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ORGANOMETALLIC COMPOUNDS IN ORGANIC SYNTHESIS: REACTIONS OF SOME TRICARBONYLCYCLOHEXADIENYLIUMIRON COMPLEXES WITH 1,2-BIS(TRIMETHYLSILOXY)-1-CYCLOPENTENE. A NOVEL ROUTE TO 2-(SUBSTITUTED)-2-CYCLOPENTEN-1-ONES.

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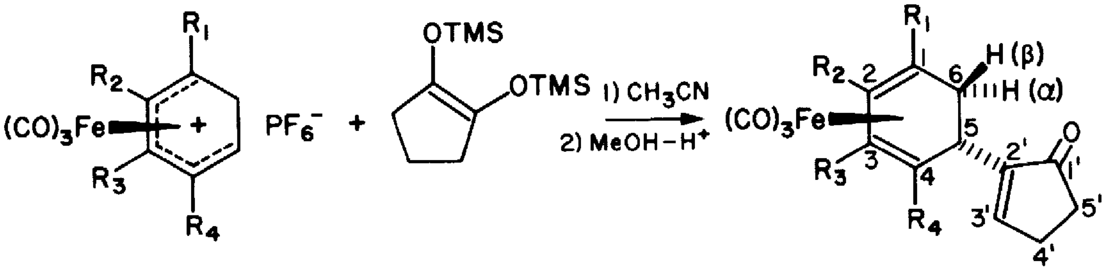
Summary: 1,2-Bis(trimethylsiloxy)-1-cyclopentene reacts with a range of tricarbonylcyclohexadienyliumiron cations to give initially siloxy acyloins, treatment of which with MeOH-HCl gives the 2-(substituted)-2-cyclopenten-1-one in good yields (56-78%).

Trimethylsilyl enol ethers, derived from ketones, were shown to react in good yields with tricarbonylcyclohexadienyliumiron cations under mild conditions, to form products with new carbon-carbon bonds.[1] Reports on a wide range of such O-silylated enolates will be made elsewhere.[2] The reactions are stereospecific, and the expectation is that in common with other such irreversible nucleophilic processes, attack is α-(opposite) to the face carrying $Fe(CO)_3$.

The class of enolates which can be used includes the 1,2-bis(trimethylsiloxy)-1-cycloalkenes and we now describe reactions of several tricarbonylcyclohexadienyliumiron cations with the readily available[4] 1,2-bis(trimethylsiloxy)-1-cyclopentene. The products are first the 2-substituted-2-siloxy-cyclopentan-1-ones, which can be converted into 2-substituted-2-cyclopenten-1-ones of a type which is of growing interest[5] in connection with the synthesis of prostaglandins and analogues. Stereospecificity is accompanied by a large measure of regiospecificity (Table), reaction occurring at the terminus of the cation more remote from substituents such as Me and OMe.

This process is of a novel type, although a few examples have been reported[6] of alkylations of 1,2-bis(trimethylsiloxy)-1-cycloalkenes, and there have been some recent studies of enolate salts derived from acyclic and alicyclic 1,2-enediols.[7] Synthetically, the reaction is equivalent to the ability to employ a 2-anion of a cyclopent-2-enone.[8] Our alkylations, in contrast[9] to previous electrophilic substitutions involving silylated enols,[10] do not require catalysis by Lewis acids or fluoride anion.



TABLE

SALTS	YIELDS (%)	2-(SUBSTITUTED)-2-CYCLOPENTEN-1-ONES
1: $R_1 = R_2 = R_3 = R_4 = H$	(76)	6: $R_1 = R_2 = R_3 = R_4 = H$
2: $R_1 = R_3 = R_4 = H$; $R_2 = OMe$	$(56)^a$	7: $R_1 = R_3 = R_4 = H$; $R_2 = OMe$
3: $R_1 = R_3 = R_4 = H$; $R_2 = Me$	$(78)^a$	8: $R_1 = R_3 = R_4 = H$; $R_2 = Me$
4: $R_1 = R_2 = R_4 = H$; $R_3 = Me$	$(60)^a$	9: $R_1 = R_2 = R_4 = H$; $R_3 = Me$
5: $R_1 = R_4 = H$; $R_2 \frown R_3 = -(CH_2)_4-$	(78)	10: $R_1 = R_4 = H$; $R_2 \frown R_3 = -(CH_2)_4-$

[a] Reaction temperature ∿-20°C

Obvious extrapolations of the type of process to ring systems of different sizes are being successfully pursued.

In a typical experiment, 1,2-bis(trimethylsiloxy)-1-cyclopentene (∿ 3.5 mmole) is stirred with an appropriate salt (1 mmole) in dry acetonitrile at or below room temperature. Reaction is usually complete in less than 10 mins. as indicated by the appearance of $[Fe(CO)_3]$ bands at ∿2040, 1980 cm^{-1} and disappearance of $[Fe(CO)_3]^+$ bands at ∿2105, 2050 cm^{-1} in the infra-red spectrum. After solvent removal under reduced pressure (0.2 mm, room temperature), the silylated acyloin is reacted[11] with oxygen-free, dry MeOH (10 ml) containing 10 N HCl (4-5 drops) for 24 hr at room temperature under nitrogen. Ether extraction from water, and chromatography (silica or alumina) gives the desired 2-substituted-2-cyclopenten-1-ones:

Tricarbonyl-5-(1'-oxo-2'-en-2'-cyclopentyl)cyclohexa-1,3-dieneiron (6): IR(CCl_4): 2048, 1983, 1975, 1709 cm^{-1}. ^{1}H-NMR:[12] 1.44 (C-6, α H); 2.25 (C-6, β H); 2.36 (C'-5, 2H); 2.52 (C'-4, 2H); 3.0-3.20 (C-1 and C-4 2H, C-5 β H); 5.41 (C-2 and C-3, 2H); 7.30 (C'-3, 1H). *Mass*[13] : *m/e* 300 $C_{14}H_{12}O_4Fe$ ($M^{+\cdot}$).

Tricarbonyl-2-methoxy-5-(1'-oxo-2'-en-2'-cyclopentyl)cyclohexa-1,3-dieneiron (7): IR(CCl_4): 2048, 1980, 1975 and 1708 cm^{-1}. ^1H-NMR: 1.54 (C-6, α H); 2.20 (C-6, β H); 2.37 (C'-5, 2H); 2.51 (C'-4, 2H); 2.66-3.35 (C-1 and C-4 2H, C-5 β H); 3.63 (C-2 OMe, s, 3H); 5.11 (C-3, 1H); 7.26 (C'-3, 1H). *Mass:* $^m/e$ 330 $C_{15}H_{14}O_5Fe$ ($M^{+\cdot}$).

Tricarbonyl-2-methyl-5-(1'-oxo-2'-en-2'-cyclopentyl)cyclohexa-1,3-dieneiron (8): IR(CCl): 2040, 1976, 1965 and 1706 cm^{-1}. ^1H-NMR: 1.44 (C-6, α H); 2.12 (C-2 Me, s, 3H); 2.24 (C-6, β H); 2.38 (C'-5, 2H); 2.50 (C'-4, 2H); 2.87-3.12 (C-1 and C-4 2H, C-5 β H); 5.28 (C-3, 1H); 7.24 (C'-3, 1H). *Mass:* $^m/e$ 314 $C_{15}H_{14}O_4Fe$ ($M^{+\cdot}$).

Tricarbonyl-3-methyl-5-(1'-oxo-2'-en-2'-cyclopentyl)cyclohexa-1,3-dieneiron (9): IR(CCl_4): 2042, 1975, 1965 and 1706 cm^{-1}. ^1H-NMR: 1.34 (C-6, α H); 2.12 (C-3 Me, s, 3H); 2.20 (C-6, β H); 2.32 (C'-5, 2H); 2.50 (C'-4, 2H); 2.95-3.05 (C-1 and C-4 2H, C-5 β H); 5.37 (C-2, 1H); 7.20 (C'-3, 1H). *Mass:* $^m/e$ 314 $C_{15}H_{14}O_4Fe$ ($M^{+\cdot}$).

Tricarbonyl{1-4-η-5-(1'-oxo-2'-en-2'-cyclopentyl)bicyclo[4,4,$0^{2,3}$]*deca-1,3-diene}-iron (10):* IR(CCl_4); 2050, 1980, 1970, 1708 cm^{-1}. ^1H-NMR: 1.40 (C-6, α H); 1.76-2.60(CH_2's, 8H); 2.16 (C-6, β H); 2.34 (C-5, 2H); 2.50 (C'-4, 2H); 2.74-3.14 (C-1 and C-4 2H, C-5 β H); 7.18 (C'-3, 1H). *Mass:* $^m/e$ 354 $C_{18}H_{18}O_4Fe$ ($M^{+\cdot}$).

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12. Spectra were recorded in $CDCl_3$ and chemical shifts are expressed in δ values. All signals are characteristic multiplets which agree fully with accepted standards and interpretations.

13. All mass spectra showed weak molecular ions and characteristic losses: M^+-CO, M^+-2CO, M^+-3CO and M^+-(3CO + H_2).

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