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Preliminary communication

Synthesis and reactions of η^2-(2-formylphenyl)tetracarbonylmanganese(I) complexes; cyclopentaannulation of a diterpenoid

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Abstract

Reaction of tetracarbonylmanganese(I) complexes derived from a diterpenoid aryl aldehyde or aryl methyl ketone with acetylene or ethylene leads to cyclopentaannulation to give 1*H*-inden-1-ols or 1*H*-indan-1-ols, respectively.

In earlier papers we reported the use of organotransition metal complexes as key intermediates in the elaboration of ring C of the diterpenoid podocarpic acid (**1**) in order to generate steroidal and related annulated analogues. Cyclopentaannulation has been achieved via a chromium carbene complex [1], and more recently [2] in a one-pot sequence via reaction of a cyclometallated acetophenone-related tetracarbonylmanganese(I) complex with Me_3NO and then diphenylacetylene. The phenyl groups subtended from C15 and C16 in the products from these reactions are undesirable in steroid-directed synthesis. However, attempted use of bis(trimethylsilyl)acetylene in the present work returned only protonated diterpenoid ligand.

The synthesis of 1*H*-inden-1-ols by reaction of η^2-(2-acetylphenyl)tetracarbonylmanganese and related complexes with a variety of substituted alkynes has been reported [3,4]. Furthermore, acetylene itself reacts in refluxing benzene with the tetracarbonylmanganese(I) complex derived from acetophenone to form 1-methyl-1*H*-inden-1-ol [4]. In contrast to the cyclomanganation in high yield of a wide range of substituted acetophenones [3], only benzaldehydes containing a *para*-methoxy or *para*-dimethylamino substituent have been reported to undergo η^2-complexation [5]. In the latter case, moreover, the product from reaction with acetylene in refluxing benzene [4] is an indan-1-one, which arises presumably by thermally promoted alkene isomerisation–tautomerization of a 1*H*-inden-1-ol.

After extensive experimentation we have established that the tetracarbonylmanganese(I) complex **2** can be synthesised, albeit in only 21% yield, by reaction of 2-methoxybenzaldehyde with $PhCH_2Mn(CO)_5$ in refluxing heptane for 2 h. The diterpenoid analogue **3** was formed similarly in 30% yield. More significantly,

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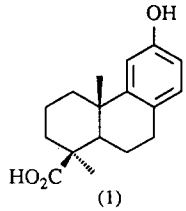
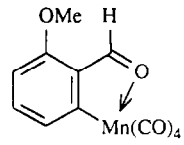


(1)



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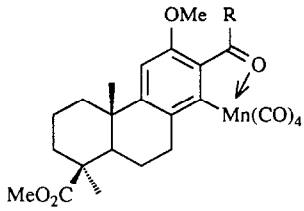
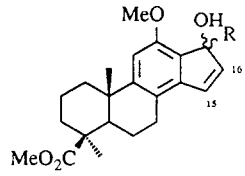


(3: R=H
4: R=Me)



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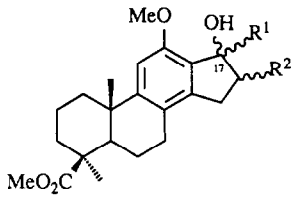
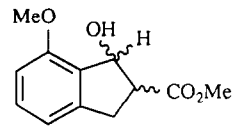


(7 :R^1=H; R^2=H
8 : R^1=Me; R^2=H
11: R^1=H; R^2=CO_2Me
12: R^1=Me; R^2=CO_2Me)



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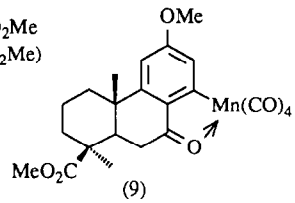

(9)

generation of coordinatively unsaturated $ArMn(CO)_3$ species by treatment of the diterpenoid complexes **3** or **4** [2] with Me_3NO (1.5 molar equiv.) in MeCN at room temperature, followed by exposure of these intermediates to acetylene (300 kPa) at room temperature for 19 h, afforded the corresponding 1*H*-inden-1-ols **5** and 1-methyl-1*H*-inden-1-ols **6** in yields of 95% and 92%, respectively. Under these mild conditions olefin isomerisation of the 1*H*-inden-1-ol, which would lead to an indan-1-one, clearly does not occur.

Although insertion of olefins carrying electron-withdrawing substituents into the aryl–Mn bond is well known, e.g. [2], there has been no report of the reaction of ethylene itself. In the context of the present work, the eventual cyclopentaannulated product **7** derived from the cyclomanganated diterpenoid aldehyde is a desirable target molecule since subsequent side-chain attachment at C17 would be more straightforward than from the tertiary alcohols **8**. In the event, treatment of **3** or **4**

with Me_3NO/MeCN at room temperature followed by exposure to ethylene (300 kPa) for 20 h at room temperature afforded the desired cyclised adduct **7** (76%) and its methyl homologue **8** (71%) as mixtures of epimers at C17. Oxidation of **7** with pyridinium chlorochromate afforded the corresponding cyclopentanone in 80% yield.

Both the aldehyde-derived benzenoid complex **2** and its diterpenoid congener **3** reacted with Me_3NO and then methyl propenoate to give a mixture of stereoisomeric 2-methoxycarbonyl-1*H*-indan-1-ols in moderate yields [53% (**10**) and 46% (**11**), respectively]. By comparison, the diterpenoid η^2-(2-acetylphenyl) complex **4** gave the 2-methoxycarbonyl-1-methyl-1*H*-indan-1-ols (**12**) in 72% yield.

Whereas the complex **9** derived from the 7-oxo diterpenoid reacted with Me_3NO/methyl propenoate to give products of insertion (but without cyclisation) (88%) [2], the use of ethylene or acetylene afforded only complicated mixtures containing no cyclised adducts.

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