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LETTERS

An Access to Homopropargylic Ketones from Propargylic Alcohols

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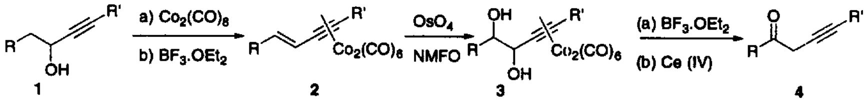
Abstract: Lewis acid treatment of $Co_2(CO)_6$-α,β-acetylenic diols, directly available by osmium tetroxide-catalyzed dihydroxylation from the corresponding $Co_2(CO)_6$-enyne complexes, afforded homopropargylic ketones in good yields. The method is compatible with many kinds of protecting groups and functionalities providing a method for the synthesis of the unstable title compounds. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *Alkynes; Ketones; Cobalt and compounds; Enynes.*

During our current synthetic studies directed to the use of dicobalt hexacarbonyl acetylenic complexes in organic synthesis[1] we became interested in the use of homopropargylic carbonyl derivatives as alkynes with peculiar structural features. However, direct oxidation from the corresponding homopropargylic alcohols is a reaction with very limited use[2] and most oxidants are ineffective.[3] Satisfactory results are only obtained in a few cases,[4] the use of alternative methods being necessary.[5]

In this communication we present a method to obtain the title functional groups in good yields from the corresponding propargylic alcohols in a straightforward manner (Scheme 1).



Scheme 1

Our method is extensively based on the use of the chemistry of $Co_2(CO)_6$-acetylenic complexes. While maintaining the acetylenic moiety complexed, we firstly eliminated the hydroxyl group to the corresponding *E*-enyne,[6] secondly performed an osmium-catalyzed dihydroxylation and thirdly Lewis acid treatment of the resulting diol, yielded, by elimination, the corresponding complexed homopropargylic ketones cleanly.

Representative examples are outlined in Table I. In all cases the propargylic alcohols were obtained by direct addition of the lithium acetylide to suitable carbonyl derivatives. Lewis acid treatment ($BF_3.OEt_2$, CH_2Cl_2, rt) provided satisfactorily the *E*-enyne derivative except in entry 6, corresponding to the situation in which an additional propargylic oxygen was present. When a THP-ether was the protecting group used (Entry 4) the unprotected enynol was the isolated product. Special attention should be paid to the fact that direct *cis*-dihydroxylation of the alkene was possible over the $Co_2(CO)_6$-enyne (OsO_4, NMO, THF:H_2O, rt). Although during the reaction some uncomplexed diol was produced (20-30%) this product was recovered by new formation of the cobalt complex [$Co_2(CO)_8$, CH_2Cl_2, rt]. Finally, the Lewis acid treatment ($BF_3.OEt_2$, CH_2Cl_2, rt) of the complexed diol provided cleanly the $Co_2(CO)_6$-homopropargylic ketones that were satisfactorily uncomplexed in the standard manner ($Ce(NO_3)_6(NH_4)_2$, acetone, rt.). The only exception was observed in entry 4 when an additional free hydroxy group was present, in which case a complex mixture was produced.

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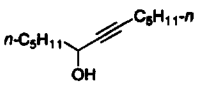
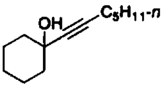
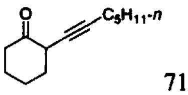
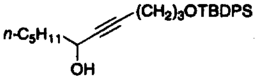
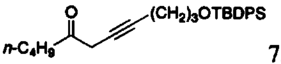
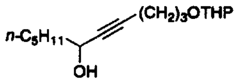
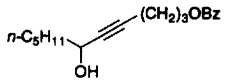
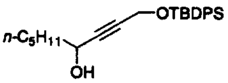
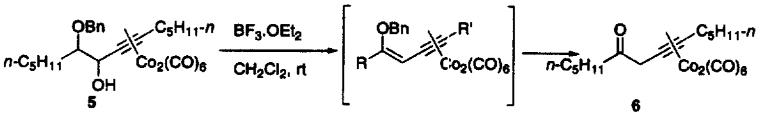
Table 1

Entry	1	2 (Yield)	3 (Yield)[a]	4 (Yield)
1.		85%	55% (76%)	 77%
2.		81%	50% (80%)	 71%
3.		82%	53% (75%)	 75%
4.		78% [b]	46% [c]	--
5.		79%	55% (73%)	 81%
6.		21%	--	--

[a]Yield obtained directly by the OsO_4 dihydroxylation (in brackets the overall yield recycling the uncomplexed diol). [b]The product was isolated as a free enynol by cleavage of the THP-ether. c) Isolated as a triol.

The method also works when the β-hydroxy group is protected as benzyl ether. Thus, Lewis acid treatment of **5** also provided cleanly the corresponding complexed ketone **6** in 82% yield.



In summary we have described a new, simple and versatile method to gain access to a rather unstable functionality scarcely described in the literature.

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References and notes

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7. Satisfactory spectral data and combustion analysis were obtained for all new compounds.