

Figure 1. 90-MHz ¹H NMR spectrum of 1*H*-cycloprop[*b*]anthracene in CDCl₃.

Scheme I



The synthesis of 1 is illustrated in Scheme I. The Diels-Alder addition of 2 to the diene 3^{14} in tetrahydrofuran at -20 °C for 24 h gave the adduct 4, mp 147-148 °C, in 76% yield.¹⁵ Treatment of 4 (650 mg, 2.1 mmol) with DDQ (715 mg, 3.15 mmol) in CCl₄ at 25 °C for 20 h followed by chromatography on silica gel (CH₂Cl₂) afforded a yellow solid, which was purified by column chromatography using silica gel (hexane, benzene) and then recrystallization from pentane to yield white needles, mp 140-141 °C, in 64% yield.¹⁶ Conversion to 1 was effected by treating 5 (51.5 mg, 0.167 mmol) with potassium *tert*-butoxide (136 mg, 1.2 mmol) at -78 °C in tetrahydrofuran. After warming to -30 °C, the solvent was removed in vacuo and the residue extracted with *n*-pentane to yield 13.2 mg of nearly pure 1 (41.5% yield).

The ¹H NMR spectrum of 1 (Figure 1) displays the expected pattern with singlets at δ 3.56 (bridging CH₂), 7.67 (H₂, H₉), 8.41 (H₃, H₈), and an AA'BB' system at 7.34–7.60 (H₅, H₆) and 7.86–8.12 (H₄, H₇). The ¹³C NMR spectrum (CDCl₃) shows signals at 18.6 (C1), 111.6 (C2, C9), 123.3 (C1a, C9a), 125.3 (C5, C6), 126.6 (C4, C7), 128.1 (C3, C8), 131.7 (C3a, C7a), and 135.2 (C2a, C8a). The ultraviolet spectrum (*n*-hexane) exhibits a maximum at 252 nm (ϵ 117000) with other absorptions at 320 (ϵ 1500), 334 (ϵ 3500), 351 (ϵ 5300), and 371 (ϵ 4700). The IR spectrum showed the characteristic benzene "double bond" at 1678 cm⁻¹. Elemental composition was provided by high-resolution mass spectrometry: calcd for C₁₅H₁₀ *m/e* 190.0783, found *m/e* 190.0781.

The ease of synthesis of 1 using the method described here and the absence of unusual spectral properties indicate that the failure to form 1 using other routes cannot be attributed to a greater degree of bond fixation (and thus destabilization) as previously suggested.^{5,7} The determination of exact bond lengths in 1 by X-ray analysis is under investigation.

Other cycloproparenes can also be prepared readily from Diels-Alder adducts of 2. Thus treatment of 4 with potassium *tert*-butoxide in tetrahydrofuran (eq 2) results in nearly quan-



titative conversion to a 77:23 mixture (NMR) of 3,8-dihydro-1*H*-cycloprop[*b*]anthracene (6^{17} and 2-methylanthracene, respectively.¹⁸ Compound **6** exhibits NMR singlets at δ 3.27 (bridging CH₂), 3.95 (H₃, H₈), and aromatic signals extending from ~7.0 to 7.5.

Finally, this route promises to be extremely useful for the synthesis of other cycloproparenes. We are currently pursuing these studies.

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Registry No. 1, 287-03-6; **2**, 88180-95-4; **3**, 65957-27-9; **4**, 88180-96-5; **5**, 88180-97-6; **6**, 88180-98-7; 1-bromo-2,2-dichloro-1-(trimethylsilyl)-cyclopropane, 88180-99-8; 2-methylanthracene, 613-12-7.

(17) This material decomposes at -20 °C after ~ 36 h. (18) A previous attempt^{5,7} to synthesize this compound by treating i with potassium *tert*-butoxide in dimethyl sulfoxide yielded only 2-methylanthracene.



Unprecedented Asymmetric Induction from a Chiral Acetate Enolate Equivalent. The Condensation of $(\eta$ -C₅H₅)Fe(CO)(PPh₃)(COCH₃) with Imines

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Various organic complexes of the $(\eta$ -C₅H₅)Fe(CO)(PPh₃) fragment, **1**, have found applications in organic synthesis because



of the unique reactivity imparted by the metal on the organic residue R^2 Although mechanistic studies using the chirality in

⁽¹⁴⁾ Thummel, R. P.; Cravey, W. E.; Nutakul, W. J. Org. Chem. 1978, 43, 2473.

⁽¹⁵⁾ NMR (CDCl₃) δ 1.24–1.68 (m, 2 H), 2.60–3.36 (m, 8 H), 7.13 (s, 4 H). Anal. Calcd for C₁₅H₁₄BrCl: *m/e* 307.9967. Found: *m/e* 307.9973. (16) NMR (CDCl₃) δ 1.34 (s, 2 H), 3.5–4.0 (m, 4 H), 7.25–7.6 (m, 2 H),

⁽¹⁶⁾ NMR (CDCl₃) à 1.34 (s, 2 H), 3.5–4.0 (m, 4 H), 7.25–7.6 (m, 2 H), 7.53 (s, 2 H) 7.6–7.9 (m, 2 H). Anal. Calcd for $C_{15}H_{12}BrCl: m/e$ 305.9811. Found: m/e 305.9813.

⁽¹⁾ Fellow of the Alfred P. Sloan Foundation, 1983-1985.

⁽¹⁾ Period of the Arnead P. Stoan Pointauton, 1983-1983.
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Table I. Stereoselective Imine Condensation	Table I.	Stereoselective	e Imine	Condensations	30
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entry	enolate 3	imine ^b	<i>Т</i> , °С	yield 4a + 4b, %	ratio 4a/4b	recovered 2 , %	mass balance, %	
1	M = Li	(E)-PhCH=NPh	-42	85	5.5:1	2	87	
2	M = Li	(E)-PhCH=NPh	-78	79	12.2:1	14	93	
3	$M = AlEt_2$	(E)-PhCH=NPh	-42	55	5.7:1	32	87	
4	$M \approx AlEt_{2}$	(E)-PhCH=N- <i>n</i> -Pr	-42	80	>20:1	0	80	
5	$M \approx AlEt_{2}$	(E)- <i>i</i> -PrCH=N- <i>n</i> -Pr	-42	68	>20:1	25	93	
6	$M = AlEt_2$	(E)-PhCH=N-c-C ₆ H ₇	-42	54	>20:1	29	83	
7	$M = AlEt_{2}$	(E) - <i>i</i> -PrCH=N-c- $\tilde{C}_{\epsilon}H_{\tau}$	-42	57	>20:1	28	85	
8	$M = AlEt_{2}$	(E, E)-PrCH=CHCH=N-p-C, H, OMe	-42	68	1.3:1	24	92	
9	$M = AlEt_{2}$	(E,E)-PhCH=CHCH=N- <i>n</i> -Pr	-42	44	2.5:1	53	97	
10	$M = AlEt_2$	(E,E)-PhCH=CMeCH=N- <i>n</i> -Pr	-42	53	11.5:1	33	86	
11	$M = AlEt_2$	(E,E)-EtCH=CMeCH=N- <i>n</i> -Pr	-42	37	>20:1	59	96	
12	$M = AlEt_2^2$	(E)-EtCH=NCH ₂ Ph	-42	36	13:1	53	89	

^a Yields are unoptimized and refer to chromatographically purified material. ^b All imine starting materials were geometrically pure E isomers about the C=N bond as judged by 'H NMR.

these pseudotetrahedral complexes (1, L \neq CO) have been common, synthetically useful asymmetric inductions from the iron have been explored very little until recently.³ Because the chiral iron acyl 2 is easily prepared as the racemate⁴ or in optically active form⁵ and $(\eta$ -C₅H₅)FeR (R = acyl) compounds can be oxidatively cleaved under mild conditions in good yield to organic acid derivatives,⁶⁻⁸ we began a study of stereoselective reactions of the enolate of 2 as a chiral acetate enolate equivalent. Aldehydes were previously shown to condense with the lithium enolate of 2 in high yield but with no effective stereoselection,⁷⁻⁹ and we now report that a variety of imines condense with the diethylaluminum enolate¹⁰ of racemic 2 (3, $M = AlEt_2$) to provide condensation products 4a,b in good to moderate yields with excellent stereofacial



bias for racemic diastereomer 4a in most cases (eq 1).¹¹ If the

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Scheme I. Transition-State Rationale of Stereoselectivity



iron acyl 2 is viewed as an acetic acid equivalent, the stereoselectivities observed in the imine condensations described in this paper are unprecedented.¹²

A list of imine condensation products and the corresponding stereoselectivity of the condensation is given in Table I. Although PhCH==NPh would condense with both the lithium enolate and the diethylaluminum enolate of 2, the N-alkyl imines required the use of the aluminum enolate to induce reaction. Products were separated from recovered acyl 2 by chromatography and analyzed

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⁽¹¹⁾ The experimental procedure for the synthesis of condensation product **4a** ($\mathbf{R} = n$ -Pr, $\mathbf{R}' = Ph$) is typical. Diisopropylamine (111 μ L, 0.79 mmol) was added to THF (2 mL) maintained at 0 °C under N₂. *n*-Butyllithium (495 μ L of 1.6 M solution in hexane, 0.79 mmol) was then added, and the solution was stirred at 0 °C for 10 min. The flask was then cooled in a dry ice-CH₂CN bath (ca. -42 °C), and a solution of $(\eta$ -C₃H₃)Fe(CO)(PPh₃)(COCH₃) (300 mg, 0.66 mmol) in THF (2 mL) was added dropwise by syringe. During the addition the initial orange color of the acyliron turned to deep red-brown. After stirring at -42 °C for 45 min., diethylaluminum chloride (1500 µL of 1.0 M hexane solution, 1.5 mmol) was added by syringe with little change in color. Typically 1.2-1.5 equiv of diethylaluminum chloride can be used with little change in product yield. The solution was stirred 15 min at -42 °C after addition of Et₂AlCl and then benzylidene-n-propylamine (117 mg, 0.79 mmol) in THF (1 mL) was added by syringe. The color of the reaction mixture slowly lightened to orange after the imine was added. After 3 h at -42 °C, the reaction was quenched with saturated aqueous NaHCO3. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the CH_2Cl_2 extracts were combined and then dried over MgSO4. Removal of volatiles on a rotary evaporator left an orange oil that was chromatographed on silica gel (60-200 evaluation for an orange on that was chromatographica on since ger (0-20) mesh, 2×20 cm, CH₂Cl₂ then diethy lether) and gave 319 mg (80%) of iron complex **4a** (R = *n*-Pr, R' = Ph) as an orange solid: mp 143–145 °C (CH₂Cl₂/ether); IR (CH₂Cl₂, cm⁻¹) 1918, 1591; ¹H NMR (270 MHz, CDCl₃) δ 7.73–7.07 (m, 20 H) 4.41 (d, 5 H, J = 1 Hz), 3.47 (dd, 1 H, J = 10, 2 Hz), 3.26 (dd, 1 H, J = 18, 10 Hz), 2.84 (dd, 1 H, J = 18, 2 Hz), 2.16 (m, 2 H), 1.36 (m, 2 H), 0.79 (t, 3 H, J = 7 Hz). Anal. Calcd for C₃₆H₃₆FeNO₂P: C, 71.89; H, 6.03; N, 2.33. Found: C, 72.00; H, 6.13; N, 2.42 2.24

⁽¹²⁾ Although spectacular stereoselectivities can be obtained from enolate condensations of chiral propionate, ^{12a,b,d} α -SOR acetate, ^{12e} α -SR methyl ketone, ^{12d} and ethyl ketone ^{12c,d} derivatives, condensations with chiral acetate^{12a,b} tone,^{12d} and ethyl ketone^{12d} derivatives, condensations with chiral acetate^{12d} and methyl ketone^{12d} derivatives have shown poor stereoselectivities: (a) Evans, D. A.; Nelson, J. V.; Taber, T. R. In "Topics in Stereochemistry"; Allinger, N. L., Eliel, E. L., Wilen, S. H., Eds.; Wiley: New York, 1982; Vol. 13, 1. (b) Evans, D. A. Aldrichimica Acta 1982, 15, 23-32. (c) Heathcock, C. H. Science (Washington, D.C.) 1981, 214, 395. (d) Masamune, S.; Choy, W. Aldrichimica Acta 1982, 15, 47-64. (e) Mioskowski, C.; Solladie, G. Tutenkedora 1090, 26, 2027, 236. Tetrahedron 1980, 36, 227-236.

for stereoselectivity by 270-MHz ¹H NMR. Most of the condensations were conducted at -42 °C (dry ice-CH₃CN); however, lower temperature significantly improved the diastereoselection in the one case investigated (compare entries 1 and 2, Table I). The mass balance of each reaction is included in the table to underscore the fact that the observed diastereoselectivities were not perturbed by significant decomposition of the products. Extensive optimization of product yields has not been investigated.

Rigorous structure proof establishing the major diastereomer formed by condensation of enolate 3 (M = Li) with (E)-PhCH=NPh as 4a (R = R' = Ph) was secured by X-ray diffraction.¹³ Assignment of structure 4a to the major diastereomer of the other imine condensation products rests upon comparison of their 270-MHz ¹H NMR spectra with those obtained for 4a and 4b (R = R' = Ph). All major diastereomers 4a showed the higher field methylene hydrogen absorption (H_a, H_b) coupled to the methine H_c with a smaller vicinal coupling constant than the corresponding coupling of H_c to the lower field methylene hydrogen. The minor diastereomer absorptions that could be clearly observed in entires 1, 3, and 8 in Table I had reversed magnitudes of vicinal coupling of the methine H_c to the higher field and lower field methylene hydrogens. These collective data are consistent with all major diastereomers possessing the same relative stereochemistry as that confirmed for 4a (R = R' = Ph).

Selective formation of diastereomer 4a can be qualitatively rationalized by formation of the condensation products as shown in Scheme I. Coordination of the nitrogen of the (E)-imine to the aluminum enolate would provide a cyclic transition state for product formation in which the substituent on the carbon of the imine double bond is forced toward the chiral iron. The presumption that bond formation occurs from a conformation of the enolate that places the very bulky PPh₃ 180° away from the approaching imine leads to discrimination between the two diastereotopic faces of the enolate (Scheme I, 5a and 5b). Therefore, selective reaction should occur from 5a that would lead to selective formation of diastereomer 4a.

The β -aminoiron acyls prepared herein should provide β -lactams on oxidative decomposition since Rosenblum has shown that oxidation of β -aminoiron alkyls (prepared by addition of amines to cationic $(\eta$ -C₅H₅)Fe(CO)₂ alkene complexes) gives β -lactams presumably via oxidatively assisted migratory insertion to transient iron(III) β -aminoacyls.¹⁴ In a brief unoptimized study we have treated 4a (R = R' = Ph and R = n-Pr, R' = Ph) with I_2/R_3N in CH₂Cl between -42 and 0 °C and observed facile β -lactam formation (eq 2).



The present diastereoselective condensations using racemic iron acyl 2 should extend to enantioselective condensations using optically active 2 and thus might prove significant in asymmetric organic synthesis. Complete details of this study will be published as a full paper.

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Supplementary Material Available: Spectral and analytical data for iron complexes and β -lactams and a typical experimental procedure for β -lactam formation (5 pages). Ordering information is given on any current masthead page.

Application of Marcus Theory to Metal Ion Catalyzed **Group Transfer Reactions**

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Particularly pertinent to questions regarding the role that metal ions play in biological systems are those model reactions in which complexing metal ions act on a substrate in concert with another catalyst (often a general base) to yield enhanced catalysis.¹⁻⁵ We have observed such behavior for the rates of enolization (eq I) and hydration (eq II) of oxalacetate (oxac2-) and found that these

$$O_{2}CCCH_{2}CO_{2}^{2} + B \xrightarrow{\text{slow}} O_{2}CC = CHCO_{2}^{2} + BH + \frac{\text{fast}}{1} O_{2}CC = CHCO_{2}^{2} + B$$

$$1 \qquad 2 \qquad (1)$$

$$\underline{1} + B + H_{2}O \xrightarrow{\text{slow}} -O_{2}CCCH_{2}CO_{2}^{2} + BH^{+} \xrightarrow{\text{fost}} -O_{2}CCH_{2}CO_{2}^{-} + B(\Pi)$$

rates, along with those for decarboxylation (eq III),^{6,7} conform to the Marcus equation for group transfer.⁸ This equation relates the free energy of activation to ΔG° , the thermodynamic change in free energy, and ΔG_o^* , the average of the self-exchange (or intrinsic) barriers for substrate and catalyst. Available information regarding complex stabilities9 permits accurate predictions of metal ion induced changes in ΔG° . No quantitative guidelines exist for the effect on ΔG_0^* , because the Marcus relation appears not to have been previously applied to these types of reactions. We report here that the influence of Mg^{II} (and also of Zn^{II} in decarboxylation) on reaction rates is essentially accounted for by the thermodynamics of the interactions with the strong chelating centers formed on the intermediates, 2, 3, 4, and the ΔG_0^{\dagger} values for a given catalytic mode are metal ion independent. This discovery should apply to other systems, and once ΔG_o^* for a reaction pathway is determined, say, from a single rate measurement on uncomplexed substrate, it appears possible to make reasonable predictions of rate constants for similar paths involving complexed substrate and general acids or general bases.

Forward rate constants for base-catalyzed enolization¹⁰⁻¹³ are given in Table I. For free oxac²⁻, base catalysts having oxygen donor atoms, imidazole, and the hindered tertiary amine, 2-(diisopropylamino)ethanol (DPEA), show normal behavior conforming to a Brønsted relationship.^{10,12} Less hindered tertiary amines show higher catalytic rates relative to their basicities¹⁰⁻¹² and are claimed¹² to react via a carbinol amine mechanism. In Table I the rate constants for unprotonated and monoprotonated N, N, N', N'-tetramethylethylenediamine (TMEN and HTMEN⁺)

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