Tetrahedron xxx (2016) 1–8

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Metal-stabilized carbocations derived from monoterpenes: dicobalt hexacarbonyl complexes of alkynyl-verbenols

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ARTICLE INFO

Article history:
Received 20 February 2016
Received in revised form 2 May 2016
Accepted 16 May 2016
Available online xxx

Keywords:
Monoterpenes
Alkynes
X-ray crystallography
^{31}P NMR spectroscopy
Cobalt-stabilized cations
Nuclear overhauser effect

ABSTRACT

Nucleophilic attack by alkynyl anions on the verbenone skeleton occurs on the face opposite to that occupied by the *gem*-dimethyl group. The resulting alkynols react with dicobalt octacarbonyl to form tetrahedral (μ^2-alkyne)$Co_2(CO)_6$ clusters in which the tricarbonylcobalt moieties are diastereotopic, and treatment with dppm tags each of these vertices with a ^{31}P NMR label. Protonation yields a single cobalt-stabilized carbocation, **13a**, in which the cobalt is situated on the side bearing the methylene bridge, thus avoiding the *gem*-dimethyl group, and pulls the capping phenyl substituent proximate to the hydrogen atom at C(3). All new molecules were characterized by NMR spectroscopy and by X-ray crystallography for *syn*-trimethylsilylethynylverbenol, **6**, *syn*-ethynyl-verbenol, **7**, and for the (2-phenylethynyl-4-methylene-6,6-dimethyl-(1*S*,5*S*)-bicyclo[3.1.1]hept-2-ene)$Co_2(CO)_4$(dppm) cluster, **12**. The 2-ethynyl-4-methylene-6,6-dimethyl-bicyclo[3.1.1]hept-2-ene ligand, **15**, was also prepared and characterized for the first time.

1. Introduction

The ability of alkyne-dicobalt clusters to stabilize an α-cationic site is the basis of the Nicholas reaction[1–5]—a synthetically valuable procedure used, for example, in the preparation of enediynes,[6] (+)-begamide E,[7] blastinomycine,[8] cyclocolorenone,[9] tetrapyrroles,[10] insect pheromones,[11] vitamin A derivatives,[12] carotenes,[13] pyrones,[14] benzofurans,[15] and benzopyrans.[15] Moreover, such stabilization by a metal allows the convenient generation and isolation of otherwise inaccessible species such as the bornyl[16–18] and fenchyl[19] cations, anti-aromatic indenyl or fluorenyl cations,[20] and cations bearing a strongly electron-withdrawing substituent such as trifluoromethyl.[21] Interestingly, in several recent reports it has been shown that protonation of the precursor alcohols in diethyl ether or tetrahydrofuran leads to products derived from radicals rather than cations.[22,23]

This stabilization can be attributed to partial delocalization of the charge onto a cobalt atom through overlap of a filled metal d orbital with the vacant p orbital on the electron-deficient α-carbon, and is facilitated by a structural perturbation such that the carbocationic centre leans toward a metal vertex,[17,24–28] as illustrated in Scheme 1.

Alkynyl cluster complexes of natural products have been used not only as precursors to chiral clusters[29,30] with the long-term goal of developing catalysts for asymmetric synthesis, but also in the burgeoning field of bio-organometallics[31] where steroidal derivatives in particular have been extensively investigated.[32–34] In their pioneering studies[35] Cadiot and Chodkiewicz reported the direction of attack by alkynyl anions on a range of alkyl-substituted five- and six-membered ring systems. However, these cannot be predicted simply from Cram's rule;[36] the torsional strain transition model proposed by Felkin,[37,38] and subsequently supported by Ahn and Eisenstein,[39,40] has been used to rationalize the experimentally observed stereoselectivities of nucleophilic additions to cyclic ketones. In this model, it is suggested that the direction of nucleophilic attack is controlled not only by steric effects but also by the torsional strain imposed on the system in the transition state. In the case of cyclohexanones, this involves a distorted chair conformation whereby the axial transition state is perfectly staggered, whereas equatorial attack proceeds through a transition state that affords partial eclipsing.

Focussing now on monoterpenoid systems (Scheme 2), we note that the reaction of alkynyl-lithiums with (-)-menthone yields a mixture of axial- and equatorial-alkynols, **1** and **2**, respectively.[41–44] [Strictly speaking, *axial* and *equatorial* designations should refer to the position of the hydroxyl group since it has priority over the alkynyl substituent in the Cahn-Ingold-Prelog

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http://dx.doi.org/10.1016/j.tet.2016.05.044
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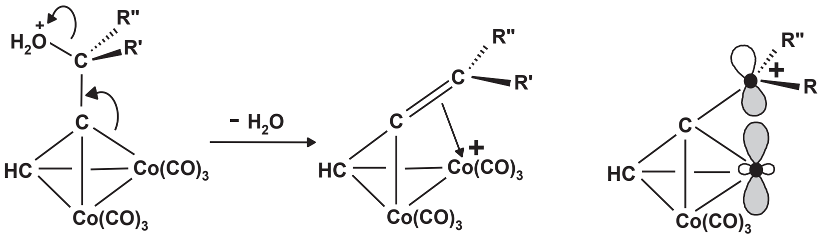
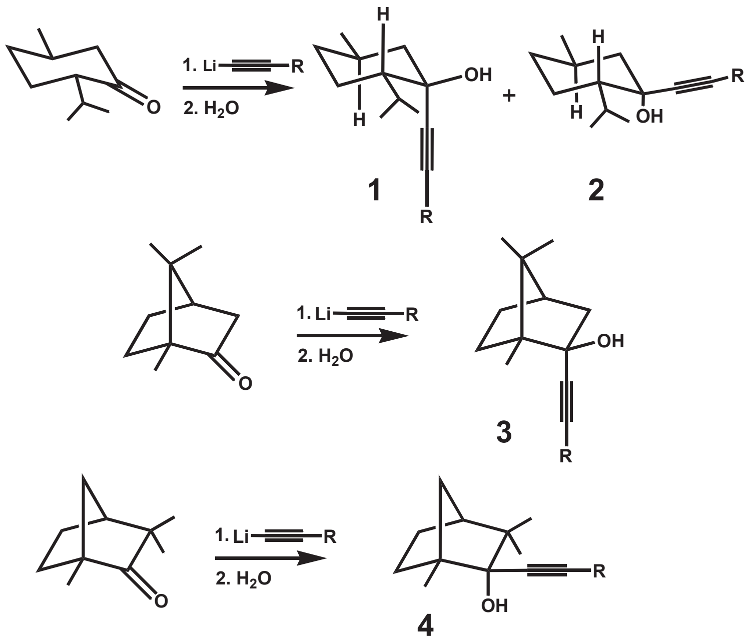


Scheme 1. Generation of cobalt-stabilized propargyl cations.

rules.] In the original study, the major isomers were assigned on the basis of NMR chemical shifts of their derived allenyl phosphine oxides as possessing an equatorial alkynyl substituent,[45] and in more recent work X-ray crystallography unequivocally established that the major isomer contains an equatorial alkynyl substituent.[46] The corresponding reactions of alkyne anions with camphor and fenchone were more straightforward. In the former case, nucleophilic attack led only to the *endo* alkynyl-borneol, **3**,[16–18] whereas in the latter system the sole product was the *exo* alkynyl-fenchol, **4**.[19] In each case the direction of approach is apparently controlled by the presence of the bulky *gem*-dimethyl functionality.



Scheme 2. Products of alkynyl-lithium attack on menthone, camphor and fenchone.

Verbenone, a chiral monoterpene with a pinene skeleton, is found in a variety of plants, has a pleasant odour and is widely used in perfumery, aromatherapy, herbal teas, spices and herbal remedies. The ketone itself plays an important role in the control of the Southern Bark Beetle, and *cis* and *trans* verbenols are pheromones for *Ips paraconfusus*, another species of bark beetle.[47] (1*S*)-(-)-Verbenone and (*S*)-*cis*-verbenol are both commercially available. We here report the reaction of (1*S*)-(-)-verbenone with alkynyl anions of the resultant alkynols, their reactions with $Co_2(CO)_8$ and $(C_5H_5)_2Mo_2(CO)_6$, and the structure of a cobalt-stabilized carbocation.

2. Results and discussion

Treatment of (1*S*)-(-)-verbenone with phenylethynyl- or trimethylsilylethynyl-lithium yields the corresponding 2-alkynyl-4,6,6-trimethyl-(1*S*,2*S*,5*S*)-bicyclo[3.1.1]hept-3-en-2-ols, **5** and **6**, respectively (Scheme 3). The structures were readily determined from their ^{1}H and ^{13}C NMR spectra, in particular the NOE data. In each case, irradiation of the hydroxyl proton revealed clear enhancement of one of the *gem*-dimethyl resonances, not only establishing the *syn* arrangement of the hydroxyl with respect to the CMe_2 unit, but also clearly identifying C(8), the *endo* methyl attached to C(6), as previously noted in *cis*-verbenol.[48,49] The protons of the bridging methylene group at C(7) exhibit mutual 9.5 Hz geminal coupling, but only one of them shows clear vicinal coupling to H(1) and H(5). This must be H(7-*exo*) since molecular models indicate that its methylene partner should make dihedral angles H(1)-C(1)-C(7)-H(7-*endo*) and H(5)-C(5)-C(7)-H(7-*endo*) of ~90°, thus giving rise to very small $^3J_{H-H}$ values. We note also the $^4J_{H-H}$ W-coupling of ~6 Hz between H(1) and H(5), a common feature of rigid cyclobutane systems.[48]

These structural assignments were corroborated X-ray crystallographically as shown for *syn*-2-trimethylsilylethynyl-verbenol, **6**

Please cite this article in press as: Moore, A.; et al., Tetrahedron (2016), http://dx.doi.org/10.1016/j.tet.2016.05.044