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Reaction of nucleophiles with alkoxycarbene complexes of chromium: a general access to polycyclic substituted butenolides

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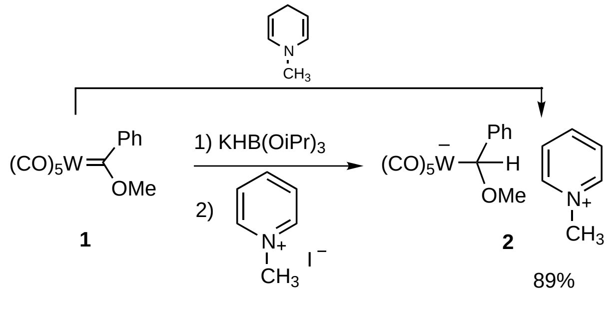
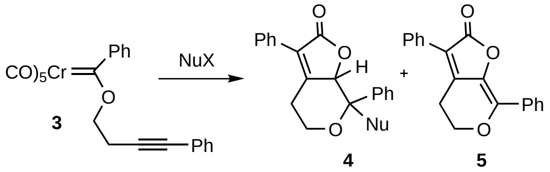
Abstract—A series of new substituted butenolides has been obtained either by reacting alkynylalkoxycarbene complexes **3** with simple nucleophiles such as metal hydrides, metal alkoxides and metal alkyls, or by reacting simple alkoxycarbene complexes **6** with more elaborate nucleophiles such as metal alkynolates or metal alkynyls. © 2002 Elsevier Science Ltd. All rights reserved.

Carbene complexes of the group 6 metals are known to react with nucleophiles to lead to tetravalent carbon intermediates upon attack at the electrophilic carbene carbon. Some of these intermediates are fairly stable since they have been isolated and fully characterized.[1–3]

Very recently, we have discovered that such a nucleophilic addition occurs also upon interaction of chromium and tungsten carbene complexes with dihydropyridines with transfer, in a biomimetic way, of a hydride to the carbene carbon. This is clearly demonstrated by the fact that the same complex **2** could be obtained either upon reduction of complex **1** with KHB(O*i*Pr)$_3$ followed by cation exchange with *N*-methylpyridinium iodide, or directly upon reduction of **1** with *N*-methyldihydropyridine.[4,5]



However, in the case of alkynylalkoxycarbene complexes such as **3**, the reduction of the carbene function with *N*-methyldihydropyridine was followed by a series of CO and triple bond insertions leading finally to butenolides.[6–8] In this paper, we demonstrate that the latter reaction is not only triggered by hydrides originating from dihydropyridines, but surprisingly also by simple metal hydrides, alkoxides and various lithium alkyls, leading in most of the cases examined so far to substituted butenolides. This is exemplified via the three following transformations. Thus, when a freshly prepared 0.83 M solution of KHB(O*i*Pr)$_3$ in THF (845 μL) was added to a solution of complex **3** in THF (15 mL) kept at −10°C under argon, the red color faded rapidly. After warming to room temperature, the solution turned again to red. Stirring for 15 h followed by extraction and silica gel chromatography gave **4a** (20.9%) as a white solid mp 59°C.



		4	5
NuX= NMedihydrop.	Nu= H	75%	
a NuX= KH(BOiPr)$_3$	Nu= H	20.9%	
b NuX= MeONa	Nu= OMe	21.6%	7.7%
c NuX= MeLi	Nu= Me	66%	
d NuX= BuLi	Nu= Bu	43%	
e NuX=Me$_3$SiCH$_2$Li	Nu=CH$_2$SiMe$_3$	40%	

Similarly, when a 30% solution of MeONa in methanol (66 μL) was added to a solution of complex **3** (0.36 mmol) in THF (15 mL) kept at 0°C, a color change from red to yellow was observed. Heating to room temperature restored the dark-red color. After stirring for a further 12 h, extraction followed by silica gel chromatography gave two new complexes in, respec-

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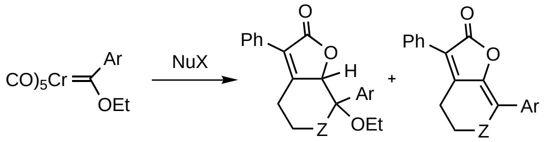
tively, 21.6 and 7.7%, which, according to their NMR data agreed with structures **4b** and **5b**. A similar behavior was observed in the case of methyllithium. In this latter case, two isomeric lactones **4** were obtained (66%, *de*, 20%). The structure of the major isomer, mp 132°C, was secured by an X-ray analysis which confirms the position of the methyl group C-8, *trans* to the hydrogen at the ring junction, and thus its fixation on the former carbene–carbon. Butyllithium and (trimethylsilylmethyl) lithium reacted similarly, leading to the expected butenolides **4d** (40%, *de* = 90) and **4e** (40%, *de* = 100).

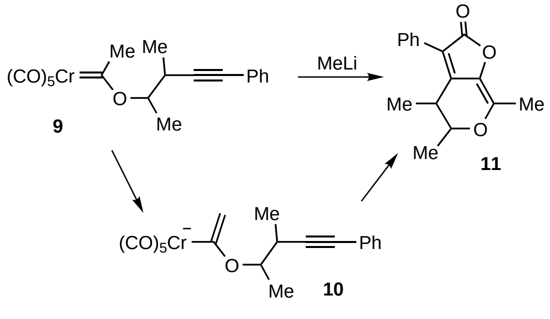
Conversely, elaborate butenolides could also be obtained starting from **6**, the most simple carbene complex of chromium: under the same conditions as above, complex **6** reacted indeed with sodium 1-phenyl-1-butyn-5-oate to afford a mixture of the expected butenolide **7f** and of **8f** the butenolide resulting from the elimination of ethanol. In the case of 1-phenylpent-1-yn-5-yllithium, however, only the butenolide **8g** was observed.



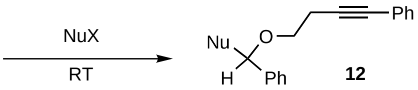
6 **7** **8**

f NuX= $NaO(CH_2)_2C{\equiv}CPh$ Z= O 18% 6.5%
g NuX= $Li(CH_2)_3C{\equiv}CPh$ Z=CH_2 17%

Even complex **9** led to a butenolide, yet in a low 10% yield, upon its interaction with MeLi: as expected, hydrogen abstraction in α to the carbene–carbon took place leading to a vinyl chromate **10** which underwent the same transformations as the previous chromates to give **11**. Up to now, no attempts have been made to improve the yields of these reactions.



We finally attempted to use as nucleophiles tetraethylammonium cyanide and sodium thiophenate, both of which are known to interact with carbene complexes of the Fischer-type.[9,10] Although the deep-red color of the starting complex **3** disappeared rapidly, upon addition of the nucleophiles, even at low temperature, the expected corresponding butenolides were not obtained: instead, compounds **12** originating from the successive addition of the nucleophiles to the carbene–carbon, and the cleavage of the carbon–chromium bond, were observed.



12

h NuX= Et_4NCN Nu= CN 23%
i NuX= NaSPh Nu= SPh 46%

It is thus clear that in all the cases addition of the nucleophiles to the electrophilic carbene–carbon took place but that the course of the transformation of the first addition product is strongly dependent on the nature of the nucleophile. One of the prerequisites for the transformation of complexes **3** into butenolides **4** is the insertion of a CO group and the coordination of the triple bond to the metal. Previous observations by Fischer,[11] Casey,[12] and Cooper[13] indicated that both the insertion and the labilization of coordinated CO groups in $[(CO)_5MR]^-$ are linked to the build-up of negative charge on the metal.[14,15] This is induced in the present case by the entering negatively charged nucleophiles.

The use of dihydropyridines, e.g. dihydronicotine, is especially interesting for the preparation of butenolides,[16,17] in an enantioselective way. However, the discovery that nucleophiles different from hydrides can trigger the same transformation broadens even more the scope of application of these cascade insertions.

Supplementary material

Spectral data for **4b**, **4c**, and **5b** and crystal data for **4c** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 184028. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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