# Tungsten-mediated Syntheses, Skeletal Rearrangement and Synthetic Applications of $\eta^1$-2,5-Dihydro-3-furanyl Rings

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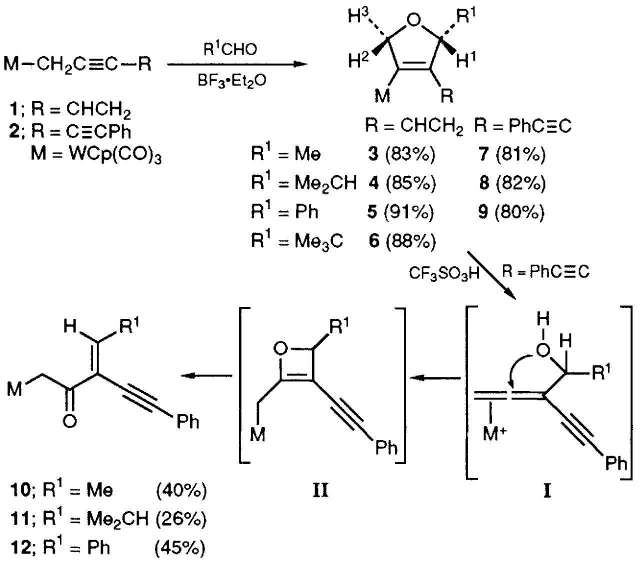
The syntheses, acid-catalysed rearrangements and demetallation chemistry of $\mathrm{CpW(CO)_3(\eta^1\text{-}\overline{C{=}CR{-}CHR^1{-}O{-}C}H_2)}$ ($\mathrm{R = CHCH_2, C{\equiv}CPh}$; $\mathrm{R^1}$ = alkyl, phenyl; $\mathrm{Cp = C_5H_5}$) are reported, and their synthetic utility in organic reactions is demonstrated.

A major goal of organometallic chemistry is to develop the synthetic utility of organometallic compounds in organic reactions.[1] Transition metal-mediated organic reactions may provide an easy and efficient synthesis of useful organic molecules which are not readily produced by common methods. In organic chemistry, dihydrofuran rings are of special interest because they are important constituents of numerous natural products.[2] We describe here a novel tungsten-mediated synthesis of new classes of functionalized 2,5-dihydrofurans which provide potential utility in organic synthesis.

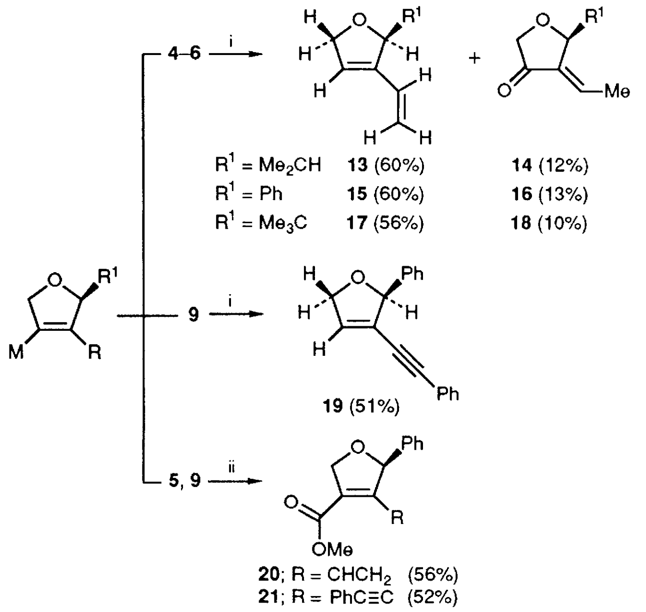
Although in a recent paper[3] it was reported that a transition-metal–$\eta^1$-allyl compound failed to undergo acid-catalysed cyclization with aldehydes, the reaction between the



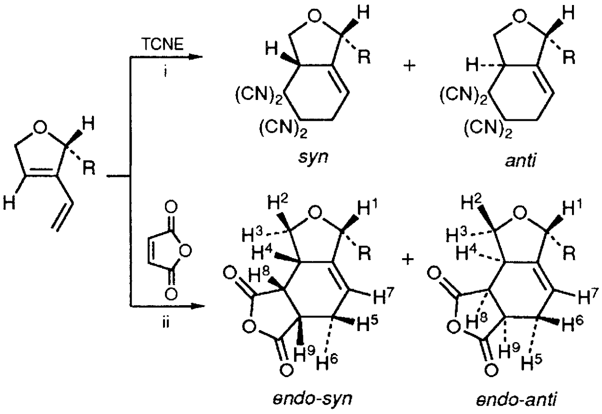
**Scheme 1**

tungsten η$^1$-propynyl compounds **1** and **2**[4] and a mixture of RCHO (R = Me, Me$_2$CH, Me$_3$C, Ph, 1.2 equiv.)–BF$_3$·Et$_2$O (1.0 equiv.) in cold toluene (−40 °C, 2 h) produced the tungsten–η$^1$-2,5-dihydro-3-furanyl compounds in good yields (>80%). The five-membered ring structure is supported by both the long-range coupling parameters $J_{1,2}$ 4–5 and $J_{1,3}$ 1.5–2 Hz and an X-ray diffraction study† of **5**. The mechanism of their formation is believed to follow a [3 + 2] cycloaddition[5] involving an allene zwitterionic intermediate.

Compounds **7–9** are prone to acid-catalysed skeletal rearrangement. Treatment of **7–9** with anhydrous CF$_3$SO$_3$H (0.5 equiv.) in CH$_2$Cl$_2$ (1 h, 0 °C) afforded **10–12** in 42–25% yield, characterized as unsaturated ketone derivatives based on mass, IR, $^1$H and $^{13}$C NMR data.‡ In a proton NOE experiment, irradiation of the C*H*$_2$CO signal (δ 2.75) of **10** produced a 1.5% increase in the signal of =CH (δ 7.08) whereas the Me signal was unaffected; therefore the (*E*)-configuration is assigned. In contrast, no skeletal isomerization was observed for the vinyl compounds **3–6**, which gave a dark red insoluble solid of undetermined composition under the same conditions. As shown in Scheme 1, the H$^+$ can be envisaged to initiate furan ring opening, regenerating the α-hydroxyallene cation **I**, which undergoes further intramolecular cyclization to give the unstable four-membered ring dihydrooxete **II**. A subsequent acid-catalysed isomerization of **II** is expected to give compounds **10–12**. Our preliminary results reveal that this skeletal rearrangement is also achieved by BF$_3$·Et$_2$O (1.0 equiv.) which nevertheless decreases the yields (**10**, 26%; **11**, 18%; **12**, 22%).



**Scheme 2** M = CpW(CO)$_3$: i, Me$_3$NO·H$_2$O (5 equiv.), CH$_2$Cl$_2$ (23 °C, 5 h); ii, CO (1 atm), (NH$_4$)$_2$Ce(NO$_3$)$_6$ (3.0 equiv.), MeOH–CH$_2$Cl$_2$ (1 : 1, −78 °C, 4 h)



| R | Dienophile | Product (yield, syn : anti) |
|---|---|---|
| Me$_2$CH | TCNE | **22** (72%, anti only) |
| Me$_2$CH | MA | **23** (66%, anti only) |
| Me$_3$C | TCNE | **24** (62%, anti only) |
| Ph | TCNE | **25** (88%, 10/1) |
| Ph | MA | **26** (90%, 8/1) |

**Scheme 3** TCNE = tetracyanoethylene, MA = maleic anhydride: i, benzene, 2 h, 25 °C, TCNE (1.2 equiv.); ii, MeCN, 80 °C, 10 h, MA (2.0 equiv.)

Demetallation of the organometallics above has been studied to explore their utility in organic reactions. As shown in Scheme 2, treatment of **4–6** with an excess of Me$_3$NO·H$_2$O§ (5.0 equiv.) in CH$_2$Cl$_2$ gave the new dienes **13**, **15** and **17**, respectively in reasonable yields. Additional α, β-unsaturated ketones **14**, **16** and **18** were also isolated in pure forms in *ca.* 10% on a preparative SiO$_2$-TLC plate.

Similarly, the enyne **19** can be obtained from **9** in 51% yield under the same conditions. Following a known procedure,

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† Compound **5** crystallizes in the monoclinic space group $P2_1/n$, $a$ = 7.444(1), $b$ = 29.676(4), $c$ = 8.224(2) Å, β = 90.63(2)°, $Z$ = 4, final $R$ = 0.021 and $R_w$ = 0.016 for 1928 reflections with $I > 2\sigma(I)$ out of 2340 unique reflections.

‡ *Selected spectra data* for complex **10**: $^1$H NMR (300 MHz, CDCl$_3$) δ 2.02 (d, $J$ 7.0 Hz, 3 H, Me), 2.75 (s, 2 H, CH$_2$CO), 5.54 (s, 5 H, C$_5$H$_5$), 7.08 (q, $J$ 7.0 Hz, C*H*=CMe), 7.32 (m, 3 H, Ph-H) and 7.48 (d, 2 H, *o*-Ph-H); $^{13}$C NMR (75 MHz, CDCl$_3$) − 5.3 (W–CH$_2$), 16.8 (Me), 85.6, 97.2 (C≡C), 92.2 (C$_5$H$_5$), 123.3, 126.8, 127.9, 131.2 (Ph-C), 129.3, 143.8 (C=C), 204.1 (CO), 217.1 and 228.2 (2 × W–CO); IR (Nujol) ν(CO)/cm$^{-1}$ 2019s, 1920s and 1645s. For complex **23**: $^1$H NMR (400 MHz, CD$_3$CN) δ 0.83 (d, 3 H, Me), 0.91 (d, 3 H, Me′), 1.78 (m, 1 H, C*H*Me$_2$), 2.23 (m, 1 H, H$^5$), 2.68 (ddd, 1 H, H$^6$), 2.79 (m, 1 H, H$^4$), 3.53 (m, 1 H, H$^9$), 3.64 (dd, 1 H, H$^8$), 4.02 (dd, 1 H, H$^1$), 4.07 (dd, 1 H, H$^2$), 4.16 (dd, 1H, H$^3$) and 5.74 (m, 1 H, H$^7$), $J_{1,7}$ 3.0, $J_{1,\mathrm{CHMe_2}}$ 6.8, $J_{2,3}$ 9.1, $J_{2,4}$ 6.9, $J_{3,4}$ 8.4, $J_{4,8}$ 8.3, $J_{5,6}$ 15.5, $J_{5,7}$ 6.1, $J_{5,9}$ 7.0, $J_{6,7}$ 1.6, $J_{6,9}$ 1.7, $J_{8,9}$ 8.7 and $J_{\mathrm{CHMe_2}}$ 6.8 Hz.

§ Me$_3$NO·H$_2$O was prepared by mixing equimolar amounts of anhydrous Me$_3$NO and H$_2$O. We have performed an isotopic study involving Me$_3$NO·D$_2$O in the reaction. According to $^1$H and $^{13}$C NMR spectra, the three alkenic protons HC=C and =CH$_2$ were all deuteriated equally, *i.e. ca.* 1/3 deuterium content, indicating that D$_2$O serves as proton source.

$Ce^{IV}$-promoted[6] carbonylation of **5** and **9** in $MeOH–CH_2Cl_2$ (−78 °C, 2 h) smoothly produced the esters **20** and **21** in *ca.* 55% yield. The dienes **13**, **15** and **17** belong to a novel class¶ of plane-nonsymmetric endocyclic dienes. We are particularly interested in their Diels–Alder reaction chemistry because it may provide easy access to some natural tetracyclic terpenes[7,8]. The three dienes above react smoothly with maleic anhydride (MeCN, 80 °C, 12 h) and tetracyanoethylene (benzene, 23 °C) to give the adducts **22–26**. Notably only a single diastereoisomer was observed for TCNE or maleic anhydride adducts **22–24** of **13** and **17**. Good diastereofacial selectivities were observed for the cycloaddition of **15** with TCNE and maleic anhydride. We have carefully determined the stereochemistries of the major (single) isomer of each reaction by means of $^1H$ NMR NOE-difference spectra.[11] The results are given in Scheme 3. In the particular case of **26**, irradiation of the $H^4$-signal at δ 2.98 led to an Overhauser increase in the intensities of $H^1$ and $H^9$ by 1.9 and 1.4%, respectively. This information indicates that maleic anhydride approaches the diene *cis* to the phenyl group with its anhydride orientation *endo* to the diene fragment. In contrast, the $Me_2CH$ and $Me_3C$ substituents preferentially form *anti*-cycloaddition adducts **22–24** as deduced from the proton NOE-difference data. The *syn*-directed effect of the phenyl case is surprising. A possible secondary orbital interaction[9] between the phenyl π-electrons (HOMO) and the frontier orbitals of the dienes and dienophiles may be responsible for its stereochemistry.

*Received, 25th February 1992; Com. 2/01004F*

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¶ In contrast, the derivatives of related endocyclic dienes bearing a dihydrofuran ring such as 4-vinyl-2,5-dihydrofurans[10] and 3,4-bis-(methylidene)-2,5-dihydrofurans[11] have been recently reported, see refs. 10 and 11.

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