Reaction of Ethyl Diethoxyacrylate with Alkynylalkoxycarbene Metal (Cr,W) Complexes: New Procedure for Preparation of 6-Ethoxy-2*H*-pyrones

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The reaction of ethyl diethoxyacrylate with alkynylalkoxycarbene metal complexes affords 6-ethoxy-2*H*-pyranylidene metal complexes (M = Cr, W) through a plausible [2 + 2] cycloaddition, followed by conrotatory cyclobutene opening and final cyclization at the carbene centre; mild dimethylsulphoxide (DMSO) oxidation of the resulting complex gives the free ligand quantitatively.

Cycloaddition reactions involving transition metal carbene complexes are being intensively investigated[1,2] owing to their potential application in the synthesis of heterocyclic derivatives.[3—5] Our interest with the chemistry of highly polarized alkynes[6] led us to explore the reactivity of alkynylalkoxycarbene complexes with activated alkenes and alkynes. Recently, this type of reaction has been described as giving cyclobutene complexes through [2 + 2] cycloadditions.[7] Here we report a dramatic change in the reaction course caused by the use of ethyl diethoxyacrylate (**2**).

When complex (**1**) (R^2 = Ph, M = Cr) was reacted with a 3 M excess of (**2**) at room temperature for 3 h, a red compound (**4**) (30—45%) was isolated together with minor amounts of a yellow complex (**3**) (14%). Complex (**3**) was formed almost exclusively when the reaction was performed with equimolar amounts of (**2**) and shorter reaction times. Both complexes (**3**) and (**4**) could be easily separated by flash chromatography using a 1 : 9 ethyl acetate:hexane eluent mixture. These results would suggest that complex (**3**) was originally formed in the reaction and subsequently transformed into complex (**4**). This was confirmed when pure (**3**) was completely converted into (**4**) on standing for one day at room temperature.

Structures (**3**) and (**4**) were assigned from the corresponding spectral and microanalytical data† related to other reported complexes.[7,8,9] Similar results were obtained with other carbene complexes as shown in Scheme 1. The structure of (**4**) was confirmed by single crystal *X*-ray diffractometry (Figure 1).‡

Some features of the present reaction are remarkable when compared to the previous work in this area reported by Wulff *et al.* Firstly, the expected intermediate resulting from a [2 + 2] cycloaddition was not detected by us, indicating the occurrence of a fast conrotatory ring opening to (**3**) due to the high dipolarity brought about by the alkene§ addition. Further transformation of (**3**) into (**4**) requires the formal transfer of one carbonyl group and one proton from the diethoxy methylene moiety to the metal and to the C(3) 2*H*-pyranylidene ring, respectively, with concomitant cyclization. Similar processes involving de-ethoxylation and carbonylation have been invoked in the formation of pyrone rings mediated by iron carbene complexes.[10]

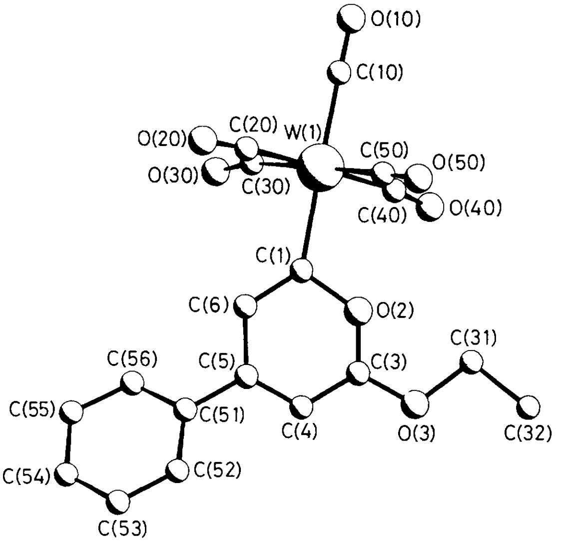
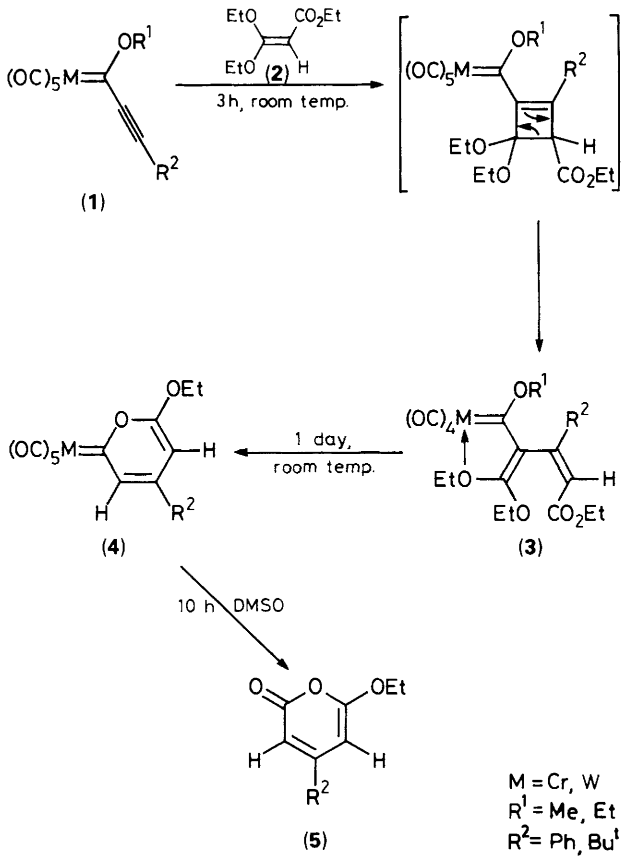


Figure 1. A view of the structure of (**4**).



Scheme 1. Preparation of 6-alkoxy-2*H*-pyranylidene metal complexes through sequential [2 + 2] cycloaddition, conrotatory cyclobutene opening and final carbene-*O*-closure.

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† For (**3**); M = Cr, R^2 = Ph, R^1 = Et. I.r. ($CHCl_3$) cm^{-1}, 2015, 1910, 1835; ^1H n.m.r. ($CDCl_3$): δ, 7.37 (5H, s), 6.45 (1H, s), 4.7 (2Hq, *J* 7.2 Hz), 4.65 (2Hq, *J* 7.1 Hz), 4.2 (4Hq, *J* 7.3 Hz), 1.52 (3Ht, *J* 7.1 Hz), 1.28 (3Ht, *J* 7.1 Hz), 1.2 (6Ht, *J* 7.3 Hz); ^{13}C n.m.r. $(CD_3)_2CO$: δ 316.2, 231.8, 228.9, 215.3, 213.9, 173.25, 165.9, 146.5, 140.3, 130.3, 129.5, 127.7, 120.9, 120.15, 76.6, 76.17, 72.5, 60.6, 14.9, 14.7, 14.2, 14.1; fast atom bombardment (f.a.b.) m.s.: M^+ 510, other important peaks 398 (M^+-4CO). For (**4**); M = Cr, R^2 = Ph, R^1 = Et. I.r. ($CHCl_3$) cm^{-1}, 2045, 1925; ^1H n.m.r. ($CDCl_3$): δ 7.95 (1Hd, *J* 1.5 Hz), 7.83 (5H, m), 6.77 (1Hd, *J* 1.5 Hz), 4.8 (2Hq, *J* 7 Hz), 1.55 (3Ht, *J* 7 Hz); ^{13}C n.m.r. $(CD_3)_2CO$: δ 260.1, 224.4, 219.12, 175.8, 153.2, 135.8, 132.8, 131.6, 130.3, 128.9, 96.0, 68.3, 14.6; electron impact (e.i.) m.s.: M^+ 392, other important peaks 252 (M^+-5CO). For (**5**); R^2 = Ph. I.r. ($CHCl_3$) cm^{-1}, 1725, 1610; ^1H n.m.r. ($CDCl_3$): δ 7.55 (2H, m), 7.2 (3H, m), 6.45 (1H, m), 4.10 (2Hq, *J* 7 Hz), 3.7 (1H, s), 1.2 (3Ht, *J* 7 Hz); u.v. (MeOH) nm, λ_{max} 390. For (**4**); M = W, R^2 = Ph, R^1 = Et (yield, 40%); i.r. (C_6H_{14}) cm^{-1}, 2078, 1944; ^1H n.m.r. ($CDCl_3$): δ 7.95 (1Hd, *J* 2.0 Hz), 7.55 (5H, m), 6.42 (1Hd, *J* 2.0 Hz), 4.75 (2Hq, *J* 8.0 Hz), 1.57 (3Ht, *J* 8.0 Hz); ^{13}C n.m.r. $(CD_3)_2CO$: δ 273.7, 239.7, 199.0, 173.3, 154.0, 135.1, 132.9 131.9, 129.6, 127.7, 95.8, 67.3, 14.5. f.a.b. m.s.: M^+ 524, other important peaks, 384 (M^+ $-5CO$). For (**4**); M = W, R^1 = Bu, R^2 = Et (yield, 31%). I.r. ($CHCl_3$) cm^{-1}, 2075, 1940; ^1H n.m.r. ($CDCl_3$): δ 7.65 (1Hd, *J* 2.0 Hz), 6.25 (1Hd, *J* 2.0 Hz), 4.70 (2Hq, *J* 8.0 Hz), 1.55 (3Ht, *J* 8.0 Hz), 1.27 (9H, s); ^{13}C n.m.r. [$(CD_3)_2CO$]: δ 199.9, 174.8, 171.3, 133.1, 97.7, 68.3, 36.6, 29.6, 14.6. The assignment for the carbene and *trans*-carbonyl atoms could not be made.

‡ *Crystal data*: $C_{18}H_{12}O_7W$; $M = 523.9$, monoclinic, $a = 30.81(2)$, $b = 7.445(6)$, $c = 17.28(2)$ Å, $\beta = 112.76(5)°$, $U = 3656$ Å^3, $Z = 8$, $D_c = 1.90$ g cm^{-3}, Mo-K_α radiation (graphite monochromator), $\lambda = 0.71069$ Å, $\mu = 65$ cm^{-1}, space group $C2/c$, $F(000) = 2000$, $T = 215$ K. A single crystal was mounted at the end of a glass fibre and centred in the Enraf-Nonius CAD4 diffractometer geometry. The crystal was kept in a continuous flux of nitrogen gas stabilized at 215 ± 2 K. Cell parameters were determined by least-squares fitting of 25 high angle reflections. Lorentz and polarization effects were corrected, but not for absorption. The structure was solved by application of automated Patterson search (ROTSEARCH[12]). Once positioned the tungsten atom, a weighted Fourier synthesis shows the remaining non H-atoms. Refinement was carried out using full-matrix least-squares methods (SHELX-76[13]) with anisotropic thermal parameters for non H-atoms converging to $R = 0.089$ and $R_w = 0.093$. The final difference Fourier synthesis showed several hydrogen atoms, which were not included in the refinement, and residual peaks around W-atom (at about 1 Å). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ 1,1-Diethoxyethene is reported to give the corresponding cyclobutene complex which does not open.[7] Furthermore, from our experience, tetramethoxyethene gives high yield of a very stable cycloadduct (80%). Therefore, from these preliminary results one can conclude that in the absence of electron withdrawing substituents the more alkoxy groups are on the starting alkene the higher is the stability of the cycloadduct complex.

The organic ligand was quantitatively released from (**4**) by dimethyl sulphoxide (DMSO) oxidation at room temperature to yield the corresponding 6-ethoxy-2*H*-pyrone (**5**). These compounds are promising intermediates in the synthesis of bioactive compounds with therapeutic application.[11]

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