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Mechanism of Oxidation of Tungsten η^1-2,5-Dihydrofur-3-yl Compounds to η^1-Fur-2-yl and Further to η^1-Δ^3-Butenolide Derivatives

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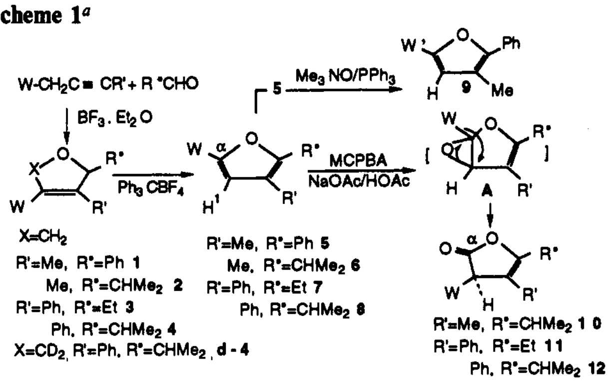
The [3 + 2] cycloaddition of transition-metal η^1-allyl, -allenyl, and -propargyl compounds with electron-deficient olefins has been known for two decades.[1,2] That only special olefins undergo this reaction makes these compounds much less useful than their main group metal analogues.[3] We have successfully achieved the BF_3-mediated [3 + 2]-cycloaddition reaction of tungsten–propargyl derivatives with aldehydes to yield the corresponding η^1-2,5-dihydrofur-3-yl[4] compounds. Furans and butenolides are important structural units for numerous natural products.[5,6] Here, we report the oxidation of metal η^1-2,5-dihydrofur-3-yl compounds to furans, and further to Δ^3-butenolide derivatives; both involve a 1,2-shift of the metal fragment.

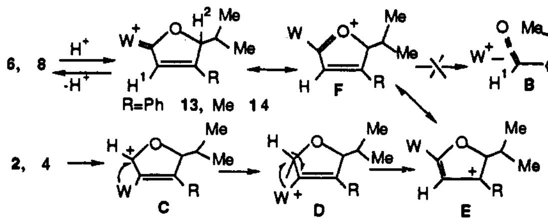
As shown in Scheme 1, compounds **1–4** were readily synthesized from suitable η^1-propargyls, aldehydes and $BF_3{\cdot}Et_2O$.[4] Treatment of **1-4** with purified Ph_3CBF_4 (1.5 equiv) in CH_2Cl_2 (0.5 h, 0 °C), followed by quenching with $NaHCO_3$ (aqueous) solution, afforded **5–8** in good yields (>80%) after workup. Although spectral data[7] of **5–8** are consistent with the furan structure, the proton NOE difference spectra and the H^1 (δ 6.20–6.70) and C*H*^{1} (δ 130–135) NMR chemical shifts indicate that the $CpW(CO)_3$ fragment has undergone a 1,2-shift to the C_α position and left a hydrogen at the C_β carbon. Further substantiation for the 1,2-shift is provided by the X-ray structure[8] of **9** derived from Me_3NO-promoted substitution of PPh_3 for one of the CO ligands of **5**. The ORTEP drawing confirms a mutual switch of the $CpW(CO)_3$ and C*H*^{1} positions, as well as the furan structure.

Scheme 1[a]



[a] W = $CpW(CO)_3$; W' = *cis*-$CpW(CO)_2(PPh_3)$.

Scheme 2[a]



[a] W = $CpW(CO)_3$.

To confirm the source of C_β–H hydrogen of **5–8**, we prepared a deuterated sample **d-4** (deuterium content ca. 70%) *via* $PhC{\equiv}CCD_2OH$, obtained by successive reduction/oxidation of $PhC{\equiv}CCHO$, each performed twice, by $NaBD_3CN$/pyridinium chlorochromate, respectively. The ^{1}H NMR spectra of the furan derived from **d-4** showed deuterium content ca. 88% in the C*H*^{1} position, confirming a 1,2-hydrogen shift. A kinetic isotopic effect accounts for the greater deuterium content of the furan according to the proposed mechanism (Scheme 2, *vide infra*).

Further oxidation of furans **6–8** was achieved with *m*-chloroperbenzoic acid (MCPBA, 1.2 equiv) in hexane (5 °C, 1 h) over an aqueous HOAc/NaOAc buffer solution, to yield **10–12** in 65–70% yields. Mass and elemental analyses reveal that **10–12** are related to **6–8** by incorporation of an oxygen atom to form a lactone structure (ν(CO) 1778 (s) cm^{-1}). The ORTEP drawing[9] of **11** confirms the Δ^3-butenolide structure; the $CpW(CO)_3$ fragment undergoes a 1,2-shift to the C_β carbon.

The oxidations above deserve special attention because both involve a 1,2-migration of the metal fragment. In the second step, MCPBA preferentially oxidizes the $WC_\alpha{=}C_\beta$ double bond due to the electron-donating ability of the $CpW(CO)_3$ moiety. Rearrangement of the epoxide intermediate (**A**) is expected to give the Δ^3–butenolide structure.[10]

To approach the mechanistic problem of the Ph_3C^+ oxidation, we monitored the reactions by *in situ* NMR measurements. At –60 °C, t = 15 min, a NMR sample (CD_2Cl_2) containing **4** and Ph_3CBF_4 (1.5 equiv) showed new proton NMR signals due to **13**[7]

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(7) Spectral data: **13**, IR (Nujol): ν(CO) 2070 (vs), 2005 (vs). ^{1}H NMR (400 MHz, CD_2Cl_2) 7.77 (1H, s, H^1), 7.60–7.75 (5H, m, Ph), 6.35 (1H, H^2, d, *J* 2.9 Hz), 6.07 (5H, s, Cp), 2.55 (1H, m, C*H* Me$_2$, $J_{\text{H-2}}$ 2.9 Hz, $J_{\text{H-Me}}$ 6.9 Hz), 1.50, 0.55 (d, d, 2Me, *J* 6.9 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2) 273.2 (W═C), 213.3, 212.5 (2W–CO), 174.2 (═*C*Ph), 140.2, 140.1, 130.2, 127.4 (Ph), 135.3 (CH^1), 108.5 (CH^2), 95.1 (Cp), 34.7 (*C*HMe$_2$), 20.5, 13.8 (2Me); **14**, IR (Nujol) ν(CO) 2070 (vs), 2005 (vs); ^{1}H NMR (400 MHz, CD_2Cl_2) 7.32 (1H, s, H^1), 6.02 (5H, s, Cp), 5.67 (1H, H^2, d, *J* 2.9 Hz), 2.52 (1H, m, C*H*Me$_2$, $J_{\text{H-2}}$ 2.9 Hz, $J_{\text{H-Me}}$ 6.9 Hz), 2.43 (3H, s, Me), 1.47. 0.68 (d, d, 2Me, J 6.9 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2) 278.4 (W═C), 213.6, 212.6 (2W–CO), 179.0 (═*C*Me), 130.1 (CH^1), 110.1 (CH^2), 95.8 (Cp), 38.2 (*C*HMe$_2$), 30.4, 21.4. 14.2 (3Me).

(8) Crystal data for **9**: triclinic space group $P1$, a = 12.5055(19) Å, b = 13.4555(18) Å, c = 21.251(5) Å, α = 95.548(16)°, β = 104.082(17)°, γ = 108.023(12)°, V = 3240.5(10) Å^3, Z = 4. Each asymmetric unit contains two independent molecules. Of the 8461 unique reflections, 6463 were considered observed having $I > 2\sigma(I)$. Final R = 0.027 and R_w = 0.019.

(9) Crystal data for **11**: monoclinic space group $P2_1/c$, a = 19.031(6) Å, b = 14.309(3) Å, c = 13.148(3) Å, β = 90.25(2)°, V = 3580.3(16) Å^3, Z = 8. Each asymmetric unit contains two independent molecules. Of the 6300 unique reflections, 3919 were considered observed having $I > 3\sigma(I)$. Final R = 0.0438 and R_w = 0.0494.

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(yields >85%), in addition to minor features assignable to Ph_3C^+, Ph_3CH, and **4**. When this NMR sample was kept at −60 °C for 2 h, the signals of **13** completely disappeared to leave **8** as the only species (yields >95%). Structural information about this intermediate **13** was provided by addition of CF_3SO_3H (7.5 equiv) to **8** in a NMR sample (CD_2Cl_2, −60 °C), which regenerated this cation slowly and completely (t = 3 h, yield >90%). This cation is stable at 23 °C but only in a highly acidic medium; treatment of **13** with Na_2CO_3 (aqueous) solution regenerated the furan **8**. Similarly, **14** was obtained in 65% yield from **6** and CF_3SO_3H (6.5 equiv) in CD_2Cl_2 (−60 °C).

The most likely structures for **13**–**14** are Fisher-type carbenes, illustrated in Scheme 2. The possibility of a vinyl ketene complex **B** is opposed by the NMR chemical shifts of H^1 (δ 7.70, **13**; 7.32, **14**) and $\mathit{C}H^1$ (δ 135.3, **13**; 130.1, **14**), which are much too far from those of the related $CpFe(CO)_2(\eta^2\text{-}H_2C{=}C{=}O)^+$ cation[11–13] and organic ketene compounds.[14,15] These NMR signals, however, are near those of M(=C(OMe)*CH*=CHR)[16] [M = $Cr(CO)_5$, (η^6-benzene)Ru(CO)(PPh_3)$^+$].[17] For **13** and **14**, the W=*C* carbon NMR resonances appear reasonably upfield[16c] (δ 272.6, **13**; 278.4, **14**) relative to those (δ 295–305) of the $CpW(CO)_2L(=CHR)^+$ (L = PR_3, R = H, Ph) cations.[18] A quaternary carbon signal (δ 174.2, **13**; 179.0, **14**) is assigned to =Cγ carbon due to the resonance form **E**. The $\mathit{C}H^2$ carbon signals (δ 108.5, J_{C-H^1} = 152 Hz, **13**; δ 110.1, J_{C-H^1} = 150 Hz, **14**) are comparable to those (δ 94.0 and 94.3) of **2** and **4**. Finally, the highly downfield $C\mathit{H}^2$ proton chemical shifts (δ 6.35, **13**; 5.67, **14**) are caused by heavy deshielding from the neighboring positive centers, i.e., oxonium and C_γ^+ centers in the two resonance forms **E** and **F**, respectively.

To account for the carbene intermediate, we believe that the Ph_3C^+ oxidation of **1**–**4** is initiated by a hydride abstraction of the methylene CH_2O protons. This suggestion implies that a cyclic η^2-allene intermediate **C** is formed since the $CpW(CO)_3$ fragment is capable of stabilizing an adjacent carbocation[19] by donation of its d electrons. A metal complex of a highly strained η^2-allene ring has been reported recently.[20] We propose a 1,2-hydrogen shift of this η^2-allene species to give the observed carbenes, of which the OC*H*–R″ proton is highly acidic and readily dissociates to give **5**–**8**.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, bond distances and angles, thermal parameters, and ORTEP drawings for **9** and **11** (20 pages); listing of observed and calculated structure factors for **9** and **11** (52 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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