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Conjugate addition of alcohols to alkynylalkoxycarbene metal (Cr, W) complexes

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Abstract

Reaction of alkynylalkoxycarbene metal (Cr, W) complexes with alcohols gives the corresponding (2-alkoxyalkenyl)alkoxycarbene metal complexes in moderate to good yields. A high degree of stereoselectivity is found with linear aliphatic alcohols.

Recently we reported the reaction of alkynylalkoxycarbene metal (Cr, W) complexes with ethyl diethoxyacrylate and tetraalkoxyethylene to give, after metal removal, 6-ethoxy-2-pyrones [1] and 3,4-dioxocyclobutenecarboxylate derivatives [2], respectively. In continuation of this research, we describe here the nucleophilic addition of alcohols to the acetylenic bond of the above carbene complexes to give the corresponding (2-alkoxyalkenyl)alkoxycarbene complexes, which are useful synthetic intermediates in benzannulation reactions [3] and cyclopropanation of external olefins by the carbene moiety, usually to be followed by a further ring expansion [4].

Our straightforward synthesis represents a remarkable improvement over the previously described procedure, which requires an aldol condensation at the α-carbene carbon atom, since the corresponding vinyllithium derivatives used in the conventional Fischer method are unstable.

A precedent for the reaction can be found in the reported reactivity of alkynylalkoxycarbene metal complexes with amines in which addition to the triple bond is preferred to aminolysis at the carbene center at temperatures above $-20\,^\circ$C. [5] We expected that such behaviour might also be displayed by alcohols, and this proved to be the case.

As shown in Table 1, moderate to high yields of (2-alkoxyalkenyl)alkoxycarbene metal complexes were obtained when the corresponding alkynylcarbene complexes were allowed to react with a 5–10 molar excess of various alcohols at room temperature in dry THF for 6–96 h (method A) (Scheme 1).

Table 1

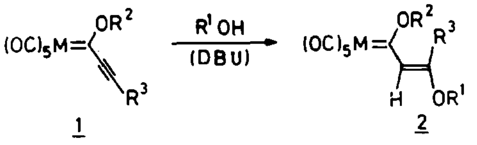
Yields and E/Z ratios of various (*Z*-alkoxyalkenyl)alkoxycarbene metal complexes [a]

	R^1	R^2	R^3	M	Method	Time (h)	Reaction yield (%)	*E*/*Z* [b] ratio
2a	Me	Et	Ph	Cr	A	24	62	9
2b	Me	Me	Ph	W	A	24	70	9.4
2c	^{i}Pr	Et	Ph	W	B	48	26	4.1
2d	Allyl	Et	Ph	W	B	96	24	9.5
2e	Ph	Et	Ph	Cr	B	5	68	3.4
2f	Benzyl	Et	Ph	Cr	B	5	45	6.1
2g	Me	Et	Pr	Cr	A	9	72	*E* only
2h	Me [c]	Me	Me_3Si	Cr	A	11	68	a single stereoisomer

[a] In a typical experiment (method A) a solution of **1** (1 equiv.) in dry THF containing an excess (5–10 equiv.) of the alcohol or phenol was stirred at room temperature until reaction was complete (TLC monitoring). The solvent was evaporated *in vacuo* and the residue purified by flash chromatography (1/20 ethyl acetate/hexane). The yellow to orange coloured complexes crystallised after concentration of the solutions. In method B 0.04 equiv. of DBU was added to reaction mixture.
Representative data for **2a** are as follows: IR ($CHCl_3$) 2062sh, 1973w, 1935s cm^{-1}. ^1H NMR ($CDCl_3$) (*E*): δ 7.5–7.1 m (5H), 6.95 s (1H), 4.40 q (*J* 8 Hz) (2H), 3.95 s (3H), 0.82 t (*J* 8 Hz) (3H); (*Z*): 7.5–7.1 m (5H), 6.85 s (1H), 4.87 q (*J* 8 Hz) (2H), 4.07 s (3H), 1.63 t (*J* 8 Hz) (3H).

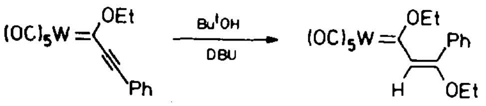
[b] E/Z ratios were determined from ^1H NMR integration data. Those for **2b** were identical to those previously reported [6]. For **2e**, data were assigned to the two stereoisomers on the basis of the reported ^1H NMR data for the corresponding uncomplexed isomers [7].

[c] With **2h** a single stereoisomer was obtained. Since during the experiment there was complete desilylation, with potential concurrent isomerization, and the value of the coupling constant for the final product (*J* 12 Hz) lies in between the values for similar *E* and *Z* complexes [3b] its stereochemistry could not be assigned.



Scheme 1

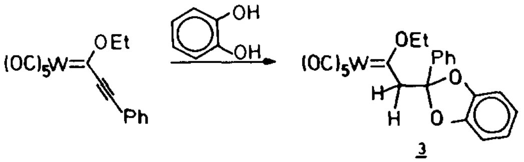
As can be seen from Table 1 all the alcohols and phenols add to various extents, to the triple bond. While methanol and ethanol react quite fast (6 h with the alcohol used as the solvent) phenols and bulky aliphatic alcohols require far longer times. In these cases addition of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) greatly shortened the reaction time (method B). However, even under these conditions t-butyl alcohol did not bring about any addition reaction, and the only well-defined isolable product in this case was that resulting from addition of a carbene-bonded ethoxy moiety to the triple bond (Scheme 2). Alongside formation



Scheme 2

of this product (≈ 20%), the base-promoted extensive decomposition of the starting complex gives very unstable ionic complexes and $Cr(CO)_6$.

In all cases a high stereoselectivity leading to predominant or exclusive formation of the *E* isomer was found. Less hindered alcohols (cf. Table 1, **2a**,**b**,**d**,**g**) gave higher *E*/*Z* ratios than aromatic and secondary aliphatic alcohols (cf. Table **1**, **2c**,**e**,**f**). Furthermore, in all cases, the regioselectivity was complete, as expected for a Michael-type reaction.



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Scheme 3

Catechol leads to a double addition at the same acetylenic carbon atom (Scheme 3). Although similar ketal complexes have been postulated as intermediates in the Lewis acid-catalysed aldol condensation of orthoesters with metal carbene complex carbanions they have never so far been isolated, since under the necessary reaction conditions elimination of alcohol gives rise to the alkenylalkoxycarbene complexes [6]. As reported for amines, alcohol addition to the triple bond deactivates the carbenic center towards nucleophilic substitution, and so a second alcohol addition to the double bond is preferred to competing alcoholysis at the carbenic center.

The present results are in agreement with an unusually high dipolarity of the triple bond of alkynylalkoxycarbene metal complexes, which is for the occurrence of additions as well as for the ease of polar cycloadditions [1,2,8,9].

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