2-Methyl-4-alkenyl-2,3-dihydrofurans by Cleavage of the Metal–Carbon Double Bond in α,β-Unsaturated 2-Oxacyclopentylidene Pentacarbonyl Chromium Complexes

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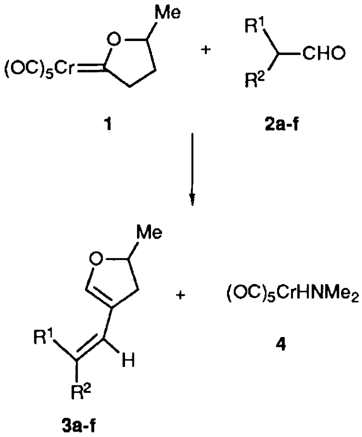
The reaction between the complex $(CO)_5Cr{=}\overline{C\text{-}CH_2CH_2CH(Me)O}$ **1** and aliphatic aldehydes bearing α-H atoms, in the presence of dimethylamine hydrochloride and potassium carbonate, leads directly to 1,3-dienes **3a–f**; in one case the formation of the intermediate **5** can be demonstrated.

Among organometallic compounds, pentacarbonyl(alkoxyalkylcarbene) chromium complexes are of increasing interest as a useful source of various organic compounds, *e.g.* β-lactams,[1] anthracyclinone derivatives,[2] β-hydroxycarboxylic acid derivatives[3] and cyclobutanones.[4] Moreover, modifications within the carbene ligand permit a large variety of carbene complexes to be obtained which are not accessible by direct synthesis. From a synthetic point of view, one of the most useful ways in which the carbene ligand in pentacarbonyl(alkoxyalkylcarbene)chromium complexes can be cleaved is the oxidation of the metal–carbon double bond.



Scheme 1 *Reagents and conditions*: K_2CO_3 $Me_2NH{\cdot}HCl$, anhydrous DMF, room temp.

Displacement of the carbene ligand from complexes with tertiary bases yielding enol ethers is also known; however despite the intrinsic synthetic interest, only a few examples of this reaction have been reported.[5]

Here we report a general and mild synthesis of 1,3-diene derivatives **3a–f** by reaction of pentacarbonyl-3-methyl-2-oxacyclopentylidenechromium **1** with aldehydes **2a–f** in the presence of dimethylamine (Scheme 1).† This reaction implies the condensation between the methylene group α with respect to the carbene carbon atom of compound **1** and aldehydes **2a–f** to give the α,β-unsaturated carbene complexes analogous to **5** which immediately eliminate the $Cr(CO)_5$ group in the form of the $(CO)_5Cr{-}HNMe_2$ complex, with shift of a hydrogen atom from the allylic position to the carbene carbon atom.

We could demonstrate that the overall process is promoted by dimethylamine. In fact, when the reaction between carbene

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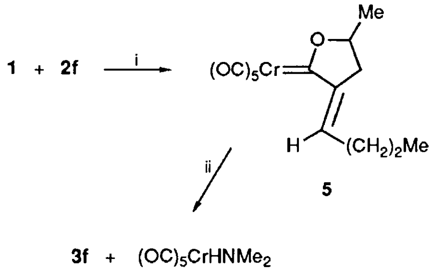
† *Typical procedure*. Dimethylamine hydrochloride (14.4 mmol) and potassium carbonate (5.4 mmol) were added to a solution of carbene complex **1** (1.8 mmol) and aldehyde **2a** (1.8 mmol) in anhydrous dimethylformamide (10 ml). The reaction was allowed to proceed at 20°C, under argon, for the time indicated in Table 1. The reaction mixture became intensely red and then yellow, indicating the end of the reaction. The mixture was diluted with water and extracted with diethyl ether. The organic layer was then dried over Na_2SO_4. The residue left by evaporation of the solvent under reduced pressure was purified by flash column chromatography; compound **3a** was then distilled (see Table 2); ^1H NMR of **3a** (200 MHz, $CDCl_3$), δ 1.30 (d, 3H, *J* 7.5 Hz, $CHCH_3$), 1.75 (s, 6H, $CH_3{-}C{-}CH_3$), 2.45 (m, 1H, CH_2), 3.00 (m, 1H, CH_2), 4.70 [m, 1H, $O{-}CH(CH_3)$], 5.70 (s, 1H, =CH) and 6.20 (s, 1H, O–CH); IR (neat) ν/cm^{-1} 2950, 2910, 2850, 1660, 1600, and 1110.



Scheme 2 *Reagents and conditions*: i, K_2CO_3, anhydrous DMF, room temp., 5 h; ii, $Me_2NH{\cdot}HCl$, K_2CO_3, anhydrous DMF, room temp., 1.5 h

1 and butanal **2f** was run in the absence of secondary amine, only the α,β-unsaturated cyclic chromium carbene complex **5**‡ was isolated in 50% yield. This complex, treated with dimethylamine hydrochloride and potassium carbonate in dimethylformamide (DMF) at room temperature, was quantitatively converted to diene **3f** (Scheme 2).

Doetz[6] has reported the breaking of the carbenic carbon–oxygen bond of pentacarbonyl-2-oxacyclopentylidenechromium by dimentylamine to give the corresponding open-chain amino carbene complex; it is noteworthy that we have never observed such a reaction. This could be due to the different experimental conditions we have used.

Dienes **3a–f** have not been previously described in the literature;§ in our hands they were stable enough to distillation and could all be obtained in a pure form (see Table 1). Since compounds **3a–f** can be regarded as both dihydrofuran derivatives and conjugated dienes, work currently in progress in our laboratory is aimed at exploiting this double synthetic potential.

Table 1 Reaction times, yields and boiling points of compounds **3a–f**

Diene[a]	R^1	R^2	t/h	Yield (%)	B.p., t/°C (p/mmHg)
3a	Me	Me	4	75	90 (0.35)
3b[b]	H	Ph	3	23	—
3c	H	$(CH_2)_7Me$	1.5	89	140 (0.25)
3d	$-(CH_2)_5-$		5.5	68	155 (0.6)
3e	H	$(CH_2)_4Me$	3	50	140 (0.5)
3f	H	Et	3	45	130 (0.5)

[a] All compounds produced satisfactory elemental analyses, and ^1H NMR, IR and mass spectra. [b] Compound **3b** was not distilled until 160°C at 0.5 mmHg; it was characterized as such.

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‡ *Spectroscopic data* for compound **5** (oil): ^1H NMR (80 MHz, $CDCl_3$), δ 1.50 (d, 3H, $CHCH_3$), 1.60 (m, 2H, CH_2CH_3), 2.00 (m, 1H of the CH_2 of the ring), 2.30 (m, 2H $=CHCH_2$), 2.74 (m, 1H of the CH_2 of the ring), 5.20 (m, 1H, $OCH(CH_3)$] and 7.30 (m, 1H, =CH); IR (neat) ν/cm^{-1} 2060, 2000, 1990, 1980, 1970–1900, 1640, 650 and 640; ^{13}C NMR (200 MHz, $CDCl_3$), δ 318.7($C_{carbenic}$), 224.2 (C≡O *trans*), 217.6 (C≡O *cis*), 155.2 (C=CH), 153.2 (>C=), 91.9 (CH–O), 34.0 ($=CHCH_2$), 31.8 ($=CCH_2$), 21.9 (CH_3CHO), 21.5 (CH_2CH_3) and 13.2 (CH_2CH_3), *m/z* 330 (M^+), 302, 274, 218, 190 and 138.

§ Only one article[7] has been reported in which a 4-alkenyl substituted tetrahydrofuran, together with other products was obtained, from a [3 + 2] cycloaddition rcaction between α,β-acetylenic ketones and alkenes.