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Synthesis of substituted iron carbonyl conjugated dienyl complexes from 4-vinylcyclohexenes under kinetic or thermodynamic control

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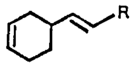
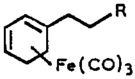
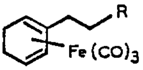
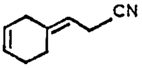
Abstract : It is shown that substituted conjugated cyclohexadienyl iron carbonyl complexes can be easily prepared, under thermodynamic control by isomerisation with $Fe(CO)_5$ of easily accessible 4- vinylcyclohexene derivatives. When an HCl modified $Fe(CO)_5$ catalyst is added, the reaction proceeds under kinetic control.

Cyclohexadienyl derivatives are most commonly obtained from aromatic products by Birch reduction (1) ; they can be further isomerized to conjugated systems by $Fe(CO)_5$ which is a powerful synthetic auxiliary (2). In the present paper we describe our results (see Table) which show that 1 and 2-substituted cyclohexadienyl iron tricarbonyl complexes can be prepared from easily accessible 4-vinylcyclohexene (3) or derivatives thereof (4). This overall procedure for the preparation of substituted conjugated cyclohexadiene derivatives can replace advantageously the Birch reaction. Using 1.2 equivalents of $Fe(CO)_5$ in $(nBu)_2O$ under reflux, the 2-substituted cyclohexadienyl complexes 3, 6 and 9 are obtained with good yields and high selectivity (entries 1,3,5). This selectivity is completely reversed (entries 2,4,6) by the addition to the reaction mixture of catalytic amounts of complex I prepared independently by bubbling gazeous HCl in an n-butyl ether solution of $Fe(CO)_5$ (5). Under these conditions 1-substituted cyclohexadienyl complexes 2, 5 and 8 are obtained as major products, with a good selectivity. Inspection of the Table shows that the reaction selectivity is not much altered by the nature of R (compare for instance entries 1 and 3 or 2 and 4) or the position of the double bond (compare entries 3 and 5 or 4 and 6). The kinetic nature of 1-substituted complexes 2, 5 and 8 was demonstrated by equilibration experiments. Treatment of reaction mixtures (see entries 2,4,6) where these derivatives are the major components, under equilibrating conditions (6) (98% H_2SO_4, for a few minutes, or in refluxing $(nBu)_2O$ for 24 h) yielded a mixture containing mainly 2-substituted complexes 3, 6 and 9, which are therefore the thermodynamic products of the reaction.

The reactions described provide a new efficient way of preparing selectively conjugated cyclohexadienyl iron tricarbonyl complexes substituted in either position 1 or 2. The latter are known to offer an interesting synthetic potential particularly in cycloaddition reactions (7). The mechanistic questions raised by the present results, as well as the structure of complex I are presently under investigation.

TABLE

Entry	R	Starting Material	Reaction Conditions	Yield (c) (%)	Products (Ratio)	
						
1	H	1	a, 24h(d)	90	2(1)	3(9)
2	H	1	b, 24h	95	2(6)	3(4)
3	COOMe	4	a, 24h	76	5(1,5)	6(8,5)
4	COOMe	4	b, 24h	77	5(7)	6(3)
5		7	a, 24h	91	8(2)	9(8)
6			b, 24h	85	8(8)	9(2)

a) In a typical experiment diene 1 (1.08 g) is reacted with $Fe(CO)_5$ (2.35 g) in refluxing n-butyl ether (25ml).

b) Complex I (0.2 g) (5) is added to the reaction mixture (see above).

c) Isolated by chromatography on silica gel.

d) See reference (8).

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5 - When gazeous HCl is bubbled into a $(n-Bu)_2O$ solution of $Fe(CO)_5$ an amorphous light yellow solid precipitates and is filtered and washed with dry diethyl-ether. This complex I is used as such (entries 2,4 and 6). At the present stage it is difficult to propose a structure for this material as the common spectroscopic methods do not provide exploitable informations. Furthermore this complex decomposes on melting and does not yield an informative microanalysis. However its preparation can be easily reproduced.
6 - N.S.Nametkin, V.D.Tyurin, H.Slupchin'sky and Al-Laddaui, J.Organomet.Chem., 154, 289, 1978.
7 - see reference 2, p.1729.
8 - The selectivity we observe (2/3 ratio) is opposite to the one previously reported by P.McArdle and T.Higgins, Inorg.Chim.Acta, 30, L303, 1978.

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