% EtOH to give 34% of (R)-**2**,⁵ [α]_D²⁵ -413° (c 0.9, EtOH), and 39% of (S)-**2**,⁵ [α]_D²⁵ +413° (c 1.1, EtOH). From (R)-**3** was obtained 93% of (R)-**1**, [α]_D²⁵ -410° (c 1.1, EtOH). The mass spectral cracking patterns of **1** and **2** confirmed their structures.

(7) We warmly thank Dr. S. Bruce Brown for developing the practical synthesis of the 2,2'-dicarboxy-1,1'-dinaphthyl used in the preparation of racemic (R)- and (S)-**3**.

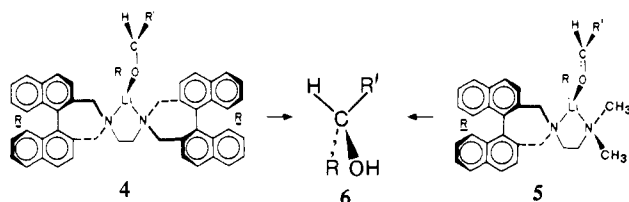
Table I. Chiral Catalysis in Additions of Alkyl- or Aryllithiums to Aldehydes in 150 mL of Et₂O at -120 °C

run no	diamine		RLi		R'CHO	C ₆ H ₅ CH(OH)R				$\Delta(\Delta G^\ddagger)^c$ kcal mol ⁻¹	
	struct	mmol	R	mmol		R'	mmol	% optical yield (ee)	yield, %		config
1	(R,R)-1	5	CH ₃ (CH ₂) ₃	4.4	C ₆ H ₅	1.2	95	89	73	R	1.0
2	(R,R)-1	3.8	C ₆ H ₅	3.1	CH ₃ (CH ₂) ₃	1.2	43	55	47	S	0.3
3	(R,R)-1	3.6	CH ₃ (CH ₂) ₂	3.4	C ₆ H ₅	1.2	59	63	63	R	0.4
4	(R,R)-1	3.4	CH ₃ CH ₂	3.3	C ₆ H ₅	1.2	66	67	75	R	0.5
5	(R,R)-1	3.9	CH ₃	3.1	C ₆ H ₅	1.2	36	35	35	R	0.2
6 ^d	(R)-2	3.3	CH ₃ (CH ₂) ₃	3.0	C ₆ H ₅	1.0	58	55	71	R	0.4
7	(R)-2	3.4	CH ₃ (CH ₂) ₂	3.0	C ₆ H ₅	1.2	53	54	75	R	0.4
8	(R)-2	3.3	CH ₃ CH ₂	2.2	C ₆ H ₅	1.2	30	30	73	R	0.2
9	(R)-2	3.6	CH ₃	3.0	C ₆ H ₅	1.2	23	22	65	R	0.1

^a Reference 8 lists maximum rotations used. ^b From ¹H NMR of (+)- α -methoxy- α -[(trifluoromethyl)phenyl]acetic esters. ^c $\Delta(\Delta G^\ddagger) = RT \ln$ [dominant enantiomer/subordinate enantiomer]. Values of ee determined by the two methods were averaged. ^d Volume of Et₂O was 20 mL.

than pentanal as the aldehyde component.

Without exception, the configurational bias is correlated by the formulations of generalized transition states **4** and **5** to give **6**.

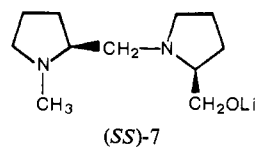


Although we examined only 14 out of many possible combinations of solvents, temperatures, reagents, catalysts, and orders of attaching groups to the asymmetric centers, the fact that all 14 reactions fit this correlation suggests that a single mechanistic feature dominates the chiral tilt. Examination of CPK molecular models of **4** with R = CH₃(CH₂)₃ and R' = C₆H₅ in advance of experiment provided the correct prediction of the configuration of the dominant product. Because of the rigid polyspirane structures of the presumed transition states, the only degree of freedom is the placement of the H and R' groups. In **4** and **5**, that diastereomer is formulated in which the H is directed toward the face of the upper left naphthalene and, in **4**, R is directed alongside the face of the lower right naphthalene. Models of **4** and **5** appear less sterically constrained than those of their diastereomers in which the positions of the H and R' groups are interchanged. Since N: rapidly inverts, catalyst (R,R)-1, in effect, contains three C₂ axes, and **4** can be generated four different ways from (R,R)-1, R'CHO, and RLi. Since catalyst (R)-2 in effect contains one C₂ axis, **5** can be generated two different ways from (R)-2, R'CHO, and RLi. This degeneracy reduces the number of transition states that compete with one another, the averaging of compensating effects, and probably is at least partly responsible for the high chiral recognition of the catalysts.

This correlation shows the following similarities to the rule of steric control of asymmetric induction for additions to carbonyl groups adjacent to chiral centers.¹² In both correlations, the differences in free energies between the diastereomeric transition states cover about the same range and depend on steric effects. An inversion in the order of attachment of groups to the forming asymmetric center inverts the configuration of that center.

Seebach et al. have used optically active amino ethers derived from tartaric acid to get 56–15% ee in stoichiometric catalysis of additions of organometallics to aldehydes.¹³ However, Mukaiyama et al. reported the highest observed stoichiometric catalysis of additions of alkylorganometallics to aldehydes to provide

alcohols.¹⁴ When RLi complexed by (S,S)-**7** was added to C₆H₅CHO, the optical yields varied from 83¹⁵ to 21% ee, and the



dominant isomer produced depended on the R of RLi and the solvent. The highest optical yield (92% ee) involved Et₂Mg reacting with C₆H₅CHO.

(14) Mukaiyama, T.; Soai, K.; Sato, T.; Shimizu, H.; Suzuki, K. *J. Am. Chem. Soc.* **1979**, *101*, 1455-1460.

(15) These authors based their optical yields on a maximum rotation for C₆H₅CH(OH)(CH₂)₃CH₃ of $[\alpha]_D^{25} 31.3^\circ$ (c 3, C₆H₆). We have corrected their ee values to a maximum of $[\alpha]_D^{25} 35.7^\circ$ (c 3, C₆H₆) so that their results and ours can be compared (see ref 9).

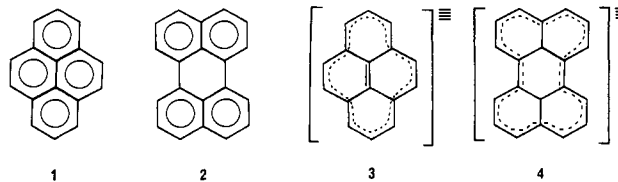
Aromatic Polycyclic Benzenoid Tetraanions: Pyrene and Perylene Anions Revisited

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Received February 17, 1981

Recently, it has been reported that four-electron reduction of conjugated hydrocarbons is feasible.¹ Conjugated systems of (4n + 2) π electrons in their periphery are of particular interest, being predicted to acquire aromatic character as a consequence of a four-electron reduction process.²

No information exists on quadruply charged ions which originate from 4n + 2 peripheries of the "ultimate aromatics", i.e., benzenoid systems. We wish to report a reduction of two polycyclic benzenoid (4n + 2) π systems which occupy a cardinal position in the understanding of aromaticity, i.e., pyrene (**1**) and perylene (**2**) leading to the formation of the respective tetraanions. These



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