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ScienceDirect
Mendeleev Commun., 2008, **18**, 205–206
Mendeleev Communications

Oxidative transformation of the dicobalthexacarbonyl complexes of γ-hydroxyalkynes

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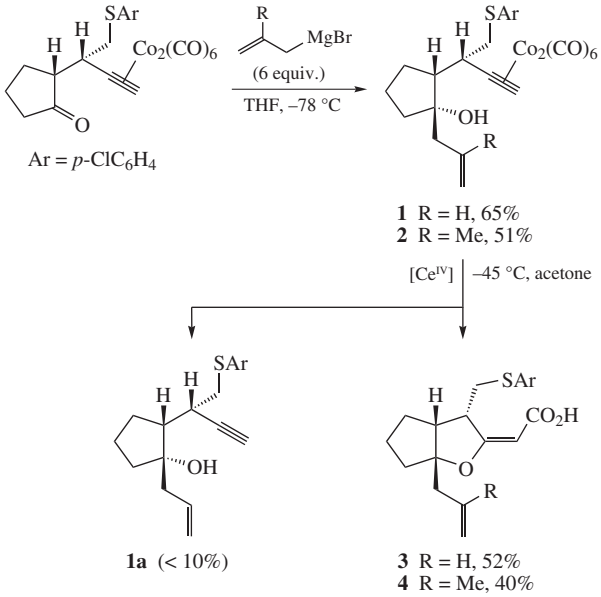
DOI: 10.1016/j.mencom.2008.07.012

The title compounds were found to undergo an oxidative cyclization–hydrocarbonylation reaction under the standard conditions of decomplexation by treatment with cerium(IV) ammonium nitrate.

To study the synthesis of 1,7-enyne derivatives, dicobalthexacarbonyl (DCHC) complexes **1** and **2**, which are potentially useful substrates for the intramolecular Pauson–Khand cyclization, were prepared following the procedure outlined previously.[1] Due to the lability of the adducts, their structure is most often ascertained from data for the decomplexed products easily prepared upon the treatment of the DCHC complexes with oxidants such as cerium(IV) ammonium nitrate.[2] However, an attempt to apply this routine procedure to the decomplexation of **1** and **2** led to surprising results. According to the TLC data, expected product **1a** was formed only in trace amounts (< 10%, TLC data†). Instead, the formation of a substantially more polar compound was observed. This compound was isolated in a satisfactory yield by TLC and identified as (*E*)-bicyclic β-alkoxyacrylic acid derivative **3**, as was established by NMR spectroscopy‡ and X-ray analysis.§ Product **4** was formed upon an oxidative treatment of DCHC complex **2** (Scheme 1).‡



Scheme 1

† The structure of the decomplexed material **1a** was established by comparison with the authentic sample prepared by the independent route, which involved the sequence of steps inversed to those presented in Scheme 1, namely: (i) decomplexation of the starting cyclopentanone derivative followed by (ii) allylation with allylmagnesium bromide.

The observed transformation is very similar to the Pd^{II}-catalysed oxidative cyclization–methoxycarbonylation of cyclic and acyclic

‡ The preparation of DCHC complexes **1** and **2** was carried out by analogy with the procedure described previously.[1]

(E)-2-{(3S,6aR*)-6a-Allyl-3-(4-chlorophenylthiomethyl)hexahydrocyclopenta[b]furan-2-ylidene}acetic acid* **3**. A purple solution of DCHC complex **1** (383 mg, 0.62 mmol) in acetone (1 ml) was added to a solution of $(NH_4)_2Ce(NO_3)_6$ in acetone (15 ml) at –45 °C. Immediate decoloration was observed and TLC data revealed the complete disappearance of the starting material. The reaction mixture was quenched with water and extracted by diethyl ether. Ether removal followed by column chromatography on silica gel furnished adduct **3** as colourless crystals; yield 122 mg (52%); R_f 0.26 (EtOAc–hexane, 1:5). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.58–2.06 (m, 6H), 2.37 (d, 2H, *J* 7.2 Hz), 2.72 (m, 2H), 3.65 (m, 1H), 4.20 (dd, 1H, J_1 3.3 Hz, J_2 13.1 Hz), 5.08 (d, 1H, *J* 3.3 Hz), 5.14 (s, 1H), 5.38 (s, 1H), 5.72 (m, 1H), 7.25 and 7.40 (2d, 2×2H, *J* 8.5 Hz). Found (%): C, 62.82; H, 5.56. Calc. for $C_{19}H_{21}ClO_3S$ (%): C, 62.54; H, 5.80.

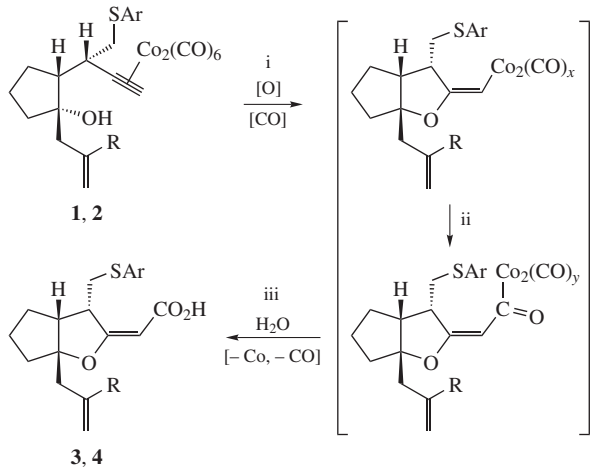
Compound **4** was prepared using the same procedure and was isolated in 40% yield as pale yellow oil, R_f 0.26 (EtOAc–hexane, 1:5). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.69 (m, 2H), 1.76 (s, 3H), 1.85 (m, 3H), 2.01 (m, 1H), 2.26 and 2.33 (2d, 2×1H, *J* 14 Hz), 2.72 (m, 2H), 3.66 (m, 1H), 4.24 (dd, 1H, J_1 2.8 Hz, J_2 13.3 Hz), 4.74 (s, 1H), 4.87 (s, 1H) 5.38 (s, 1H), 5.36 (s, 1H), 7.26 and 7.40 (2d, 2×2H, *J* 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 24.0, 25.2, 28.1, 29.7, 32.3, 37.2, 45.6, 46.2, 48.6, 91.1, 101.0, 115.3, 128.8, 129.1, 131.3, 132.3, 134.0, 141.5, 173.2, 179.8. Found (%): C, 63.65; H, 6.32. Calc. for $C_{20}H_{23}ClO_3S$ (%): C, 63.40; H, 6.12.

§ *X-ray analysis*. Crystals of **3** ($C_{19}H_{21}ClO_3S$, M = 364.87) are triclinic, space group $P\bar{1}$, at 100 K: a = 7.4641(4), b = 9.3187(5), c = 13.9722(8) Å, α = 87.090(1)°, β = 83.897(1)°, γ = 67.860(1)°, V = 895.03(9) Å^3, Z = 2, (Z' = 1), d_{calc} = 1.354 g cm^{-3}, μ(MoKα) = 3.44 cm^{-1}, F(000) = 384. Intensities of 10742 reflections were measured with a Bruker SMART APEX II CD diffractometer [λ(MoKα) = 0.71073 Å, ω-scans, $2\theta < 59°$] and 4736 independent reflections (R_{int} = 0.0277) were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The position of hydrogen atoms were located from the Fourier density synthesis and refined in the isotropic approximation in riding model. Refinement converged to wR_2 = 0.0940 and GOF = 1.067 for all independent reflections [R_1 = 0.0333 was calculated against F for 3792 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0. X-ray diffraction investigations has been performed by K. A. Lyssenko (X-ray Structural Centre, A. N. Nesmeyanov Institute of Organoelement Compounds, RAS).

CCDC 691811 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2008.

4-yn-1-ols in the presence of an oxidant (air or *p*-benzoquinone) in methanol solution under a carbon monoxide atmosphere, which is elaborated as a general route toward the formation of (*E*)-cyclic β-alkoxyacrylate derivatives.[3(*a*)–(*c*)]

In accordance with the generally accepted mechanism of Pd-induced alkyne carbonylation reactions,[3(*a*)] the formation of bicyclic products **3** or **4** upon the oxidative treatment of DCHC complexes **2** or **3** could be schematically described as a sequence of the following steps (Scheme 2): (i) the oxidative removal of a carbonyl monoxide ligand concomitant with the intramolecular nucleophilic addition at the complexed triple bond, (ii) carbonyl insertion at the cobalt–carbon bond with the formation of an acylcobalt intermediate, and (iii) the hydrolytic cleavage of the cobalt–acyl bond.



Scheme 2

Note that the β-alkoxyacrylate fragment is known to be present in biologically active natural products.[3(*b*),(*d*)] Hence, the exploration of alternative routes leading to the formation of such systems seems to be well-warranted.

This work was supported by the Russian Foundation for Basic Research (project no. 06-03-33016).

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Received: 17th December 2007; Com. 07/3062