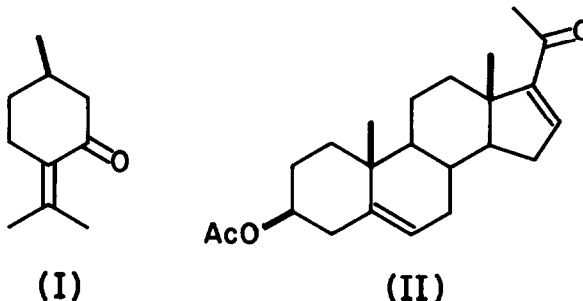


ASYMMETRIC SYNTHESIS OF OPTICALLY ACTIVE TRICARBONYLIRON COMPLEXES OF 1,3-DIENES

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**Summary:** Asymmetric coordination of prochiral 1,3-dienes to form optically active (diene)Fe(CO)<sub>3</sub> complexes has been achieved by direct transfer of the Fe(CO)<sub>3</sub> group from chiral enone complexes.

Complexation of an unsymmetrically substituted 1,3-diene produces a chiral molecule, with one face of the diene distinguished by bonding to the metal. Here we report a complexation process which enables the two faces of a prochiral diene to be differentiated for the first time, resulting in the production of optically active tricarbonyliron complexes.



Various  $\alpha,\beta$ -unsaturated ketones, which form moderately stable tricarbonyliron complexes, are known to act as a convenient source of an iron carbonyl moiety for transfer to 1,3-dienes.<sup>1</sup> Analogous transfer reagents prepared simply from two readily available chiral enones, (+)-pulegone (I) and (-)- $3\beta$ -acetyloxypregna-5,16-diene-20-one (II), (16-DHA) were used without isolation to provide a direct synthesis of optically active complexes of 1-methoxycyclohexa-1,3-diene (III), 1-methoxy-4-methylcyclohexa-1,3-diene (IV) and methyl sorbate (V), as shown in the Table.

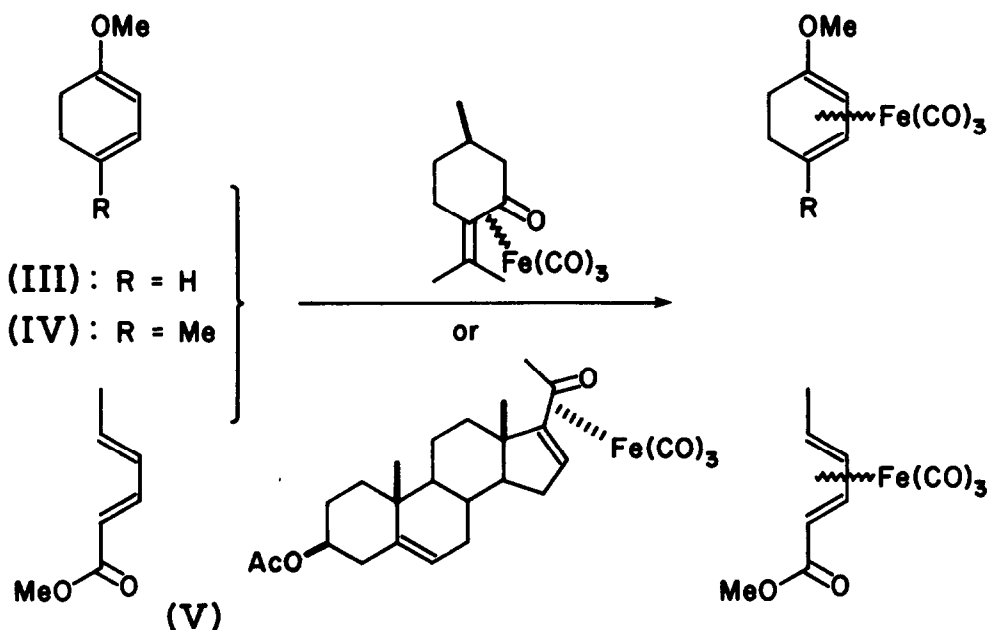
Complexes of pulgone<sup>3</sup> were prepared thermally from Fe<sub>2</sub>(CO)<sub>9</sub> (light petroleum, b.p. 40-60°, 5 hrs). After filtration through celite, evaporation of solvent and Fe(CO)<sub>5</sub>, addition of the 1,3-diene in degassed benzene, toluene or light petroleum (b.p. 40-60°) and heating at reflux for the appropriate time, the crude product was distilled and chromatographed on silica gel. The compounds were distilled a second time and optical rotations measured on analytically pure samples. A similar method was used for  $3\beta$ -acetyloxypregna-5,16-diene-20-one, except that crystallisation of the crude product from hexane resulted in

recovery of the steroid (> 60%). Chromatography of the supernatant after concentration yielded the diene complex which was then distilled.

**TABLE**

Diene	Reaction Conditions for Transfer of $\text{Fe}(\text{CO})_3$		Reagent Quantities (gm)			Wt Diene Complex (gm)	Yield (c)	$[\alpha]_D$ ( $\text{CHCl}_3$ ) 4-12 gm/100 ml	
	Solvent	Time	Pulegone or (16-DHA)	$\text{Fe}_2(\text{CO})_9$	1,3-Diene				
$(\text{III})^2, (\text{a})$	(i)	Benzene	18 hrs	1.25	3.25	0.5	0.94	83%	+15°
	(ii)	Benzene	90 hrs	1.25	3.25	0.5	0.66	58%	+13°
	(iii)	Petrol	240 hrs	8.5	22.0	11.0	6.2	27%	+9°
$(\text{IV})^2, (\text{a})$	(iv)	Benzene	90 hrs	2.5	6.5	1.5	1.5	48%	+6°
	(v)	Toluene	6 hrs	2.5	6.5	1.5	1.8	58%	+4°
	(vi)	Petrol	270 hrs	3.7	10.0	4.0	6.7	79%	+13°
(V), (a)	(vii)	Petrol	300 hrs	2.9	7.3	3.15	2.5	38%	+7°
$(\text{III})^2, (\text{b})$	(viii)	Benzene	17 hrs	1.0	1.5	0.6	0.14	10%	-29°
$(\text{IV})^2, (\text{b})$	(ix)	Benzene	19 hrs	1.0	1.5	0.68	0.32	22%	-42°
(V), (b)	(x)	Benzene	19 hrs	1.0	1.5	0.69	0.23	16%	+28°

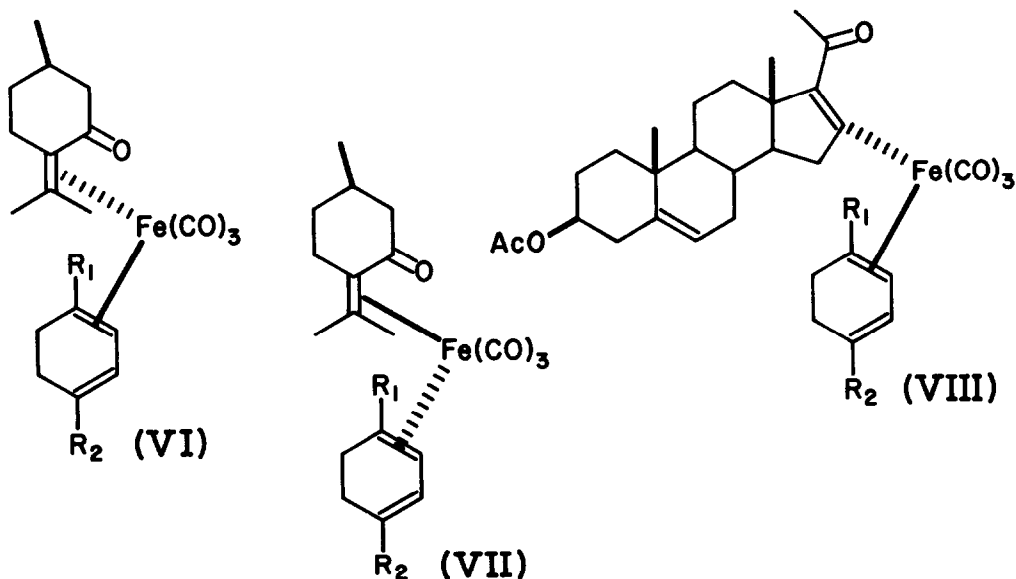
(a): from Pulegone/ $\text{Fe}_3(\text{CO})_9$ ; (b): from (16-DHA)/ $\text{Fe}_3(\text{CO})_9$ ; (c): yield based on 1,3-diene<sup>2</sup>.



Optically active tricarbonyl(cyclohexadienyl)iron cations were obtained from the complexes by the usual procedures.<sup>4</sup> Tricarbonyl(1-methoxycyclohexa-1,3-diene)iron ( $[\alpha]_D = +8.3^\circ$ , C=12,  $\text{CHCl}_3$ ) reacted with triphenylmethylm tetrafluoroborate to give tricarbonyl(2-methoxycyclohexadienylm)iron hexafluorophosphate, ( $[\alpha]_D = +4.8^\circ$ , C=6,  $\text{CH}_3\text{CN}$ ).<sup>5</sup> Treatment of tricarbonyl(1-methoxy-4-methylcyclohexa-1,3-diene)iron ( $[\alpha]_D = +12.6^\circ$ , C=4,  $\text{CHCl}_3$ ) with concentrated sulphuric acid gave tricarbonyl(2-methylcyclohexadienylm)iron hexafluorophosphate, ( $[\alpha]_D = -2.5^\circ$ , C=9,  $\text{CH}_3\text{CN}$ ).

Conversion of these salts into R-(-)-cryptone, and S-(+)- $\alpha$ -phellandrene, respectively, will be described elsewhere. Although accurate optical yields cannot be given at this stage, the results indicate that the 1,3-diene complexes are formed in less than 20% enantiomeric excess.

The optical yield may be limited by two factors: thermal liberation of free iron carbonyl species, and lack of specificity in the initial complexation of the enone. While complexation of 16-DHA may reasonably be expected to occur only on the  $\alpha$  face, pulegone forms both  $\alpha$  and  $\beta$  complexes.<sup>3</sup> Although unstable, the pulegone complexes can be isolated in low yield by crystallisation and sublimation ( $40^\circ$ , 0.001 mmHg) as an inseparable mixture of the two isomers. (Found C: 53.25, H: 5.59; Calc. C: 53.45, H: 5.52;  $\text{M}^+-\text{CO}$ : 264 - 2CO;  $\nu_{\text{CO}}$ , 2051, 1991, 1965  $\text{cm}^{-1}$ , cyclohexane). The PMR spectrum of the mixture included four methyl singlets of about equal intensity ( $\delta = 1.39, 1.42, 1.55, 1.57$  ppm,  $\text{C}_6\text{D}_6$ ) and two doublets ( $\delta = 0.89, 0.93$  ppm,  $J = 6$  Hz).  $^{13}\text{C}$  resonances of the enone system show pairs of peaks for each carbon (99.1, 99.5 ppm : C4 and 68.8, 69.8 ppm : C8,  $\text{C}_6\text{D}_6$ ). The PMR spectrum of the crude material used for the transfer of  $\text{Fe}(\text{CO})_3$  was similar to that of the purified complexes, indicating the production of approximately equal amounts of the  $\alpha$  and  $\beta$  isomers.



The displacement of the enone by dienes is thought to proceed by dechelation of the ketone function and partial coordination of the diene.<sup>6</sup> This suggests that the stereochemical outcome of the reaction is determined during the first approach of the diene to the coordinately unsaturated species formed by cleavage of the metal ketone bond, involving the formation of the presumed intermediates VI, VII or VIII. These then decompose under the reaction conditions to give the observed products in which the metal remains bonded to the same face of the diene. Reaction of similar, transient, coordinately unsaturated (polyene)Fe(CO)<sub>3</sub> intermediates in which the iron is bonded to a single olefinic linkage in the conjugated polyene has been shown to proceed with no detectable scrambling of the iron between the two faces of the molecule.<sup>7</sup> The ambiguity resulting from the presence of both  $\alpha$  and  $\beta$  complexes of pulegone in the reaction mixture may account for the superior asymmetric induction observed with 16-DHA under comparable conditions. (Reactions (ii) and (viii), (iv), and (ix)). However, until more information concerning the reaction pathway is available, further speculation on the steric basis of asymmetric complexation is premature. The preparation of a variety of optically active  $\alpha,\beta$ -unsaturated ketones, and their evaluation as asymmetric transfer reagents is currently in progress.

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