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ORGANOMETALLIC COMPOUNDS IN ORGANIC SYNTHESIS—PART 17[1]

REACTIONS OF TRICARBONYLCYCLOHEXADIENYLIRON SALTS WITH O-SILYLATED ENOLATES, ALLYL SILANES AND ASPECTS OF THEIR SYNTHETIC EQUIVALENTS

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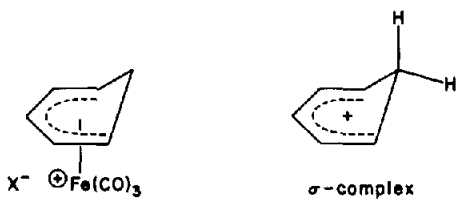
Abstract—Efficient C–C bond formation results during reactions of O-silylated enolates and allytrialkysilanes with a range of tricarbonylcyclohexadienyliron salts to give tricarbonylcyclohexadieneiron complexes in good to excellent yields. This represents a new and efficient type of conversion of aldehydes, ketones, esters and lactones, through enol TMS ethers, into synthetically useful products. An advantage of the allylsilane process is that C–C formation occurs at the end of the double bond remote from the silane group. The cations employed can be defined as synthetic equivalents of the 5-cation of substituted cyclohexadienes, or of the 4-cation of cyclohex-2-enones, or alternatively of specifically substituted aryl cations, dependent on their structures and the subsequent treatment of the reaction product.

Carbon-carbon bond formation is central to the art and science of organic synthesis.[2] Any new and wide-ranging methods are therefore important. Classical methods employ commonly the reaction of anionoid with cationoid reagents. A recently developed type of anionoid reagent involves the trialkylsilylenolether group, which, compared[3,4] with classical enolates, or organometallic groups is monomeric, non-basic, non-solvated, but reacts regiospecifically on carbon with cationoid reagents.[5] The formally similar allylsilanes are stable to air and water and are non-basic, and have been reacted with standard cationoid reagents such as halides and carbonyl derivatives. Recently to the general list of cationoid reagents have been added the transition metal complexed cations, and these have been shown[6] to form new C–C stereospecifically with a range of anionoid (nucleophilic) reagents. We now report an investigation of such processes with a range of O-silylated enolates and allylsilanes on the one hand, and a range of tricarbonylcyclohexadienyliron salts on the other, which demonstrates the range and efficiency of C–C formations. Some methods of obtaining such salts in pure form have been outlined,[7] together with a discussion of $Fe(CO)_3$ as a complexing group for lateral activation and control in synthesis.[7]

Tricarbonylcyclohexadienyliron cations (**1**) are formally a stabilised version of the σ-protonated benzene (**1a**) formed in super acids,[8] and their general reactivity trends have recently been attempted using simple Frontier Molecular Orbital (FMO) considerations.[9] While the σ-complex (**1a**) is incompatible for C–C bond formation with anionoid reagents discussed above, the tricarbonylcyclohexadienyliron salts form C–X bonds (X = O, S, P and C) bonds efficiently with high regio- and total stereo-



(**1**) (**1a**)

specificity, the group X[10] being attached on the face opposite to $Fe(CO)_3$. The fundamental reactivities as cations of such salts are independent of the presence of attached classical anionoid or cationoid groups, except that these control regio-specificities in mesomeric systems. Such novel reactivity patterns are usually not amenable to classical organic methodology.[11] Although our discussion to follow is limited to the tricarbonylcyclohexadienyliron salts, the principles apply more widely to other transition metals and other ligands, which need to be chosen according to the synthetic end desired.

The range of carbon nucleophiles (anionoid reagents) employed so far includes thermodynamic enols[12] from ketones and 1,3-dicarbonyls, anions of malonic esters,[13] enamines,[14] organometallic derivatives of zinc,[15] cadmium,[15] copper,[16] boron,[17] and more recently[18] organolithium reagents. The versatility of synthetic procedures has recently been increased by the use of trimethylsilyl (TMS) enol ethers,[19] 1,2 - bis(trimethylsiloxy) - 1 - cycloalkenes[20] and allylsilanes.[21]

Reactions of TMS-enol ethers with tricarbonylcyclohexadienyliron salts

A quick perusal of the list of anionoid reagents which form C–C bonds efficiently with these cations reveals that the most widely employed enolate ions are missing, the reason being that attempted reactions have resulted

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in the formation of complex reaction mixtures.[22] Thus we were led to examine TMS-enol ethers as their reaction partners.

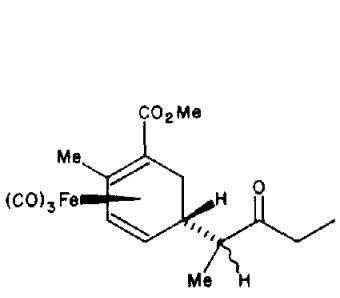
Smooth and rapid reaction occurs on mixing the reagents in dry acetonitrile at, or below room temperature. Catalysis such as Lewis acids[23] or fluoride ion[24] which have been used in alkylation or aldol-type condensations with TMS-enol ethers are not needed here.

To define optimum experimental conditions, the TMS enol ether of cyclohexanone was examined with a variety of salts, the best yield based on salt was found with use of 3–5 equivalents of TMS enol ether in acetonitrile at room temperature. For reasons not at present clear, the use of 1.1 equivalent of TMS enol ether did not consume the salt completely. This result puts limitations on its usage in synthesis, if the TMS enol ether is the rare component.

1-Trimethylsiloxycyclohexene with the tricarbonylcyclohexadienyliron salts (**1** and **2**) gave the known[12] products (**3** and **4**) with the expected regiospecificity at the 5-position of **2** directed by OMe. The presence of 1-COOMe in the salt **5** does not interfere with the process, the regiospecific product (84% yield) being **6**. Reaction with unsymmetrical salt **11** gave the neutral complex **12** in 91% yield.

stituted - 6 - methylcyclohexanones (**9**, **10**, **8** and **13**). Structural confirmation was obtained by conversion of complex **9** into the known 6 - methyl - 2 - phenyl - cyclohexanone.[26] In the case of 2-methoxy complex (**10**), the diastereomers could be separated by fractional crystallization.

Z - 3 - Trimethylsiloxy - 2 - pentene reacted with the 1-carbomethoxy salt (**7**) to yield the keto-ester (**14**) in 88% yield, and there seems no doubt that the process is generally applicable.



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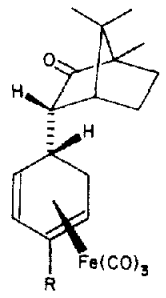

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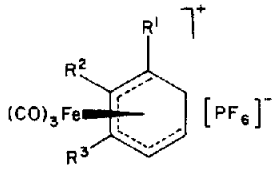
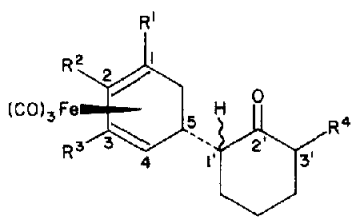
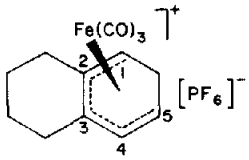




(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = R^3 = H$, $R^2 = OMe$
(2a) $R^1 = R^2 = H$, $R^3 = OMe$
(5) $R^1 = CO_2Me$, $R^2 = H$, $R^3 = Me$
(7) $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = H$

(3) $R^1 = R^2 = R^3 = R^4 = H$
(4) $R^1 = R^3 = R^4 = H$, $R^2 = OMe$
(6) $R^1 = CO_2Me$, $R^2 = R^4 = H$, $R^3 = Me$
(8) $R^1 = CO_2Me$, $R^2 = R^4 = Me$, $R^3 = H$
(9) $R^1 = R^2 = R^3 = H$, $R^4 = Me$
(10) $R^1 = R^3 = H$, $R^2 = OMe$, $R^4 = Me$



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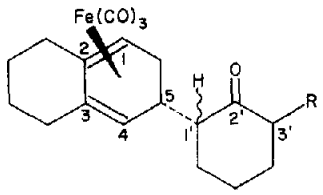


(12) R = H
(13) R = Me

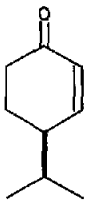
The availability of specific TMS enol ethers from unsymmetrical ketones by kinetic or thermodynamic enolization[25] led us to test whether the specificity is retained in the reaction, with such isomers. Ketones themselves react slowly, but only through the stable enol.[12]

Thus, 6-methyl-1-trimethylsiloxycyclohexene was reacted with several salts (**1**, **2**, **7** and **11**) and its regiochemical integrity was found to be maintained, the product being in each case a diastereoisomeric mixture (presumably due to the centre adjacent to the CO since α-attack on the cation would be expected) of 2 - substituted - 6 - methylcyclohexanones (**9**, **10**, **8** and **13**). Structural confirmation was obtained by conversion of complex **9** into the known 6 - methyl - 2 - phenyl - cyclohexanone.[26] In the case of 2-methoxy complex (**10**), the diastereomers could be separated by fractional crystallization.

Z - 3 - Trimethylsiloxy - 2 - pentene reacted with the 1-carbomethoxy salt (**7**) to yield the keto-ester (**14**) in 88% yield, and there seems no doubt that the process is generally applicable.

2-Trimethylsiloxy-2-bornene derived from (+)-α-bromocamphor was used to examine both the reaction of a rather hindered enol ether, and a possible enantiospecificity of reaction with a chiral compound. With the symmetrical salt (**1**), the product was a mixture of isomers which could be equilibrated (MeOH–KOH, room temperature) to >90% of one of them, presumably the *endo*-isomer (**15**, R = H).[28] Interestingly in the case of the (±)-2-methoxy salt (**2**), if the reaction was not allowed to go to completion, recovered salt **2** was found to be optically active $[\alpha]_D$ (C = **5**, MeCN) varying between −1° to −18° depending upon experimental conditions

(Experimental). The enantiomeric excess of the enriched 2-methoxy-salt (**2**) $[\alpha]_D$ −18° was ~15% as indicated by the Eu(fod)$_3$ induced ^{1}H-NMR analysis of the diastereoisomers produced by its reaction with (−)-1-phenylethylamine. The absolute configuration[29] of 2-methoxy salt (**2**) has been deduced by direct correlation of its enantiomer with (−)-cryptone (**16**), and is indicated by structure **17**. This represented the first example of a



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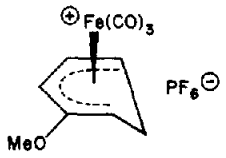


(17)

direct resolution, even though partial, of a potentially asymmetric cation of this type. While not at present very useful as a practical resolution, this process holds promise to define the transition state of this alkylation. Most likely an SN_2 type process is operative.[9]

2-Methyl-1-trimethylsiloxypropene[30] reacted with salts (**1**, **7** and **11**) giving the neutral complexes (**18**, **19** and **20**) respectively. This example provides a novel approach to the introduction of a gem dimethyl group adjacent to either a potential cyclohexa - 1,3 - diene, cyclohex - 2 - en - 1 - one or the related aryl derivatives. Similar products are also accessible through the use of a related enamine.[14]

1 - Oxa - 2 - trimethylsiloxycyclopent - 2 - ene which is readily available[31] from γ-butyrolactone reacts with salts (**1**, **2**, **7** and **11**) to give high yields of γ-lactone adducts (**21**, **22**, **23** and **24**). Likewise phenyl ketene methyl-TMS-acetal[32] readily gave the expected complexes (**25**, **26** and **27**) upon reaction with the cations (**1**, **7** and **11**). The diastereomers thus produced were separable by fractional crystallization.

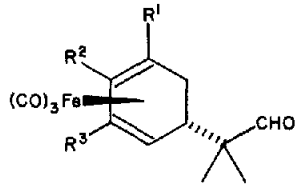
Extension of the above reaction to 1,2 - bistrimethylsiloxy - 1 - cyclopentene gave initially siloxy acyloins, treatment of which with MeOH–HCl resulted in a novel route to 2 - (substituted) - 2 - cyclopenten - 1 - one. Some aspects of this work have been reported[20] in a preliminary form.

Reactions of some allylsilanes with tricarbonylcyclohexadienyliron salts

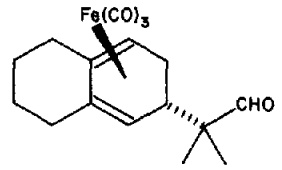
Allylsilanes are closely related to TMS enol ethers with C instead of O. The reactions are formally analogous, with development of a negative charge at the terminus of the initial double bond. A wide range of cationoid reagents react with allylsilanes, resulting in a net transfer of an allyl unit.[33]

Transfer of an allyl group to tricarbonylcyclohexadienyliron salts has previously been achieved employing allyl cadmium reagents.[15] In many cases the yield of the product was poor and there is some doubt whether cations bearing a COOMe group would be compatible with the reaction.

Efficient reaction proceeds by gently refluxing the appropriate salt (**1**, **2**, **2a**, **7** and **11**) and allyl trimethylsilane



(18) $R^1 = R^2 = R^3 = H$
(19) $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = H$



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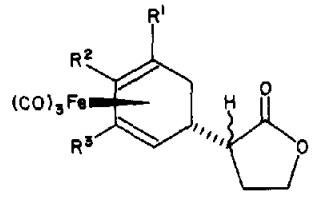
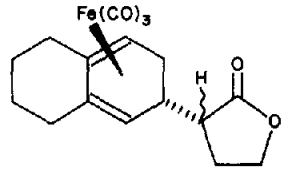


(21) $R^1 = R^2 = R^3 = H$
(22) $R^1 = R^3 = H$, $R^2 = OMe$
(23) $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = H$



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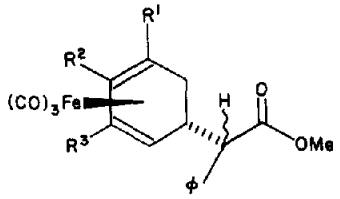
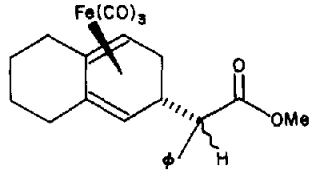
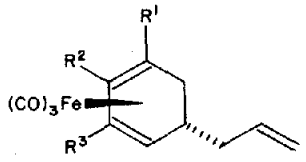


(25) $R^1 = R^2 = R^3 = H$
(26) $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = H$



(27)

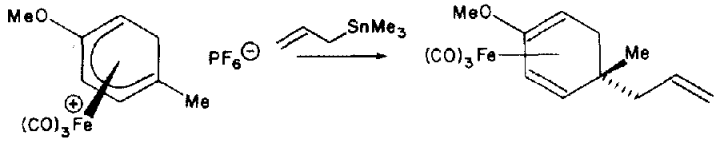
(2-3 molar excess) in dry methylene chloride, the products being **28**, **29**, **30**, **31** and **32**.



(28) $R^1 = R^2 = R^3 = H$
(29) $R^1 = R^3 = H$, $R^2 = OMe$
(30) $R^1 = R^2 = H$, $R^3 = OMe$
(31) $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = H$
(32) $R^1 = H$, $R^2 \frown R^3 = -(CH_2)_4-$

In the case of salt **2**, the reaction was best performed in a higher boiling solvent (1,2-dichloroethane, b.p. 83°), since it is known that the –OMe substituent at C-2 deactivates the cation towards anionoid reagents.

The reaction is subject to steric hindrance since cation **33** failed to react with allyl trimethylsilane in both CH_2Cl_2 and $ClCH_2CH_2Cl$. However, the more reactive allyl trimethylstannane gave in ~30% yield the complex **34** in refluxing methylene chloride for 15 hr, with nearly



(33) (34)

50% recovery of the salt. Some other minor components of this reaction were not identified. It is significant to note however, that deprotonation of the salt **33** at the terminus of Me group was not observed under the above conditions, although this may be a dominant reaction with basic nucleophiles.

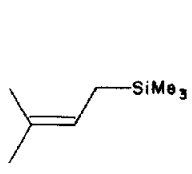
The silane (**35**) reacted smoothly with salt **7** giving compound **36** in 95% yield. Although benzylsilanes are analogous to allylsilanes, the attempted reactions were too slow to be observed. It is of interest to note that Birch reduction products **37** and **38**,[34] which are readily accessible from respective benzyl silanes react very smoothly with cation **11** to produce novel products (**39** and **40**).

Reactions of these types though illustrated above with the cyclic complexed cations, should in principle be possible with other cations, including the open-chain ones.

Vinyltrimethylsilane though known[33] to react with cationoid reagents, showed no favourable reactivity with our cations, despite the rather forcing conditions of a sealed tube experiment (100°, 24 hr). We have, however, not studied the more reactive vinylsilanes.

Tricarbonylcyclohexadienyliron cations and their organic synthetic equivalents

To emphasize the structural results of the synthetic C–C bond forming process with these cations, it is desirable to relate them to their synthetic equivalents. These cations can be expressed as several organic *cationic* equivalents according to alternative experimental sequences (a) removal of $Fe(CO)_3$ from the product; (b) removal of $Fe(CO)_3$ from a complex carrying OR, followed by acid hydrolysis, or (c) removal of $Fe(CO)_3$ with dehydrogenation. Synthetic equivalents are then respectively C-5 cations of cyclohexa-1,3-dienes or cyclohex-2-enones or are specifically substituted aryl cations. A further discussion of related synthetic equivalents has already appeared,[7,35] and some useful synthetic procedures towards this end are noted in the experimental. In this way complexes **8**, **14**, **20**, **23** and **27** were converted to the aromatic substrates **41**, **42**, **43**, **44** and **45** respectively, while the methoxy substituted complexes **29** and **30** were converted to cyclohexenone derivatives **46** and **47**.



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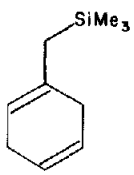

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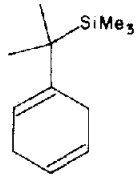

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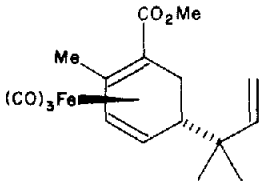

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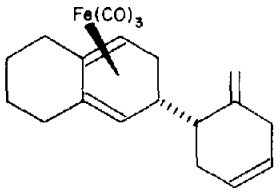

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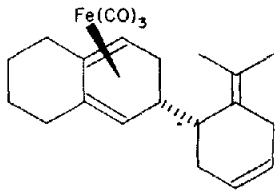

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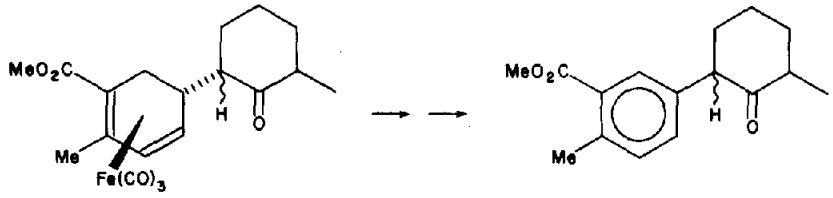

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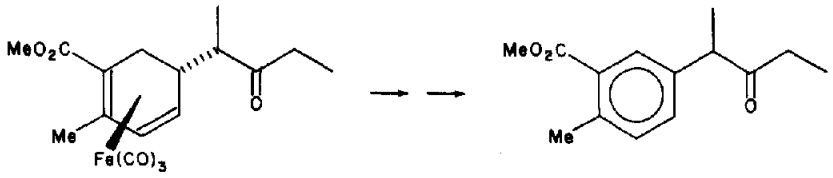

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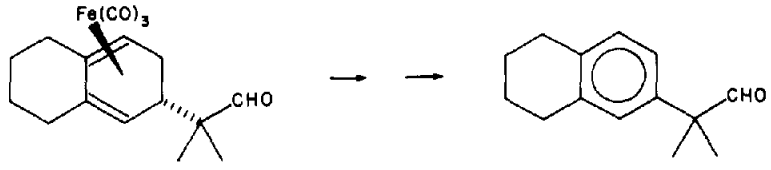
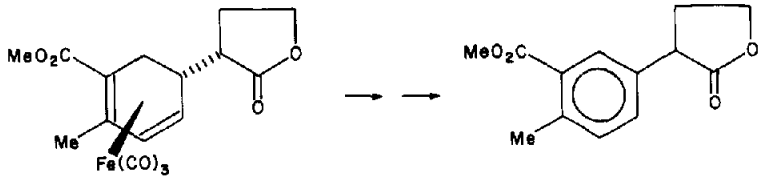
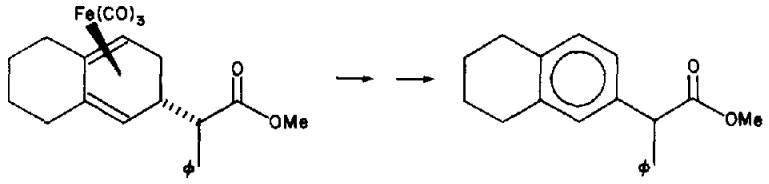


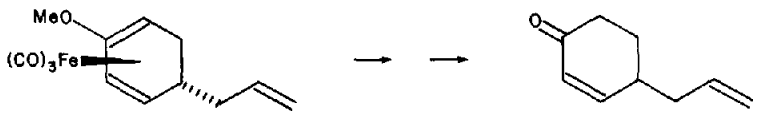
(20) (43)



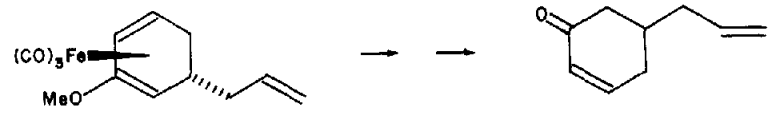
(23) (44)



(27) (45)



(29) (46)

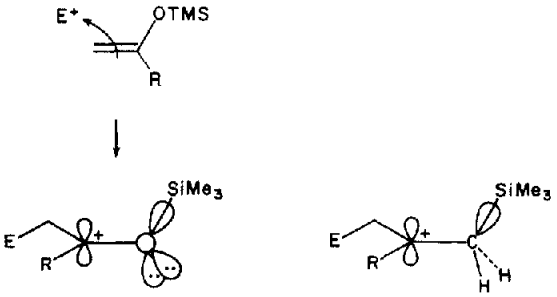


(30) (47)

Some observations on the possible mechanism of the reaction between cyclohexadienyliron cations and O-silylated enolates

One possible type of mechanism for the enol-TMS derivatives might involve attack on Si by PF_6^- (or $F^\ominus$ derived from it) to generate the enolate ion, which then reacts with the cation. This is however, most unlikely on two grounds. PF_6^- is non-nucleophilic and therefore would not be expected to react with the electron rich TMS enol ether and also salts of enolate anions are known to produce complex reaction mixture.[22] Additional evidence comes from the fact that (1) cyclohexanone TMS enol ether failed to react with benzyl bromide in the presence of $PF_6^\ominus$ (see known[24] $F^\ominus$ assisted alkylation of O-silylated enolates with benzylbromide); (2) competition between the reaction of TMS and t-butyldimethylsilyl enol ether derived from cyclohexanone with tricarbonylcyclohexadienyliron salt as monitored by glc showed that contrary to expectation on this basis, the latter disappeared more rapidly. Reaction of pure kinetically derived TMS enol ether from 2-methylcyclopentanone, gave products completely void of any equilibration, again confirming that free enolates are not the likely intermediates.

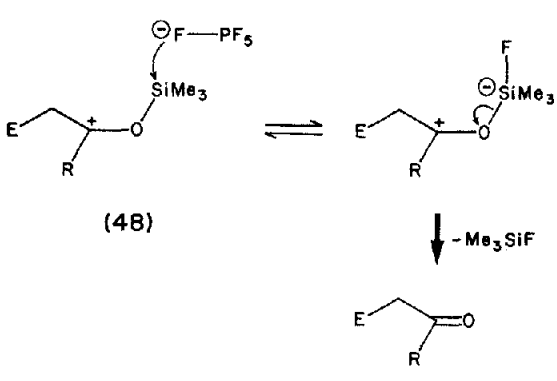
Alternatively, the π electrons of the TMS enol ether could attack the cation (E^+) to generate a carbonium ion β to the trimethylsilyl group, e.g. **48**, which could be

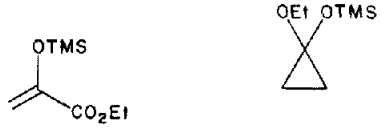


(48) (49)

stabilized either by the eclipsing O–Si bond through σ-π conjugation, which is completely analogous to the well studied all carbon case **49** or by the eclipsing oxygen lone pair. The latter possibility would clearly afford better overlap of orbitals.

Jung has earlier suggested[36] that oxidation of TMS ethers via hydride abstraction with $\phi_3C^+BF_4^\ominus$, proceeds via the initial formation of an intermediate such as **48**, and since the carbonyl products are formed before the addition of H_2O to the reaction mixture, it implies that the cation **48** probably decomposes by attack of fluoride from $BF_4^\ominus$ to give Me_3SiF and carbonyl compound directly. In support of this mechanism, when the reaction mixture was heated, Jung detected the evolution of acidic gas, probably BF_3 or Me_3SiF. We also are able to detect acidic gas in our reaction, and NMR evidence was obtained for the formation of Me_3SiF (Experimental), though we favour the initial formation of penta-coordinate silicon by attack of $F^\ominus$ from $PF_6^\ominus$, followed by decomposition to give carbonyl compound and acidic gases (PF_5, $(CH_3)_3SiF$). The ability of silicon to form penta-coordinate species is well known.[37] In support of this mechanism we note that when an electron withdrawing substituent is situated on the double bond of a TMS enol ether (such as **50**), no reaction was observed.





(50) (51)

Also compound **51** did not show any reactivity with our cations.

EXPERIMENTAL

For general see Part XI. *Tetrahedron* **37**, 289 (1981).

THF was dried over Na/benzophenone. Trimethylsilyl chloride was distilled from dry quinoline prior to use. Triethylamine and diisopropylamine were dried by distillation from KOH. Pentane and ether were dried over Na wire. All reactions involving enolate formations and Si compounds were performed in an atmosphere of dry N_2.

Glc measurements were taken on a Perkin–Elmer 881 equipped with a flame-ionisation detector. The column used was 2 m in length and 6 mm outer diameter packed with 2% OV17 supported on 80–100 chromosorb W. ^{19}F NMR spectra were recorded on a Bruker B-KR 322s using external trifluoracetic acid as reference.

Preparation of cyclohexadienyl-$Fe(CO)_3$ *complexes* (**1**, **2**, **2a**, **5**, **7** *and* **11**). Compound **1** was prepared according to the procedure of Birch and Haas,[38] using conc H_2SO_4 demethoxylation of the mixed $Fe(CO)_3$-complexes formed from dihyrdroanisole.[39] Compound **2** was prepared according to the procedure of Birch and Chamberlain.[39] Compound **2a** was prepared[40] by the action of CF_3COOH on tricarbonyl [(1,2,3,4-η) - 1,3 - dimethoxy - 1,3 - cyclohexadiene)]iron(O). Compound **5** was prepared according to the procedure of Bandara.[41] Compound **7** was prepared as described by Bandara.[41]

Tricarbonyl[(1,2,3,5,6-η)*bicyclo*[4,4,0]*deca* - 1,5 - *dien* - 3 - *yl*]*iron*(+1) *hexafluorophosphate*(−1) (**11**). Bicyclo[4,4,0]deca - 3,6(1) - diene (10 g) which is readily available by Birch reduction of tetralin[42] was treated with $Fe(CO)_5$ (20 g) in refluxing di-n-butyl ether (100 ml) during 48 hr. After cooling, the dark soln was filtered through Celite and concentrated (80°/12 mm). The resulting dark-yellow oil was chromatographed over silica-gel (petrol-ether, 20:1) and the yellow oil so obtained, was distilled to give a mixture of *tricarbonyl*[(1,2,3,6 - η) - *bicyclo*[4,4,0]*deca* - 2,6(1) - *diene*]*iron*(0) and the (1,2,5,6-η)-1,5-diene complex (3:1) as a viscous yellow oil b.p. 100°/0.03 mm (48%); ν_{max}(neat) 2045, 1960 cm^{-1}; $\delta_H(CDCl_3)$ 5.13 (1H, d, *J* 7 Hz, 2H), 2.95 (1H, m, 3-H), 2.8–1.3 (12H, m, $(-CH_2-)_4$, 4-, 5-H); *m/z* 274 (M^+). This complex was then dissolved in conc H_2SO_4 and stirred at ambient temp during 2.5 hr. After this time the mixture was poured on to crushed ice and extracted with ether. Evaporation gave a new complex, *tricarbonyl*[(1,2,5,6 - η) - *bicyclo*[4,4,0]*deca* - 1,5 - *diene*]*iron*(0) which was purified by chromatography over silica gel (petrol)(85%); ν_{max}(neat) 2045, 1960 cm^{-1}; $\delta_H(CDCl_3)$ 2.96 (2H, br s, 2- and 5-H), 2.7–1.3 (12H, m, $(-CH_2-)_4$, 3-, 4-H); *m/z* 274 (M^+). Treatment of this complex with tritylhexafluorophosphate in the usual way[7] gave the salt **11** in 90% yield, purified by crystallization (acetone-ether); ν_{max} 2110, 2040 cm^{-1};

$\delta_H(CD_3CN)$ 5.76 (1H, d, *J* 7 Hz, 2-H), 4.28 (1H, dd, *J*7, 6 Hz, 4-H), 3.76 (1H, d, *J* 6 Hz, 1-H), 3.29–1.9 (10H, m, $(-CH_2-)_4$, 6-H).

Preparations of O-silylated enolates and allyl silanes

O-Silylated enolates. 1-Trimethylsiloxycyclohexene and 6-methyl-1-trimethylsiloxycyclohexene were prepared from cyclohexanone and 2-methylcyclohexanone essentially following the method of House *et al.*[43] *Z*-3-Trimethylsiloxy-2-pentene was prepared from 3-pentanone as described by Kuwajima.[44] 2-Trimethylsiloxy-2-bornene was prepared from (+)-α-bromo camphor according to the procedure of Joshi and Pande.[27] 2 - Methyl - 1 - trimethylsiloxypropene was prepared according to the method of Stang *et al.*[30] 1 - Oxa - 2 - trimethylsiloxycyclopent - 2 - ene was prepared[31] from γ-butyrolactone. Phenyl ketene methyltrimethylsilylacetal was prepared as described by Ainsworth *et al.*[32] 1 - Bistrimethylsiloxy - 1 - cyclopentene was prepared according to the procedure of Bloomfield.[45] 5 - Methyl - 1 - trimethylsiloxycyclopentene was prepared by the kinetic deprotonation[43] of 2-methylcyclopentanone and was separated from its thermodynamic isomer by a spinning band column distillation. 2-Trimethylsiloxy-methylacrate was prepared from methylpyruvate under equilibrating conditions, as described by House.[43]

Allyl silanes. Allyltrimethylsilane was obtained from Petrarch Chemicals.

Compound **35** was prepared by the action of trimethylsilyllithium on 1 - bromo - 3 - methyl - 2 - butene in 80–90% yield. The anion was generated according to the procedure of Still.[46] Compound **37** was prepared according to the method of Coughlin and Salomon.[47] Compound **38** was prepared by the Birch reduction of 2 - phenyl - 2 - trimethylsilyl - propane, the latter reagent can itself be readily prepared by the reaction[47] of 2 - chloro - 2 - phenyl - propane[48] with Mg and Me_3SiCl. Allyltrimethylstannane was prepared from allylmagnesium bromide and trimethylstanyl chloride as described by Abel.[49]

Reactions of TMS enol ethers with tricarbonylcyclohexadienyliron salts

General procedure. The enol ether was added dropwide over a short period to a stirred soln (*ca* 0.5 g in 10 ml) of the salt in dry acetonitrile (ex. CaH_2) under N_2 at room temp. Completion of reaction was monitored using the disappearance of the IR absorption at 2110 cm^{-1} $[Fe(CO)_3]^+$. After the required time solvent was removed by rotary evaporation and any excess TMS enol ether removed at oil-pump pressures. The residue was chromatographed on silica gel using petroleum spirit containing a small amount of ether (1–10%) as an eluent. Distillation (Kugelrohr) of the yellow oils so obtained gave the *adducts as mixtures of diastereoisomers* (*presumably due to* C-2′) which could be separated, in certain cases, by fractional crystallisation.

1-*Trimethylsiloxycyclohexene* (0.3 ml) *and salt* **1** (0.3 g) gave[12] **3** (69%) as a yellow oil, b.p. 140° (10^{-3} mmHg) which was crystallized from petroleum spirit, m.p. 44–47°; ν_{max} 2050, 1975, 1705 cm^{-1}; $\delta_H(CCl_4)$ 5.35 (2H, m, inner diene), 3.05 (2H, m, outer diene), 2.60–1.40 (11H, m, 5-, 6-H, cyclohexanone ring protons), 1.16 (1H, br d, *J* 15 Hz, 6-H); *m/z* 316 (M^+), 288 (M^+–CO), 260 (M^+–2CO), 232 (M^+-3CO), 230 (M^+-3CO, -2H); Found: C, 57.00; H, 5.10. Calc. for $C_{15}H_{16}O_4Fe$; C, 56.99; H, 5.10%).

1-*Trimethylsiloxycyclohexene* (0.5 ml) *and salt* **2** (0.3 g) gave[14] **4** (79)%, m.p. 99–103°; ν_{max} 2042, 1975, 1710 cm^{-1}; $\delta_H(CCl_4)$ 5.02 (1H, dd, *J*6, 2 Hz, inner diene), 3.59 (3H, s, OMe), 3.22 (1H, m, 1-H); 2.50 (1H, m, 4-H), 2.40–1.40 (11H, m, 5-, 6-H, cyclohexanone ring protons), 1.21 (1H, m, 6-H); *m/z* 346 (M^+), 318, 290, 262, 260; (Found: C, 55.80; H, 5.36. Calc. for $C_{16}H_{18}O_5Fe$: C, 55.52; H, 5.24%).

1-*Trimethylsiloxycyclohexene* (0.4 ml) *and salt* **5** (0.3 g) gave **6** (84%), m.p. 81–82°; ν_{max} 2060, 1985, 1705 (br) cm^{-1}; $\delta_H(CCl_4)$ 5.88 (1H, br s, inner diene), 3.62 (3H, s, CO_2Me) 3.08 (1H, br d, *J* 10 Hz, outer diene), 2.50–1.40 (11H, m, 5-, 6-H, cyclohexanone ring protons), 2.12 (3H, s, Me), 0.96 (1H, dt, *J* 14, 3 Hz, 6-H); *m/z* 388 (M^+), 360, 332, 304, 302; (Found: C, 55.30; H, 5.17. $C_{18}H_{20}O_6Fe$ requires: C, 55.69; H, 5.19).

1-*Trimethylsiloxycyclohexene* (0.4 ml) *and salt* **11** (0.3 g) gave **12** (91%), m.p. 62–67°; ν_{max} 2040, 1960, 1705 cm^{-1}; $\delta_H(CCl_4)$ 2.70 (2H, m, outer diene), 2.50–1.30 (19H, m, 3-, 4-H, cyclohexanone ring protons, $(CH_2)_4$), 1.14 (1H, br d, *J* 15 Hz, 4-H); *m/z* 370.085 2 (M^+) ($C_{19}H_{22}O_4Fe$ requires *M*, 370.086 7), 342, 314, 286, 284.

6 - *Methyl* - 1 - *trimethylsiloxycyclohexene* (1.25 ml) *and salt* **1** (0.5 g) gave **9** (81%), b.p. 130° (10^{-3} mmHg); ν_{max} 2040, 1955, 1700 cm^{-1}; $\delta_H(CCl_4)$ 5.35 (4H, m, inner diene), 3.05 (4H, m, outer diene), 2.70–1.04 (22H, br m, 5-, 6-H, cyclohexanone ring protons), 0.96 and 0.93 (6H, centres of overlapping doublets *J* 7Hz, 6′ Me's); *m/z* 330 (M^+), 302, 274.065 6 (M^+-2CO) ($C_{14}H_{18}O_2Fe$ requires: *M*-2CO, 274.065 6), 246, 244.

Conversion of the complex (**9**) *to 6-methyl-2-phenylcyclohexanone.* The complex **9** (0.335 g) was treated with $FeCl_3 \cdot 6H_2O$ in ethanolic benzene according to the method of Gunatilaka and Mateos[50] to yield diastereoisomeric 2 - (2′,4′ - *cyclohexadien* - 1′ - *yl*) - 6 - *methylcyclohexanone* (88%), b.p. 80° (0.1 mmHg); ν_{max} 3040, 2940, 2865, 1710, 1450 cm^{-1}; $\delta_H(CCl_4)$ 5.80 (8H, m, diene), 2.90–1.10 (22H, br, m, remaining ring protons), 1.00 (6H, centre of two overlapping doublets, *J* 7 Hz, 6-Me's); *m/z* 190 (M^+), 112. The diene (0.11 g) was dehydrogenated with 2,3 - dichloro - 5,6 - dicyanoquinone in ether (0.14 g in 30 ml) following the procedure of Ireland *et al.*[26] to yield 6 - methyl - 2 - phenylcyclohexanone (82%), m.p. 50–52° (lit.[168] 51–52°); ν_{max} 2965, 2930, 2860, 1715 cm^{-1}; $\delta_H(CCl_4)$ 7.30–6.94 (5H, m, aromatic protons), 3.65–3.30 (1H, m, benzyl proton), 2.60–0.90 (8H, m, cyclohexanone ring protons), 0.98 (3H, d, *J* 7 Hz, Me); *m/z* 188 (M^+).

6 - *Methyl*- 1 - *trimethylsiloxycyclohexene* (1.9 ml) *and salt* **2** (1.0 g) gave **10** (96%), b.p. 125° (10^{-3} mmHg); ν_{max} 2045, 1975, 1710 cm^{-1}; $\delta_H(CCl_4)$ 5.10 (2H, m, inner diene), 3.65 and 3.60 (6H, two singlets, diastereomeric MeO), 3.25 (2H, m, 1-H), 2.70 (2H, m, 4-H), 2.40–1.60 (20H, br, m, 5-H, cyclohexanone ring protons), 1.30 (2H, m, 6-H), 1.04 and 0.96 (6H, centres of two overlapping doublets, *J* 7 Hz, 6′-Me's); *m/z* 360 (M^+), 232, 204, 276, 274; (Found: C, 56.87; H, 5.47. $C_{17}H_{20}O_5$ Fe requires: C, 56.69; H, 5.60%).

Crystallization of this oil from petroleum spirit at −15° gave yellow crystals, m.p. 82–83°, which had $\delta_H(CCl_4)$ 4.97 (1H, dd, *J* 6, 2 Hz, inner diene), 3.60 (3H, s, OMe), 3.25 (1H, m, 1-H), 2.70 (1H, dd, *J* 6, 4 Hz, 4-H), 2.40–1.60 (10H, br, m, 5-, 6-H, cyclohexanone ring protons), 1.30 (1H, dt, *J* 15, 3 Hz, 6-H), 0.98 (3H, d, *J* 7 Hz, 6′Me) indicating the separation of diastereoisomers.

6 - *Methyl* - 1 - *trimethylsiloxycyclohexene* (1.75 ml) *and salt* **7** (1.0 g) gave **8** (93%), b.p. 150° (10^{-3} mmHg); m.p. 110–116° (pentane); ν_{max} 2060, 1985, 1710 (br) cm^{-1}; $\delta_H(CCl_4)$ 5.04 (2H, m, 3-H), 3.68 (6H, s, CO_2Me), 3.10 (2H, m, 4-H), 2.60–1.10 (22H, br, m, 5-, 6-H, cyclohexanone ring protons), 2.48 (6H, s, C-2 Me), 1.02 and 0.96 (6H, centres of two overlapping doublets *J* 7 Hz, diastereomeric C-6′ Me); *m/z* 402 (M^+), 374, 346, 318, 316; (Found: C, 57.05; H, 5.47. $C_{19}H_{22}O_6Fe$ requires: C, 56.74; H, 5.51%).

6 - *Methyl* - 1 - *trimethylsiloxycyclohexene* (2.0 ml) *and salt* **11** (1.0 g) gave **13** (95%), m.p. 113–115° (EtOH); ν_{max} 2045, 1965, 1708 cm^{-1}; $\delta_H(CCl_4)$ 2.90 (4H, m, outer diene), 2.60–1.40 (36H, br, m, 3-, 4-H, $(CH_2)_4$, cyclohexanone ring protons), 1.10 (2H, m, 4-H), 0.98 and 0.94 (6H, centres of overlapping doublets, *J* 7 Hz, diastereomeric 6′-Me); *m/z* 384 (M^+), 356, 328, 300, 298; (Found: C, 62.81; H, 6.29. $C_{20}H_{24}O_4Fe$ requires: C, 62.62; H. 6.30%).

Z-3-*Trimethylsiloxy-2-pentene* (0.85 ml) *and salt* **7** (0.78 g) gave **14** (88%), b.p. 150° (10^{-3} mmHg); ν_{max} 2055, 1980, 1710 cm^{-1}; $\delta_H(CCl_4)$ 5.12 (1H, d, *J* 6 Hz, inner diene), 3.64 (3H, s, CO_2Me), 2.80 (1H, m, outer diene), 2.45 (3H, s, 2-Me), 2.60–2.05 (5H, m, 5-, 6-H, $CHCOCH_2$), 1.30–0.78 (7H, m, 6H, C-1′ and C-5′ Me's); *m/z* 376.060 4 (M^+) ($C_{17}C_{20}O_6Fe$ requires: *M*, 376.060.9), 348, 320, 292, 290.

2-*Trimethylsiloxy-2-bornene* (2.0 g) *and salt* **1** (0.5 g) were stirred under N_2 during 24 hr at room temp. in dry acetonitrile (10 ml). The mixture was diluted with Na dried ether (50 ml) and the unreacted salt (≈10%) was collected by filtration. The organic part was worked up in the usual fashion, which, after chromatography over silica, gave a yellow oil (58%) consisting of *exo*- and *endo*-isomers (with respect to camphor) in the ratio of 2.5:1 based on the ^1H NMR data: $\delta_H(CCl_4)$ 3.32–3.05 (m, outer diene proton for *exo*-isomer), 3.80 and 2.95 (m, outer diene protons for *endo*-isomer). This oil was crystallized from MeOH

and gave a crystalline sample of the above adduct, m.p. 71–73°; $[\alpha]_D$ +67° (*c* 5, EtOH), which was equilibrated to 95% of one of them as described below.

The above adduct (64 mg) was absorbed on basic Al_2O_3 (20 g) and eluted with petroleum ether after 3 hr. Thus, 54 mg of the adduct rich in presumably *endo*-isomer was obtained, m.p. 119–121°; ν_{max} 2050, 1975, 1748 cm^{-1}; δ_H(270 MHz, $CDCl_3$) 5.39 (2H, m, inner diene), 2.94 and 3.05 (2H, m, outer diene for *endo*-isomer; note the absence of signals at 3.32–3.05), 2.15–1.04 (8H, m, 5-, 6-H, 3'-*exo* H, 5'-, 6'-CH_2's, 4'-H), 0.95–0.80 (1H, m, 6-H), 0.92 (3H, s, 1'-Me), 0.95 (3H, s, 7'-Me), 0.80 (3H, s, 7'-Me); *m/z* 370 (M^+), 342, 314, 286, 284; (Found: C, 61.50; H, 5.75; Fe, 14.97. $C_{19}H_{22}O_4Fe$ requires: C, 61.64; H, 5.99; Fe, 15.08%).

The above equilibrrations could also be achieved by using 10% KOH in MeOH (15 hr, room temp.) with identical results.

Kinetic resolution of salt (**2**) *using 2-trimethylsiloxy-2-bornene derived from (+)-α-bromocamphor.* Table 1 gives details of reactions between salt **2** and (+)-camphor TMS enol ether. The salt was recovered by pouring the reaction mixture into an excess of dry ether. The filtered solid was thoroughly washed with ether and recrystallised (acetone–ether) to constant optical rotation. The enantiomerically enriched salt had the expected physical and spectral properties.

Determination of optical purity of the recovered 2-methoxy salt. To a stirred soln of the enantiomerically enriched 2-methoxy salt $[\alpha]_D$ −18°, (0.12 g) in dry acetonitrile (2.0 ml) was added (−)-phenylethylamine (0.11 g) (optical purity >97%). After 1 hr the solvent was removed leaving a yellow oil which was dissolved in ether, filtered and the solvent again evaporated. The resulting oil was dissolved in warm hexane (20 ml) and this soln was washed five times with 5% NH_4Claq and twice with water. The organic phase was filtered through phase-separating paper, dried ($MgSO_4$) and evaporated to give (−) - *tricarbonyl*{(1,2,3,4 - η) - 2 - *methoxy* - 5 - [N - (*phenylethylamino*)] - 1,3 - *cyclohexadiene*} *iron*(0) (44%), which contained no free amine, $[\alpha]_D$ −56.5° (*c* 1.7, MeOH); $\delta_H(CCl_4)$ 7.18 (5H, s, aromatic), 4.96 (1H, m, inner diene), 3.86–3.40 (1H, m, benzylic H), 3.63 (3H, s, OMe), 3.14 (1H, m, 1-H), 2.88 (1H, m, 5-H), 2.75 (*ca.* (1/2) H, partly hidden dd *J* 3.5, 3.0 Hz, 4-H), 2.53 (*ca.* (1/2) H, dd, *J* 3.5, 3.0 Hz, 4-H), 2.26–1.92 (1H, m, 6-H), 1.50 (1H, br d, *J* 16 Hz, 6-H), 1.22 (*ca.* 1.5H, d, *J* 6 Hz, CH_3), 1.20 (*ca.* 1.5H, dd, *J* 6 Hz, CH_3), 0.90 (1H, br s, N–H). To this sample was successively added 5.0 μl of a saturated solution of Eu(fod)$_3$ in deuteriochloroform and the ^1H NMR spectrum recorded after each addition. Optimum resolution of the diastereomeric methoxy peaks was obtained with 25 μl of shift reagent. A suitable scale expansion was chosen (50 Hz) and the integrated area of each MeO peak was measured. An average value (20 scans) of 15% e.e. was thus obtained.

2 - *Methyl* - 1 - *trimethylsiloxypropene* (0.8 ml) *with salt* **1** (0.5 g) gave **18** (77%), b.p. 80° (10^{-3} mmHg); ν_{max} 2040, 1975, 1730 cm^{-1}; $\delta_H(CCl_4)$ 9.32 (1H, s, CHO), 5.36 (2H, t, *J* 3 Hz, inner diene), 2.93 (2H, m, outer diene), 2.50–0.90 (3H, m, 5-, 6-H), 0.94 (3H, s, Me), 0.90 (3H, s, Me); *m/z* 290 (M^+), 262, 234, 206, 204; (Found: C, 53.99; H, 4.77. $C_{13}H_{14}O_4Fe$ requires: C, 53.02; H, 4.86%).

2 - *Methyl* - 1 - *trimethylsiloxypropene* (0.25 ml) *with salt* **7** (0.18 g) gave **19** (81%), purified by chromatography; ν_{max} 2058, 1990, 1735, 1708 cm^{-1}; $\delta_H(CCl_4)$ 9.28 (1H, s, CHO), 5.20 (1H, d, *J* 6 Hz, inner diene), 3.65 (3H, s, CO_2Me), 2.84 (1H, br d, *J* 6 Hz, outer diene), 2.54–2.12 (2H, m, 5-, 6-H), 2.45 (3H, s, 2-Me), 1.22–0.78 (1H, m, 6-H), 0.94 (3H, s, Me), 0.92 (3H, s, Me); *m/z* 362.045 9 (M^+). $C_{16}H_{18}O_6Fe$ requires: *M*, 362.045 3), 334, 331, 306, 278, 276.

2 - *Methyl* - 1 - *trimethylsiloxypropene* (4.0 ml) *with salt* **11** (2.1 g) in CH_2Cl_2 (20 ml) gave **20** (94%), b.p. 150° (10^{-3} mmHg); ν_{max} 2040, 1975, 1725 cm^{-1}; $\delta_H(CCl_4)$ 9.25 (1H, s, CHO), 2.80–2.60 (2H, m, outer diene), 2.58–1.64 (10H), m, 3-, 4-H, $(CH_2)_4$), 1.50–1.08 (1H, m, 4-H), 0.95 (3H, s, Me), 0.92 (3H, s, Me); *m/z* 344 (M^+), 316, 288, 260, 258; (Found: C, 59.45; H, 6.05. $C_{17}H_{20}O_4Fe$ requires; C, 59.32; H, 5.86%).

1 - *Oxa* - 2 - *trimethylsiloxycyclopent* - 2 - *ene* (1.3 ml) *and salt* **1** (0.8 g) gave **21** (75%), b.p. 150° (10^{-3} mmHg); ν_{max} 2052, 1980, 1775 cm^{-1}; $\delta_H(CCl_4)$ 5.36 (2H, m, inner diene), 4.18 (2H, m, 5'-H), 3.10 (2H, m, outer diene), 2.90–1.50 (5H, m, 5-, 6-, 3'-, 4'-H), 1.20 (1H, m, 6-H); *m/z* 304.003 4 (M^+), ($C_{13}H_{12}O_5Fe$ requires: *M*, 304.003 8), 276, 248, 220, 218.

1 - *Oxa* - 2 - *trimethylsiloxycyclopent* - 2 - *ene* (0.7 ml) *and salt* **2** (0.3 g) gave, after 24 hr, **22** (76%), b.p. 150° (10^{-3} mmHg); ν_{max} 2050, 1970, 1760 cm^{-1}; $\delta_H(CCl_4)$ 5.20 (1H, over-lapping dd, *J* 6, 2 Hz, inner diene), 4.15 (2H, m, 5'-H), 3.64 (3H, s, OMe), 3.28 (1H, br s, 1-H), 2.90 (7H, dd, *J* 6, 2 Hz, 4-H), 2.50–1.50 (5H, m, 5-, 6-, 3'-, 4'-H), 1.30 (1H, br d, *J* 15 Hz, 6-H); *m/z* 334.013 8 (M^+). ($C_{14}H_{14}O_6Fe$ requires: *M*, 334.013 9), 306, 278, 250, 248.

1 - *Oxa* - 2 - *trimethylsiloxycyclopent* - 2 - *ene* (1.5 ml) *and salt* **7** (1.0 g) gave **23** (70%), m.p. 114–115° (MeOH); ν_{max} 2062, 1985, 1765, 1695 cm^{-1}; $\delta_H(CCl_4)$ 5.26 (1H, overlapping d, *J* 6 Hz, inner diene), 4.2 (2H, m, 5'-H), 3.70 (3H, s, CO_2Me), 3.29 and 2.90 (1H, dd, *J* 6, 3 Hz at each resonance position, 4-H of diastereoisomers), 2.70–2.10 (5H, m, 5-, 6-, 3'-, 4'-H), 2.50 (3H, s, 2-Me), 1.20 (1H, m, 6-H); *m/z* 376 (M^+), 348, 320, 292, 290; (Found: C, 50.91; H, 4.48. $C_{16}H_{16}O_7Fe$ requires: C, 51.09; H, 4.29%).

1 - *Oxa* - 2 - *trimethylsiloxycyclopent* - 2 - *ene* (1.5 ml) *and salt* **11** (1.0 g) gave **24** (86%), b.p. 180° (10^{-3} mmHg); ν_{max} 2050, 1965, 1780 cm^{-1}; $\delta_H(CCl_4)$ 4.18 (2H, m, 5'-H), 2.80 (2H, m, outer diene), 2.70–1.80 (13H, m, 3-, 4-, 3'-, 4'-H, $(CH_2)_4$), 1.05 (1H, m, 4-H); *m/z* 358.050 3 (M^+), ($C_{17}H_{18}O_5Fe$ requires: *M*, 358.050 4), 330, 302, 274, 272.

Phenyl ketene methyltrimethylsilyl acetal (1.2 ml) *and salt* **1** (0.73 g) gave **25** (82%), b.p. 150° (10^{-3} mmHg). Crystallisation from hexane gave a sample, m.p. 125–127°, which had ^1H NMR $\delta(CCl_4)$ 7.09 (5H, s, aromatic), 5.30 (2H, dd, *J* 3 Hz, 2-, 3-H), 3.58 (3H, s, CO_2Me), 3.10 (1H, m, 1-H), 2.86 (3H, m, 4-, 5-H, benzylic C-H), 1.86–1.54 (1H, m, 6-H), 1.13 (1H, dt, *J* 15 Hz, 6-H). The mother liquors from above were concentrated to yield a yellow oil having ^1H NMR δ (CCl_4), 7.16 (5H, s, aromatic), 5.10 (2H, m, 2-, 3-H), 3.48 (3H, s, CO_2Me), 3.00 (1H, m, 1-H), 2.90–2.00 (4H, m, 4-, 5-, 6-H, benzylic C-H), 1.30 (1H, br d, *J* 15 Hz, 6-H). Assignments of the latter sample were complicated by the presence of *ca.* 20% of the other diastereoisomer. The following

Table 1.

Salt (2) in (mmol), $[\alpha]_D^\circ$	TMS enol ether of (+)-camphor (mmol)	Time h	% adduct[1]	% recovered salt (2)	$[\alpha]_D^\circ$ (c 5, CH_3CN)	% recovered camphor[2]
1, [0.0]	2	15	< 5	70	-10.20	37
2, [0.0]	1	20	< 5	86	-3.08	33
1, [0.0]	5	7	45	56	-2.60	not measured
1, [-3.08]	5	21	53	49	-18.0	45
2, [0.0]	1	0.75	< 5	70	-1.20	not measured

[1] (15), R = OCH_3

[2] Obtained by dilution of the reaction mixture with reagent grade ether.

spectral data apply to both compounds; ν_{max} 2055, 1980, 1740 cm^{-1}; *m/z* 368.034 4 (M^+) ($C_{18}H_{16}O_5Fe$ requires: *M*, 368.034 8), 340, 312, 284, 282.

Phenyl ketene methyltrimethylsilyl acetate (1.5 ml) *and salt* **7** (1.0 g) gave **26** (89%), b.p. 180° (10^{-3} mmHg), from which a single diastereoisomer was isolated by crystallisation from MeOH, m.p. 133–135°; $\delta_H(CCl_4)$ 7.14 (5H, s, aromatic), 5.14 (1H, d, *J* 6 Hz, 3-H), 3.60 (3H, s, 1-CO_2Me), 3.56 (3H, s, 1'-CO_2Me), 3.07 (1H, dd, *J*6, 2.5 Hz, 4-H), 2.90 (2H, m, 5-H, benzylic C–H), 2.46 (3H, s, Me), 2.30–1.98 (1H, m, 6-H), 0.94 (1H, br d, *J* 15 Hz, 6-H); (Found: C, 57.33; H, 4.59. $C_{21}H_{20}O_7Fe$ requires: C, 57.30; H, 4.54%). The other diastereoisomer, isolated from the mother liquors by evaporation, could not be obtained pure. The following spectral data apply to both compounds. ν_{max} 2060, 1987, 1740, 1710 cm^{-1}; *m/z* 440 (M^+), 412, 384, 356, 354.

Phenyl ketene methyltrimethylsilyl acetal (1.5 ml) *and salt* **11** (102 g) gave **27**, (76%), b.p. 180° (10^{-3} mmHg); crystallisation from MeOH gave a mixture of diastereoisomers (4:1), m.p. 89–91°; $\delta_H(CCl_4)$ 7.25 and 7.20 (10H, two singlets, aromatic protons of diastereoisomers), 3.63 and 3.55 (6H, two singlets, MeO of diastereoisomers), 3.00–1.50 (26H, m, outer diene, 3-, 4-H, $(CH_2)_4$, benzylic H), 1.20 (2H, br d, *J* 15 Hz, 4-H). The following spectral data were obtained for the mixture of diastereoisomers; ν_{max} 2045, 1965, 1740 cm^{-1}; *m/z* 422 (M^+), 394, 366, 388, 336; (Found: C, 62.44; H, 5.31. $C_{22}H_{22}O_5Fe$ requires: C, 62.58; H, 5.25%).

1,2-*Trimethylsiloxy*-1-*cyclopentene* (1 ml) was added in one portion to a stirred soln of **11** (0.5 g) in acetonitrile at 0°. After about 0.5 hr reaction was complete (IR) and solvent, together with any excess siloxy compound, was removed under vacuum (0.5 mmHg, 25°). The residual oil was dissolved in MeOH (20 ml) and 5 drops of conc. HCl were added. This soln was stirred at room temp. for 15 hr then partitioned between water and ether. After collecting and drying the organic phase, the solvent was evaporated and the remaining oil chromatographed (alumina, basic, Act. IV/$CHCl_3$) to yield *tricarbonyl*{(1,2,5,6-η) - 3 - (1' - *oxo* - 2 - *cyclopenten* - 2' - *yl*)*bicyclo*[4,4,0]*deca* - 1,5 - *diene*}*iron*(0) (78%), m.p. 108/110° (petrol); ν_{max} 2050, 1980, 1970, 1708 cm^{-1}; $\delta_H(CCl_4)$ 7.18 (1H, m, 3'-H), 3.14–2.74 (3H, m, 2-, 5-, 3-H), 2.52 (4H, m, 4'-, 5'-H), 2.40–1.70 (9H, m, $(CH_2)_4$, 4-H), 1.40 (1H, m, 4-H); *m/z* 354 (M^+), 326, 298, 270, 268; (Found: C, 60.97; H, 5.18. $C_{18}H_{18}O_4Fe$ requires: C, 61.04; H, 5.12%).

Reactions of allyl trimethylsilanes with tricarbonylcyclohexadienyl-iron salts

General procedure. The allyl silane and salt were heated in refluxing CH_2Cl_2 (ex. CaH_2) until the mixture became homogeneous and the IR absorption at *ca.* 2100 cm^{-1} had disappeared. The cooled soln was then concentrated by rotar-vap and excess silane removed at oil-pump pressures. The residue was chromatographed on silica-gel using petrol or petrol-ether mixtures (max. 10% ether) as eluent. If necessary the oils so obtained were distilled.

Allyl trimethylsilane (2 ml) *and salt* **1** (0.5 g) gave the known[15] **28** (78%), b.p. 85° (0.005 mmHg); ν_{max} 2052, 1975, 1640 cm^{-1}; $\delta_H(CCl_4)$ 5.84–4.78 (5H, m, 2-, 3-H, allyl CH_2=CH), 3.04 (2H, m, 1-, 4-H), 2.1–1.6 (4H, m, 5-, 6-H, allyl CH_2), 1.26 (1H, m, 6-H); *m/z* 260 (M^+), 232, 219, 204, 176, 174.

Allyl trimethylsilane (0.6 ml) *and salt* **2** (0.25 g) were stirred for 15 hr in gently refluent 1,2-CH_2Cl_2. Work-up as described gave **29** (81.5%), b.p. 75° (10^{-3} mmHg); ν_{max} 2045, 1970, 1640 cm^{-1}; $\delta_H(CCl_4)$ 5.84–4.72 (4H, m, 3-H, allyl CH_2=CH), 3.62 (3H, s, OMe), 3.25 (1H, br s, 1-H), 2.64 (1H, br d, *J* 6 Hz, 4-H), 2.2–1.6 (4H, m, 5-, 6-H, allyl CH_2), 1.34 (1H, m, 6-H); *m/z* 290.024 1 (M^+) ($C_{13}H_{14}O_4Fe$ requires: *M*, 290.024 7), 262, 234, 206, 204.

Allyl trimethylsilane (2 ml) *and salt* **2a** 0.5 g) gave, after 20 hr, **30** (77%), purified by chromatography, ν_{max} 2050, 1975, 1640 cm^{-1}; $\delta_H(CCl_4)$ 5.86–4.78 (3H, m, allyl CH_2=CH), 5.08 (1H, dd, *J* 5, 2 Hz, 3-H), 3.60 (3H, s, OMe), 3.34 (1H, m, 1-H), 2.56 (1H, m, 4-H), 2.30–1.66 (4H, m, 5-, 6-H, allyl CH_2), 1.15 (1H, m, 5-H); *m/z* 290 (M^+), 262, 234, 206, 204; (Found: C, 53.62; H, 5.08. $C_{13}H_{14}O_4Fe$ requires: C, 53.82; H, 4.86%).

Allyl trimethylsilane (1 ml) *and salt* **7** (0.3 g) gave, after 1 hr, **31** (81%), b.p. 90° (10^{-3} mmHg); ν_{max} 2060, 1985, 1710, 1640 cm^{-1}; $\delta_H(CCl_4)$ 5.86–4.78 (3H, m, allyl CH_2), 5.12 (1H, d, *J* 6 Hz, 3-H), 3.64 (3H, s, CO_2Me), 3.04 (1H, dd, *J* 6, 2 Hz, 4-H), 2.48 (3H, s, Me), 2.4–1.8 (4H, m, 5-, 6-H, allyl CH_2), 1.04 (1H, d, *J* 15 Hz, 6-H); *m/z* 332 (M^+), 304, 276, 248, 246; (Found: C, 54.19; H, 4.90. $C_{15}H_{16}O_5Fe$ requires: C, 54.24; H, 4.86%).

The same reaction using only 1.1 equiv of allyl silane and heating for 2 hr gave a 61% yield of **31**, together with some aromatic materials.

Allyl trimethylsilane (1 ml) *and salt* **11** 0.5 g) gave, after 23 hr, **32** (98%), purified by chromatography; ν_{max} 2050, 1975, 1640 cm^{-1}; $\delta_H(CCl_4)$ 5.86–4.76 (3H, m, allyl CH_2=CH), 2.78 (2H, m, 2-, 5-H), 2.6–1.6 (12H, m, 3-, 4-H, (CH_2), allyl CH_2), 1.25 (1H, m, 4-H); *m/z* 314 (M^+), 286, 258, 230, 228; (Found: C, 61.41; H, 5.50. $C_{16}H_{18}O_3Fe$ requires: C, 61.17; H, 5.78%).

Allyl trimethylstannane (0.5 ml) *and salt* **2** (0.4 g) were heated for 15 hr in refluent CH_2Cl_2 (15 ml). Usual work-up gave a yellow oil, identified by spectral data as **31** (97%).

Allyl trimethylstannane (0.4 ml) *and salt* **33** (0.4 g) were treated as just described to give a yellow oil (0.11 g) and recovery of cation (0.2 g). ^1H NMR of the oil suggested the complex to be **34**, (30%), $\delta_H(CCl_4)$ 5.88–4.80 (4H, m, 3-H, allyl CH_2=CH), 3.60 (3H, s, OMe), 3.24 (1H, m, 1-H), 2.36 (1H, d, *J* 6 Hz, 4-H), 2.0–1.2 (4H, 6-H, allyl CH_2), 0.96 (3H, s, Me). A singlet at δ3.38 (< 10%) suggested the presence of some product due to alkylation at the 1-position of cation **33**.

3 - *Methyl* - 2 - *buten* - 1 - *yl trimethylsilane* (1 ml) *and salt* **7** (0.3 g) gave after 2 hr, **36** (95%), b.p. 90° (10^{-3} mmHg); ν_{max} 2060, 1990, 1710, 1640 cm^{-1}; $\delta_H(CCl_4)$ 5.8–4.72 (3H, ABC m, *J* 16, 9, 2 Hz, allyl CH_2=CH), 5.18 (1H, d, *J* 6 Hz, 3-H), 3.66 (3H, s, CO_2Me), 2.96 (1H, dd, *J* 6, 2.5 Hz, 4-H), 2.48 (3H, s, 2-Me), 2.40–1.95 (2H, m, 5-, 6-H), 0.92 (6H, s, 3'-Me's), 1.08 (1H, m, 6-H); (Found: C, 56.50; H, 5.70. $C_{17}H_{20}O_5Fe$ requires: C, 56.69; H, 5.60%).

(1,4 - *Cyclohexadien* - 1 - *yl*)*methyl trimethylsilane* **37** (0.35 ml) *and salt* **11** (0.42 g) gave after 14 hr, **39** (98%), b.p. 120–130° (10^{-3} mmHg); ν_{max} 2050, 1975, 1650 cm^{-1}; $\delta_H(CCl_4)$ 5.54 (2H, br s, 1'-, 2'-H), 4.64 (2H, m, methylidene CH_2), 3.0–1.5 (17H, br m, $(CH_2)_4$, 2-, 3-, 4-, 5-, 3'-, 5'-, 6'-H), 1.32 (1H, m, 4-H); *m/z* 366.091 8 (M^+) ($C_{20}H_{22}FeO_3$ requires *M*, 366.091 8), 338, 310, 282, 280.

2 - (1,4 - *Cyclohexadien* - 1 - *yl*) - 2 - *propyl trimethylsilane* (**38**, 2 ml) *and salt* **11** (1 g) gave after 20 hr, **40** (86%) b.p. 140–150° (10^{-3} mmHg) which solidified to a waxy solid on cooling, m.p. 75–82°; ν_{max} 2042, 1970, 1655 (weak); $\delta_H(CCl_4)$, 5.58 (2H, br s, 1'-, 2'-H), 3.0–1.5 (17H, br m, $(-CH_2-)_4$, 2-, 3-, 4-, 5-, 3'-, 5'-, 6'-H), 1.62 (6H, br s, Me's), 1.10 (1H, m, 4-H); *m/z* 394.122 8 (M^+) ($C_{22}H_{26}O_3$ Fe requires: *M*, 394.123 1), 366, 338, 310, 308).

SYNTHETIC EQUIVALENTS

A. *Arylation procedures*

Removal of metal from complexes—general procedures. (a) The method here consists of treating the complex with $FeCl_3 \cdot 6H_2O$ (excess) in a benzene-EtOH (1:1) mixture. The reaction is performed at room temp. but was found to be sluggish. Work-up involves simple extraction of the filtered mixture with petrol or ether, followed by isolation from the organic phase and purification by standard methods. Aromatisation of the metal-free diene was not found to be a problem using this method.[50]

(b) $Me_3N \rightarrow 0.2H_2O$: The complex (1 mmol) and trimethylamine-N-oxide dihydrate (8 mmol) are stirred in dimethylacetamide (10 ml) at between 40–90° (oil bath temp). A suitable temp. is chosen by observing the commencement of gas evolution. After evolution of gas has subsided, the reaction is generally cooled and worked-up by filtration and extraction with ether. Dimethylacetamide is removed by washing the organic soln with water. The reaction can be monitored for completion by removing samples from the mixture and observing the loss of the bands at *ca.* 2045 and 1970 cm^{-1}, due to $Fe(CO)_3$, in the I.R. A sample of the complex in dimethylacetamide prior to oxidation is used as reference.

Occasionally, depending on the temp. required for removal of metal, small amounts of aromatic material can be detected in the product.

Use of anhydrous trimethylamine-N-oxide in such solvents as

benzene or toluene has been recommended for oxidation of methoxy-substituted complexes where hydrolysis of the enol ether as well as aromatisation, is a problem.[51]

Aromatisation of dienes—general procedures. (a) 2,3 - *Dichloro - 5,6 - dicyanoquinone (DDQ)*: The diene (1 mmol) and DDQ (1 mmol) are heated and stirred in refluent benzene for 1 hr. The phenolic product from DDQ separates as a pale yellow solid on cooling and can be removed by filtration. Excess DDQ can be also removed by adding cyclohexa-1,4-diene to the reaction mix after about 1 hr. Work-up consists of concentration of the benzene soln followed by brief chromatography over alumina to remove any unreacted DDQ or its derived phenol. Chromatography or distillation is then used to purify the desired aromatic compound.

(b) *Palladium/charcoal.* In this process the diene (1 mmol) is stirred and heated in refluent toluene (10 ml) in the presence of Pd supported on carbon (0.5 g) usually for about 15 hr. Filtration of the cooled solution gives the desired aromatic which is purified by standard methods.

B. *Cyclohexenone*

The most convenient approach, utilised here, is a one-pot oxidation and hydrolysis. Different reagents may be used.

(a) *Cerium* IV, *acetic acid.* To a stirred soln of the methoxy complex in acetone (1 mmol in about 10 ml) is added ceric ammonium nitrate (3 mmol). Immediate evolution of a gas is observed. The mixture is further stirred for 15 min then water (20 ml) is added and the mixture poured into ether (30 ml) containing AcOH (10 ml). After partition, the organic phase is collected, washed with water and dried ($MgSO_4$). Evaporation gives an oil which is purified by standard methods.

(b) *Chromic acid, acetone (Jones' reagent).* Jones' reagent (*ca.* 1.5 ml) is added to a stirred soln of the methoxy complex (1 mmol) in acetone (10 ml). Gas is evolved immediately and when this has subsided the solution is decanted into water (20 ml) and extracted with ether to give, after usual work-up, an oil which is purified by standard methods.

(c) *Pyridinium chlorochromate.* This reagent has the advantage in oxidation of the iron that functional groups such as aldehydes are not oxidised, whereas reagents like Jones' oxidant are known to react with such sensitive functionalities. Furthermore, the reaction can be carried out under buffered conditions if required.

A soln of the complex (1 mmol) in CH_2Cl_2 (4 ml) is added dropwise to a stirred suspension of pyridinium chlorochromate (5 mmol) in CH_2Cl_2 (20 ml). The reaction is stirred for about 4–5 hr during which time a gas is evolved. Completion of reaction may be monitored for by IR. The soln is poured into ether (200 ml) and then filtered. Evaporation gives the crude product which is purified by normal procedures.

Preparation of α-arylated carbonyl compounds. 6 - Methyl - 2 - phenyl - cyclohexanone was prepared from **9** by $FeCl_3$ oxidation and DDQ dehydrogenation as described in the earlier section.

Methyl 6 - methyl - 3 - (2' - oxo - 3' - methylcyclohexyl)benzoate (**41**), was prepared without isolation of the diene intermediate as follows. Ester complex **8** (0.57 g) and $Me_3NO \cdot 2H_2O$ were heated at 80° in dimethylacetamide (25 ml) for 20 min. The dark solid was then cooled, diluted with toluene (25 ml) and filtered through Celite. Following this the soln was washed with water (3 × 50 ml; to remove dimethylacetamide), brine and again water. To the dried ($MgSO_4$) soln was added DDQ (0.5 g) and the mixture heated at 100° for 0.5 hr. A small portion was then worked-up as described and this showed incomplete dehydrogenation. The crude mixture was stirred over a weekend with a further 0.3 g DDQ to give complete aromatisation. The aromatic compound was obtained by filtering the solution through neutral alumina (Act. I) followed by evaporation (63%). The compound was further purified by preparative thin layer chromatography (SiO_2/petrol–ether, 10:1); ν_{max} 1710 (br); $\delta_H(CCl_4)$ 7.62 (1H, br s, 2-H), 7.12 (2H, br s, 4-, 5-H), 3.81 (3H, s, CO_2Me), 3.50 (1H, m, 1'-H), 2.56 (3H, s, 6-Me), 2.10–1.10 (7H, m, 3'-, 4'-, 5'-, 6'-H), 1.00 (3H, d, *J* 7 Hz, 3'-Me); *m/z* 260 (M^+).

Methyl 6 - methyl - 3 - (1' - methylbutan - 2' - one)benzoate (**42**) was prepared by successive treatment of **14** (0.36 g) with $Me_3NO \cdot 2H_2O$ (1 g) in dimethylacetamide (20 ml) and DDQ (0.23 g) in benzene (20 ml) as previously described. Elution from an alumina column with toluene gave the aromatic ester, 52%; ν_{max} 1710 (br) cm^{-1}; $\delta_H(CCl_4)$ 7.76 (1H, br s, 2-H), 7.20 (1H, br s, 4-, 5-H), 3.82 (2H, s, CO_2Me), 3.72 (1H, m, 1'-H), 2.62 (3H, s, 6-Me), 2.36 (2H, m, 3'-H), 2.38 (3H, d, *J* 7 Hz, 1'-Me), 0.96 (3H, m, 4'-H); *m/z* 234 (M^+).

1,1 - *Dimethyl - 1 - [6 - (1,2,3,4-tetrahydronophatalene)]acetaldehyde* (**43**) was prepared by reaction of **20** (1.26 g) with $Me_3NO \cdot 2H_2O$ (3.5 g) in dimethylacetamide (20 ml) at 90° for 20 min. Usual work-up gave the crude diene (ν_{max} 1738, 1660 cm^{-1}; $\delta_H(CCl_4)$ 9.28 (1H, s, CHO), 5.30 (2H, m, diene protons); *m/z* 204 (M^+) which on treatment with Pd/C (1 g, toluene, 110°, 15 H) gave the aromatic (43), b.p. 80° (10^{-3} mmHg), 78.5%; ν_{max} 1738 cm^{-1}; $\delta_H(CCl_4)$ 9.28 (1H, s, CHO), 6.84 (3H, m, aromatic protons), 2.72 (4H, m, 1'-, 4'-H), 1.79 (4H, m, 2'-, 3'-H), 1.36 (6H, s, 1-Me's); *m/z* 202 (M^+).

Dihydro - 3 - (3' - methoxycarbonyl - 4' - methyl)phenyl - 2(3H) - furanone (**44**) was prepared by treatment of **23** (0.5 g) with $Me_3NO \cdot 2H_2O$ (1.2 g) in dimethylacetamide at 80° for 1.5 hr. DDQ (0.21 g) oxidation of the crude diene gave, after chromatography on alumina (acidic, Act. I; petrol-ether, 9:1), the desired aromatic **44** 55%; ν_{max} 1765, 1720 cm^{-1}; $\delta_H(CCl_4)$ 7.79 (1H, br s, 2'-H), 7.24 (2H, m, 5'-, 6'-H), 4.30 (2H, m, 5-H), 3.82 (3H, s, CO_2Me), 3.72 (1H, br s, 3-H), 2.56 (3H, s, 6-Me), 2.80–2.10 (2H, m, 4-H); *m/z* 234 (M^+).

Methyl phenyl[6 - (1,2,3,4 - tetrahydronaphthalene)]acetate (**45**) was obtained by treatment of **27** (0.85 g) with $Me_3NO \cdot 2H_2O$ (1 g) in dimethylacetamide (20 ml) at 75° for 1 hr. The crude diene obtained as earlier described was stirred for 20 hr in refluent toluene containing Pd/C (0.1 g, 10% Pd). Work-up gave a colourless oil, b.p. 170° (10^{-3} mmHg), 60%; ν_{max} 1730 cm^{-1}; $\delta_H(CCl_4)$ 7.40–6.70 (8H, m, aromatic protons), 4.78 (1H, s, benzylic H), 3.62 (3H, s, CO_2Me), 2.8–2.3 (4H, m, 1'-, 4'-H), 1.9–1.50 (4H, m, 2'-, 3'-H); *m/z* 280 (M^+).

Preparation of substituted cyclohexenones. Compound **46** was prepared from **29** (2.14 g) and Jones' reagent as described in the earlier procedure, b.p. 80° (1 mmHg), lit.[52] b.p. 87–88° (7 mmHg), 65%; ν_{max} 1685 cm^{-1}; $\delta_H(CCl_4)$ 6.68 (1H, br d, *J* 10 Hz, 3-H), 5.92–4.88 (4H, m, allyl CH_2=CH, 2-H), 2.6–1.6 (7H, m, allyl CH_2, 4-, 5-, 6-H); *m/z* 136 (M^+).

5 - (2 - *Propenyl)2 - cyclohexen - 1 - one* (**47**) was obtained by treatment of **30** (0182 g) with ceric ammonium nitrate followed by acidic hydrolysis as described to give **47**, b.p. 85° (2.5 mmHg); ν_{max} 1685 cm^{-1}; $\delta_H(CCl_4)$ 6.90 (1H, m, 3-H), 6.0–4.9 (4H, m, allyl CH_2=CH, 2-H), 2.62–1.86 (7H, m, allyl CH_2, 4-, 5-, 6-H); *m/z* 136 (M^+).

Some observations regarding mechanism of the reaction of O-silylated enolates and salts

Reaction between cation **1** *or* **2** *and a mixture of TMS and TBDMS enol ethers of cyclohexanone.* Retention times (75°, 20 cm^3 min^{-1} N_2) were obtained for the enol ether: TBDMS-Rt 6.7 min; TMS-Rt 2.60 min. Both compounds were shown to be stable in the acetonitrile which was to be used for reaction. A mixture comprising 1-t-butyldimethylsiloxycyclohexene (3 eq), 1-trimethylsiloxycyclohexene (3 eq.) and cation **1** was prepared in acetonitrile. Glc monitoring after about 3 min showed substantial loss of both enol ethers. Repetition of this experiment using cation **2** gave the same result but it was evident here that 1-t-butyldimethylsiloxycyclohexene decreased in concentration more rapidly than 1-trimethylsiloxycyclohexene, although allowance for response factors was not established.

5 - *Methyl - 1 - trimethylsiloxycyclpentene* (1.2 ml) *and salt* **1** (0.75 g) gave tricarbonyl[(1,2,3,4-η) - 5 - (5' - methyl - 1' - oxocyclopent - 2' - yl) - 1,3 - cyclohexadiene]iron(0) (92%), b.p. 110° (10^{-3} mmHg); m.p. 50–70° (aq. MeOH); ν_{max} 2045, 1970, 1735 cm^{-1}; $\delta_H(CCl_4)$ 5.28 (4H, m, 2-, 3-H), 3.04 (4H, m, 1-, 4-H), 2.70–1.10 (18H, br m, 5-, 6-H, cyclopentanone ring protons), 1.02 (6H, d, *J* 7 Hz, 5'-Me); *m/z* 316 (M^+), 288, 270, 242, 240; (Found: C, 56.72; H, 5.09. $C_{15}H_{16}O_4Fe$ requires: C, 56.99; H, 5.10%).

Detection of TMSF. Using a 10 mm NMR tube as reaction vessel, 2-methoxy cation **2** (0.2 g) was dissolved in acetonitrile (2 ml) and the ^{19}F spectrum recorded, δ_F 6.2 (d, $J_{(P-F)}$ 703.3 Hz). Likewise samples of TMSF (δ_F − 89.5, m, $J_{(H-F)}$ 7.1, $J_{(Si-F)}$ 135 Hz),

and PF_5 (δ_F-10.99, d, $J_{(P-F)}$ 1064.5 Hz) were recorded in MeCN. As well as the expected doublet obtained for PF_5 a second broad doublet was also present due either to partial hydrolysis or complexation with the solvent.[53]

Cyclohexanone TMS enol ether (0.2 ml) was next added to the reaction vessel containing **2** and the mixture cooled to −30°. After 1 hr, there was very little change in the ^{19}F spectrum and so the mixture was allowed to warm to room temp. for 1 hr and then cooled to −30° again. The ^{19}F spectrum clearly showed the presence of the typical TMSF multiplet at δ −89.5 with correct coupling constants, and a small doublet at δ-10.2 (J 1064 Hz) suggests PF_5. After stading overnight an appreciable quantity of TMSF was present but there was no longer a doublet at around δ −10 for PF_5. IR after this time indicated complete reaction of the cation **2** even though a small doublet attributed to salt **2** was still apparent in the ^{19}F spectrum.

REFERENCES

[1]Part 16. A. J. Birch, A. J. Liepa and G. R. Stephenson, *J. Chem. Soc.* Perkin I, submitted.

[2]J. Mathieu and J. Weill-Raynal, *Formatijon of C–C Bonds*, Vols I–III. Georg Thieme, Stuttgart, Germany (1973, 1975 and 1979).

[3]T. L. Brown, *Acc. Chem. Res.* **1**, 23 (1968).

[4]L. M. Jackman and B. C. Lange, *Tetrahedron* **33**, 2737 (1977).

[5]E. W. Colvin, *Chem. Soc. Revs.* **7**, 15 (1978).

[6a]A. J. Birch, and I. D. Jenkins, *Transition Metal Organometallics in Organic Synthesis* (Edited by H. Alper), Vol. 1, pp. 7–35. Academic Press, New York (1976); [b]M. Rosenblum, *Acc. Chem. Res.* **7**, 122 (1974); [c]B. M. Trost, *Pure & Applied Chem.* **51**, 787 (1979); [d]K. M. Nicholas, M. Mulvaney and M. Bayer, *J. Am. Chem. Soc.* **102**, 2508 (1980).

[7]A. J. Birch, B. M. R. Bandara, K. Chamberlain, B. Chauncy, P. Dahler, A. I. Day, I. D. Jenkins, L. F. Kelly, T.-C. Khor, G. Kretschmer, A. J. Liepa, A. S. Narula, W. D. Raverty, E. Rizzardo, C. Sell, G. R. Stephenson, D. J. Thompson and D. H. Williamson, *Tetrahedron* **37**, Supplement 9, 289 (1981).

[8]G. Olah, *Angew Chem.* Int. Ed. Engl. **12**, 173 (1973).

[9]A. J. Pearson, *Transition Metal Chemistry* **6**, 67 (1981).

[10]A. J. Birch, K. B. Chamberlain and D. J. Thompson, *J. Chem. Soc.* Perkin I, 1900 (1973).

[11]D. Seebach, *Angew. Chem.* Int. Ed. Engl. **19**, 239 (1979).

[12]A. J. Birch, K. B. Chamberlain, M. A. Haas and D. J. Thompson, *J. Chem. Soc.* Perkin I 1882, (1973); and Ref. 10 cited.

[13]A. J. Pearson, *Ibid.* Perkin I, 2069 (1977).

[14]R. E. Ireland, G. G. Brown, R. H. Stanford Jr. and T. C. McKenzie, *J. Org. Chem.* **39**, 51 (1974).

[15]A. J. Birch and A. J. Pearson, *Tetrahedron Letters.* 2379 (1975); *J. Chem. Soc.* Perkin I, 954 (1976).

[16]A. J. Pearson, *Aust. J. Chem.* **30**, 345 (1977).

[17]A. Pelter, K. G. Gould and L. A. P. Kane-Maguire, *J. Chem. Soc.* Chem. Commun. 1029 (1974).

[18]B. M. R. Bandara, A. J. Birch and T.-C. Khor, *Tetrahedron Letters* 3625 (1980).

[19]L. F. Kelly, A. S. Narula and A. J. Birch, *Ibid.* 4107 (1979).

[20]A. J. Birch, A. S. Narula, P. Dahler, G. R. Stephenson and L. F. Kelly, *Ibid.* 979 (1980).

[21]L. F. Kelly, A. S. Narula and A. J. Birch, *Ibid.* 871 (1980).

[22]A. J. Birch, L. F. Kelly and A. S. Narula, unpublished results.

[23]T. Mukaiyama, K. Banno and K. Narasaka, *J. Am. Chem. Soc.* **96**, 7503 (1974); T. Mukaiyama, *Angew. Chem.* Int. Ed. Engl. **17**, 48 (1978); I. Paterson and I. Fleming, *Tetrahedron Letters* 2179, 993 (1979); S. Murata, M. Suzuki and R. Noyori, *J. Am. Chem. Soc.* **102**, 3248 (1980).

[24]R. Noyori, K. Yokoyama, J. Sakata, I. Kuwajima, E. Nakamura and M. Shimizu, *Ibid.* **99**, 1265 (1977); E. Nakamura, K. Hashimoto and I. Kuwajima, *J. Org. Chem.* **42**, 4167 (1977).

[25]J. d'Angelo, *Tetrahedron* **32**, 2979 (1976).

[26]A. J. Sisti and G. M. Rusch, *J. Org. Chem.* **39**, 1182 (1974); R. E. Ireland and J. A. Marshall, *Ibid.* **27**, 1619 (1962).

[27]G. E. Joshi and L. M. Pande, *Synthesis* 450 (1975).

[28]For an excellent study regarding steric effects of 7,7-dimethyl group on the reactivity of nor-bornene see: H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.* **95**, 8665 (1973); H. C. Brown, J. H. Kawakami and K.-T. Liu, *Ibid.* **95**, 2209 (1973).

[29]A. J. Birch, W. D. Raverty and G. R. Stephenson, *J. Chem. Soc.* Chem. Commun. 857 (1980).

[30]P. J. Stang, M. G. Mangnum, D. P. Fox and P. Haak, *J. Am. Chem. Soc.* **96**, 4562 (1974).

[31]J. K. Rasmussen and A. Hassner, *J. Org. Chem.* **39**, 2558 (1974).

[32]C. Ainsworth, F. Chen and Y.-N. Kuo, *J. Organometallic Chem.* **46**, 59 (1972).

[33]T. C. Chan and I. Fleming, *Synthesis* 761 (1979).

[34]C. Eaborn, R. A. Jackson and R. Pearce, *J. Chem. Soc.* Perkin Trans. 1, 470 (1975).

[35]L. F. Kelly, A. S. Narula and A. J. Birch, *Tetrahedron Letters.* 2455 (1980).

[36]M. E. Jung, *J. Org. Chem.* **41**, 1479 (1976).

[37]R. J. P. Corrin, G. Royo and A. D. Saxcé, *J. Chem. Soc.* Chem. Commun. 892 (1980); R. A. Olafson and J. Cuomo, *Tetrahedron Letters.* 819 (1980).

[38]A. J. Birch and M. A. Haas, *J. Chem. Soc.* (C), 2465 (1971).

[39]A. J. Birch and K. B. Chamberlain, *Organic Synthesis* **57**, 107 (1977).

[40]A. J. Birch, L. F. Kelly and D. J. Thompson, *J. Chem. Soc.* Perkin 1, 1006 (1981).

[41]B. M. R. Bandara, Ph.D. Thesis, Australian National University, Canberra (1981).

[42]A. J. Birch, A. R. Murry and H. Smith, *J. Chem. Soc.* 1945 (1951).

[43]H. O. House, L. J. Czuba, M. Gall and D. Olmstead, *J. Org. Chem.* **34**, 2324 (1969).

[44]E. Nakamura, K. Hashimoto and I. Kuwajima, *Tetrahedron Letters* 2079 (1978).

[45]J. J. Bloomfield, D. C. Owsley and J. M. Nelke, *Organic Reactions* **23**, 259 (1976).

[46]W. C. Still, *J. Org. Chem.* **41**, 3063 (1976).

[47]D. J. Coughlin and R. G. Salomon, *Ibid.* **44**, 3784 (1979).

[48]H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *J. Am. Chem. Soc.* **79**, 1897 (1957).

[49]E. W. Abel and R. J. Rowley, *J. Organometallic Chem.* **84**, 199 (1975).

[50]A. A. L. Gunatilaka and A. F. Mateos, *J. Chem. Soc.* Perkin 1, 935 (1979).

[51]A. J. Pearson, *Ibid.* Perkin 1, 1255 (1979).

[52]R. L. Danheiser and G. Stork, *J. Org. Chem.* **38**, 1775 (1973).

[53]*High Resolution NMR Spectroscopy* (Edited by J. W. Elmsley, J. Feeney and L. H. Sutcliff), Vol. 2, pp. 949–952. Pergamon Press, Oxford (1966).