

# Chiral Discrimination in the Reaction of the Enolate $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}_2)]\text{-Li}^+$ with Monosubstituted Epoxides: X-Ray Crystal Structure of $(RS,SR)\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\{\text{COCH}_2\text{CH}_2\text{CH}(\text{OH})\text{Me}\}]$

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In the presence of  $\text{Et}_2\text{AlCl}$ , the lithium enolate derived from the iron acetyl complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COMe})]$  discriminates between the enantiomers of monosubstituted epoxides to produce essentially only one product diastereoisomer, for example  $(RS,SR)\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\{\text{COCH}_2\text{CH}_2\text{CH}(\text{OH})\text{Me}\}]$  in the case of propene oxide.

We have recently demonstrated that the iron moiety  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)]$  is a highly versatile chiral auxiliary allowing excellent stereochemical control to be achieved in a variety of reactions of attached acyl<sup>1,2</sup> and carbene<sup>3</sup> ligands. We report here that the lithium enolate derived from  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COMe})]$  (**1**) in the presence of Lewis acids opens monosubstituted epoxides regioselectively at the unsubstituted carbon and although no new chiral centres are being generated in these reactions essentially only one product diastereoisomer is formed.

Addition of  $\text{Bu}^n\text{Li}$  to the racemic acetyl complex (**1**) in tetrahydrofuran at  $-78^\circ\text{C}$  generates the lithium enolate (**2**).<sup>1</sup> No reaction between (**2**) and racemic propene oxide or styrene oxide was observed at  $-78^\circ\text{C}$ . Addition of  $\text{Et}_2\text{AlCl}$  to (**2**) at  $-78^\circ\text{C}$  immediately followed by propene oxide gave a single product (**3a**). <sup>1</sup>H and <sup>13</sup>C N.m.r. spectroscopy clearly indicated that, as expected, epoxide opening had occurred at the unsubstituted carbon atom. This was confirmed by an X-ray crystal structure determination for complex (**3a**) (Figure 1) which also established the relative configurations of the two chiral centres as *RS,SR*. Crystal data for (**3a**):  $\text{C}_{29}\text{H}_{29}\text{FeO}_3\text{P}$ ,  $M = 512.4$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 8.426(3)$ ,  $b = 16.590(6)$ ,  $c = 18.272(4)$  Å,  $U = 2554.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.333$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 6.984$  cm<sup>-1</sup>, crystal size  $0.30 \times 0.35 \times 0.60$  mm. 1926 Reflections,  $I \geq 3\sigma(I)$ , final  $R = 0.046$ ,

$R_w = 0.055$ . Data were collected on an Enraf-Nonius CAD-4F diffractometer to  $\theta = 25^\circ$ . The crystal structure was solved by Patterson and electron density methods. Parameters including those for anisotropic thermal vibration were refined by large-block matrix least squares refinement. The majority of the hydrogen atoms were located in difference Fourier syntheses; those not found were included in their theoretical positions. Hydrogen atoms were allowed to 'ride' on their respective carbon atoms with one overall thermal parameter for the hydrogen atoms being refined.<sup>†</sup>

Under the conditions employed enolate transmetalation does not occur;<sup>4</sup> the  $\text{Et}_2\text{AlCl}$  is providing Lewis acid assistance to epoxide opening.<sup>5</sup> Similar results were obtained for other monosubstituted epoxides and are given in the Table 1. In each case both product diastereoisomers were formed in the presence of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  as Lewis acid. Since these reactions

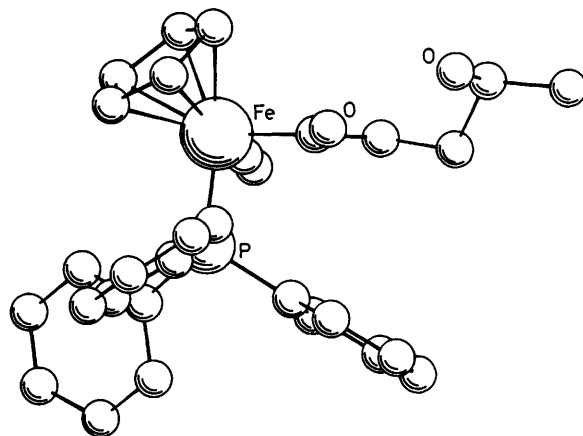


Figure 1. Molecular structure of  $(RS,SR)\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\{\text{COCH}_2\text{CH}_2\text{CH}(\text{OH})\text{Me}\}]$  (**3a**).

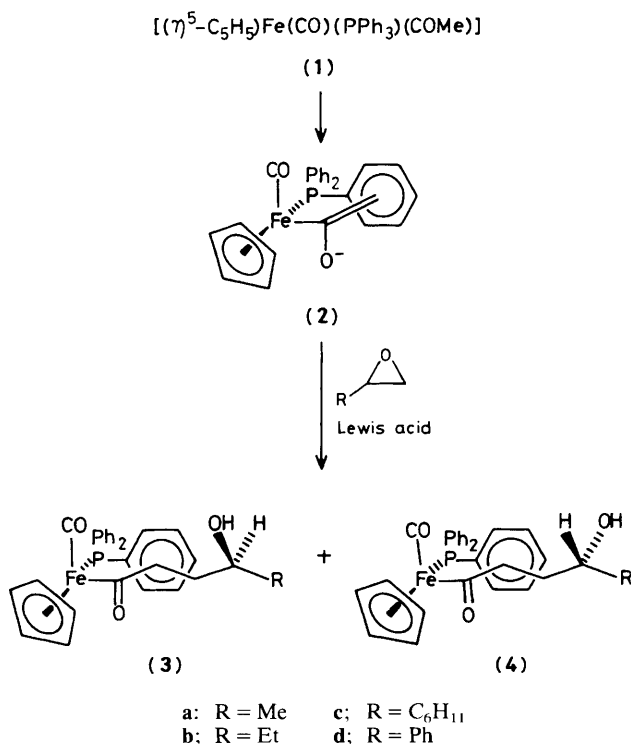


Table 1. Ratio<sup>a</sup> of (**3**) to (**4**) produced from the reaction of the enolate (**2**) with epoxides in the presence of Lewis acids.

Epoxide	Lewis acid	
	$\text{Et}_2\text{AlCl}$	$\text{BF}_3 \cdot \text{OEt}_2$
Propene oxide, ( <b>3a</b> ) : ( <b>4a</b> )	>30 : 1	55 : 45
But-1-ene oxide, ( <b>3b</b> ) : ( <b>4b</b> )	>30 : 1	60 : 40
Vinylcyclohexene oxide, ( <b>3c</b> ) : ( <b>4c</b> )	>30 : 1	70 : 30
Styrene oxide ( <b>3d</b> ) : ( <b>4d</b> ) <sup>b</sup>	13 : 1	65 : 35

<sup>a</sup> Determined by 300 MHz <sup>1</sup>H n.m.r. spectroscopy. <sup>b</sup> Ratios determined after *O*-methylation ( $\text{NaH}$ ,  $\text{MeI}$ ).

<sup>†</sup> The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

involve racemic enolate and racemic epoxides the stereoselectivities in Table 1 correspond to the rate difference in the reaction of one enolate enantiomer with the two epoxide enantiomers.<sup>6</sup> The origin of this remarkable chiral discrimination and its extension to the kinetic resolution of iron acyl complexes and epoxides is under investigation.

We thank the S.E.R.C. for a studentship (to P. W.) and a postdoctoral research assistantship (to R. H. J.) and British Petroleum plc, for financial support.

Received, 1st July 1985; Com. 921

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