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ORGANOMETALLIC COMPOUNDS IN ORGANIC SYNTHESIS: REACTIONS OF SOME TRICARBONYLCYCLOHEXADIENYLIUM-IRON COMPLEXES WITH TRIMETHYLISLYL ENOL ETHERS

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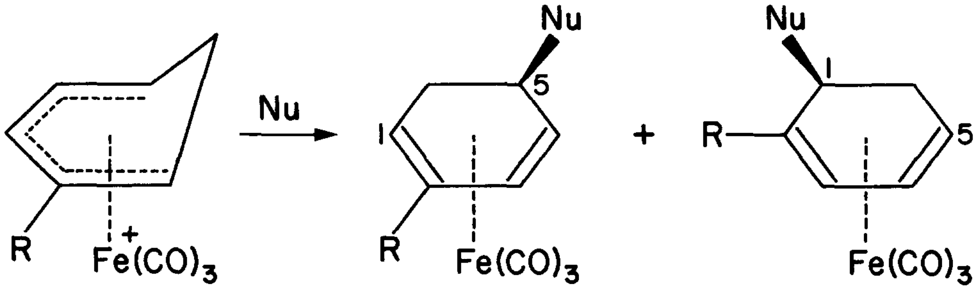
Summary: O-Silylated enolates derived from ketones react with tricarbonylcyclohexadienyl-iron cationic complexes under very mild conditions to form carbon-carbon bonds in excellent yields.

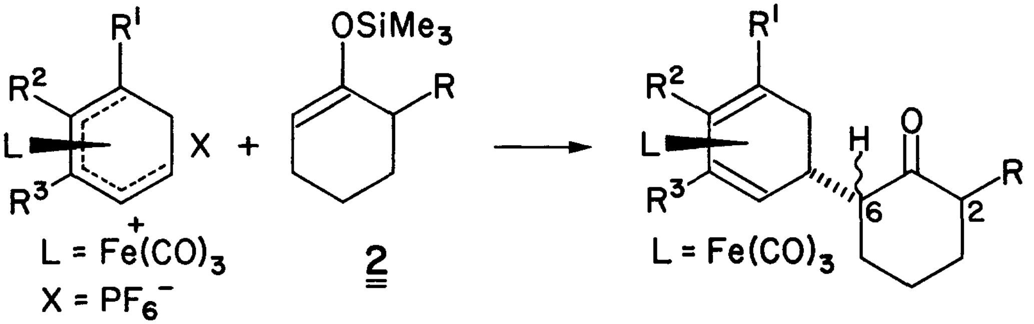
A wide range of nucleophiles is known to react with cations of type (1) at one or both termini of the charge, attack being from the α-(rear) side under kinetic control (equation 1).[1] The reaction has potential use in organic syntheses, and can result in new carbon-carbon bonds, particularly through the use of enolate anions, enols or enamines. In order to produce alternative products, pure defined enol-derivatives are required, and are often difficult to obtain. A reaction now described, using trimethylsilyl enol ethers has the double advantage that it is very smooth and rapid, and that specific enol trimethylsilyl ethers can be obtained by known methods, particularly through alternative kinetic or thermodynamic control in enolisation.[2] Trimethylsilyl enol ethers are known to react with electrophilic reagents in a range of reaction type.[3]



1 Nu = Nucleophile

Equ. I

Reactions of trimethylsilyl enol ethers derived from cyclohexanone and 2-methylcyclohexanone (2, R=H or Me) and several substituted tricarbonylcyclohexadienylium-iron complexes (3, 4 and 5) have yielded expected products (6, 7 and 8; R=H or Me) in 70-84% isolated yields calculated on the dienylium salt.



2

3 $R^1 = R^2 = R^3 = H$

4 $R^1 = R^3 = H$, $R^2 = OMe$

5 $R^1 = COOMe$, $R^2 = H$, $R^3 = Me$

6 $R^1 = R^2 = R^3 = H$

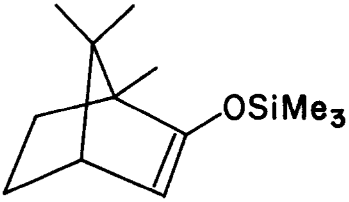
7 $R^1 = R^3 = H$, $R^2 = OMe$

8 $R^1 = COOMe$, $R^2 = H$, $R^3 = Me$

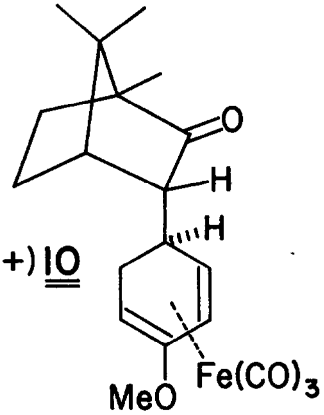
The kinetically formed 2 (R=Me) reacts at the 6-position in contrast to the enamine or the slow enolization of the carbonyl where reaction occurs at the 2-position.[4] The enol trimethylsilyl ether 2 (R=Me; ∿1.25 ml, 4-5 equivalents) was added with stirring under nitrogen to the salt 3 (0.5 g) in dry acetonitrile (6 ml). After 1.5 hr[5] the solvent was removed at 23°/0.05 mm, the product extracted with ether and chromatographed on silica in hexane containing ether (∿2% vol.). The product was finally distilled in high vacuum to yield 6 (R=Me; 0.34 g, 75%) as an oil, consisting of an epimeric mixture at C-6. Spectra were those expected: ν_{max} 1705, 1955, 2035 cm^{-1}; m/e 330 (M^+, $C_{16}H_{18}O_4Fe$), 302 (M^+-CO), 274 (M^+-2CO), 246 (M^+-3CO); $\delta(CDC\ell_3)$ 0.98 (d, J = 7Hz, $C\underline{H}_3CH$), 1.03 (d, J = 7Hz, $C\underline{H}_3CH$). 1.20-2.78 (b.m. ∿22H), 3.08 (m, overlapping, "outer" diene), 5.36 (m, overlapping, "inner" diene).

The $Fe(CO)_3$ group was removed ($FeC\ell_3.6H_2O$ - benzene, room temp.)[6] to give the cyclohexadiene (88%), dehydrogenated with DDQ[7] to the known 6-methyl-2-phenylcyclohexanone.[8] The overall process amounts to the α-arylation of a ketone.[9] With a variety of salts available the method should be a rather general one for preparing substituted aryl derivatives.

The enol trimethylsilyl ether of (+) camphor (9)[10] was found to react with salt (4) to yield a mixture of isomers which can be equilibrated (MeOH-KOH, room temperature) to >90% of one of them, presumably the endo-isomer (10).[11,12] Importantly the



(+)9



(+)10

recovered unreacted cation was found to be optically active $[\alpha]_D$ (5% acetonitrile) varying between -1° and -18° depending on conditions. The logical consequences of this observation are being pursued. It represents the first (partial) direct resolution of a potentially asymmetric cation of this type.

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12. All new compounds gave expected spectral data, as well as combustion values.

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