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New reactivity of $(RC\equiv CCH_2OH)Co_2(CO)_6$ complexes in the Pauson–Khand reaction in the presence of CF_3COOH: synthesis of methyl substituted cyclopentenones

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Abstract

The Pauson–Khand reaction of $(RC\equiv CCH_2OH)Co_2(CO)_6$ complexes give the corresponding methyl substituted cyclopentenones in presence of CF_3COOH (TFA). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt; Carbon monoxide; Propargyl alcohol; TFA; Cyclopentenones

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1. Introduction

The cobalt-mediated Pauson–Khand co-cyclization of alkyne, alkene and CO has proved to be an efficient method for the construction of cyclopentenones in synthetic organic chemistry [1–4]. Recent efforts have led to the development of several modifications in the Pauson–Khand reaction conditions. In the presence of promoters such as amine oxides, DMSO, etc. several substrates that are otherwise not reactive under usual conditions take part in this useful reaction [5–9]. The Pauson–Khand reaction of (propargyl alcohol)$Co_2(CO)_6$ complexes have not been studied under usual thermal conditions [2]. However, it has been reported that these substances react in the presence of N-oxides to give the corresponding cyclopentenone derivatives with alcohol group intact [10,11]. In continuation of our efforts toward applications of (alkyne)$Co_2(CO)_6$ complexes prepared using the $RC\equiv CH/CoBr_2/Zn/CO/THF$ combination [12–14], we wish to report that the $Co_2(CO)_6$ complexes of substituted and unsubstituted propargyl alcohols in the presence of TFA give the corresponding methyl substituted cyclopentenones.

2. Results and discussion

The reaction of the cobalt carbonyl complex of propargyl alcohol with norbornene gave only a complex mixture of products. However, the reaction of the $(HC\equiv CCH_2OH)Co_2(CO)_6$ complex with norbornene in the presence of TFA gave the corresponding methyl substituted cyclopentenone **1** in which the methyl group is α- to carbonyl group (Eq. 1).

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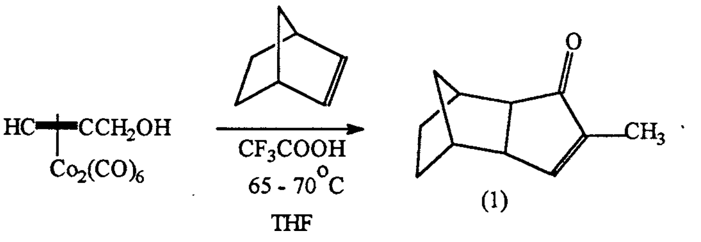
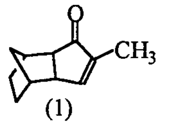
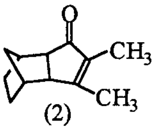
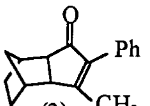
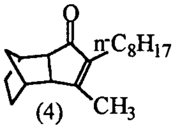
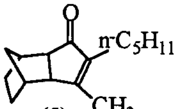
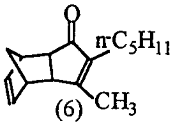


... (1)

Table 1
Reaction of $(RC{\equiv}CCH_2OH)Co_2(CO)_6$ complexes with alkene and TFA

S.No	Substrate[a]	Time	Product	Yield (%)[b,c]
1	$HC{\equiv}CCH_2OH$	12 h	 (1)	50[d]
2	$HOH_2CC{\equiv}CCH_2OH$	16 h	 (2)	40[e]
3	$PhC{\equiv}CCH_2OH$	12 h	 (3)	60
4	$n\text{-}C_8H_{17}C{\equiv}CCH_2OH$	12 h	 (4)	56
5	$n\text{-}C_5H_{11}C{\equiv}CCH_2OH$	12 h	 (5)	55
6	$n\text{-}C_5H_{11}C{\equiv}CCH_2OH$	10 h	 (6)	52

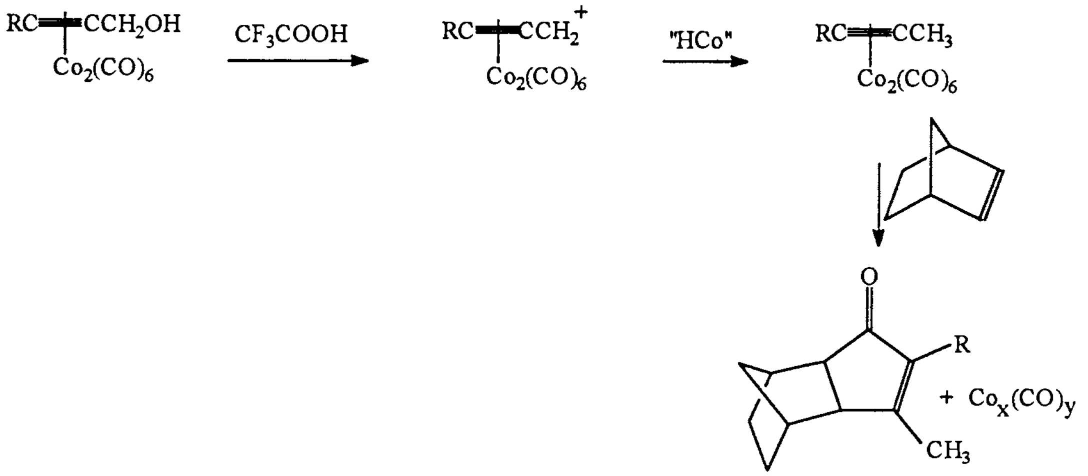
[a] $CoBr_2$ (10 mmol), Zn (10 mmol), norbornene (10 mmol) and TFA (10 mmol) were used. In entry **6**, norbornadiene (10 mmol) was used in the place of norbornene.

[b] All the products were identified by spectral data (IR, ^1H-, ^{13}C-NMR-DEPT experiments and MASS) and in comparison with the data available in the literature.

[c] Yields reported are for products separated by column chromatography on silica gel using ethylacetate in hexane as eluent and calulated on the basis of amount of alk-2-yn-1-ol used.

[d] Reaction carried out using $CoBr_2$ (20 mmol), Zn (20 mmol), norbornene (20 mmol), TFA (20 mmol).

[e] For 10 mmol diol complex, norbornene (20 mmol) and TFA (40 mmol) were used.



Scheme 1.

The product **1** has been obtained previously in the reaction of the $(CH_3C{\equiv}CH)Co_2(CO)_6$ complex with norbornene in the original version of the Pauson–Khand reaction [15–17]. Hence, it may be of interest to note that the propargyl alcohol may serve as an equivalent of the gaseous propyne in such applications.

The reactions of various $(RC{\equiv}CCH_2OH)Co_2(CO)_6$ complexes with norbornene and TFA gave the corresponding methyl substituted cyclopentenones. The results are summarised in Table 1. In all cases methyl substituted cyclopentenones were obtained in 40–60% yields. The reaction is regioselective and only one isomer has been obtained. The product **3** (Table 1) has been previously reported in the Pauson–Khand reaction of the $(PhC{\equiv}CCH_3)Co_2(CO)_6$ complex with norbornene [15–17].

The deoxygenation of the hydroxy group in acetylenic alcohols complexed with the '$Co_2(CO)_6$' moiety has been earlier reported in the reaction of TFA with $NaBH_4$ or $BH_3 \cdot SMe_2$ [18,19]. Hence, it is possible that the $-CH_3$ group would have formed from $-CH_2OH$ through reduction by the 'H–Co' species present in the medium. These 'H–Co' species may result from the reaction of cobalt carbonyl species with TFA (Scheme 1).

Polymeric cobalt carbonyl species that would be formed after the Pauson–Khand reaction could also react with acid to give hydridocobalt species [20,21]. The reaction sequence may be visualised as initial formation of carbonium ion on reaction with TFA followed by reduction with the 'H–Co' species as depicted in Scheme 1. Alternatively, since the $HCo(CO)_4$ is also acidic, it could serve both as a 'proton' and 'hydride' source [21].

The Pauson–Khand reaction with norbornene may take place after the conversion of hydroxyl group to methyl group (Scheme 1). Also, the regioselectivity observed is according to the reactivity of the dehydroxylated alkyne–cobalt complex intermediate. We have observed that the reaction of the $PhC{\equiv}CCH(OH)Ph–Co_2(CO)_6$ complex with TFA and norbornene and the $(HC{\equiv}CCH_2OH)Co_2(CO)_6$ complex, TFA and cyclopentene gave a mixture of products. Also, the reaction of the $(Me_3SiC{\equiv}CCH_2OH)Co_2(CO)_6$ complex with norbornene in the presence of TFA did not yield the corresponding cyclopentenone even after 24 h of stirring the reaction mixture at 70–80°C. Most of the complex remained unreacted besides the formation of small amounts of unidentified products. These results would throw light on the scope and limitations of this transformation.

It may of interest to note that the product obtained in the reaction of the $(n\text{-}C_5H_{11}C{\equiv}CCH_2OH)Co_2(CO)_6$ complex with norbornadiene and TFA (product **6**, Table 1) could serve as a precursor for the dihydrojasmone synthesis [22]. In conclusion, the present transformation involving certain substituted propargyl alcohols to obtain the corresponding methyl substituted cyclopentenones should widen further the synthetic utility of the $(alkyne)Co_2(CO)_6$ complexes.

3. Experimental

3.1. General methods

All reactions were carried out under an atmosphere of predried nitrogen. All transfers and manipulations of compounds were carried out under a nitrogen atmosphere. Tetrahydrofuran was freshly distilled over sodium/benzophenone ketyl. Propargyl alcohol supplied by Fluka, Switzerland was used. Substituted propargyl alcohols were prepared by following a literature procedure [23]. All IR spectra were recorded on JASCO FT-5300 instrument with polystyrene as reference. All ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Brucker-AC-200 instrument with chloroform-*d* as solvent and TMS as reference ($\delta = 0$ ppm). Column chromatography was carried out using Acme silica gel (100–200 mesh). Anhydrous $CoBr_2$ was prepared from the hydrated complex by keeping it in the air oven at 150°C for 5–6 h and further dried at 150°C for 4 h under vacuum. It was kept under nitrogen in a desiccator. Active zinc dust was prepared by treating commercial zinc dust with 1% H_2SO_4 and acetone, and drying at 150°C for 4 h under vacuum. Carbon monoxide was generated by dropwise addition of formic acid (98%) to concentrated H_2SO_4 (96%) at 90°C using an apparatus recommended for utilization in the carbonylation of organoboranes [24].

3.2. Representative procedure for the reaction of the $(HC{\equiv}CCH_2OH)Co_2(CO)_6$ complex with CF_3COOH in the presence of norbornene

The $(HC{\equiv}CCH_2OH)Co_2(CO)_6$ (10 mmol) was prepared by reducing $CoBr_2$ (4.36 g, 20 mmol) with Zn (1.43 g, 22 mmol) and $HC{\equiv}CCH_2OH$ (0.56 g, 10 mmol) in THF (60 ml) while bubbling CO at 25°C for 3 h. Norbornene (1.88 g, 20 mmol) and trifluoroacetic acid (1.54 ml, 20 mmol) were added. The contents were stirred at 65–70°C for 16 h, brought to room temperature and the metal carbonyl was oxidised with ceric ammonium nitrate in methanol. Water (20 ml) was added and the organic phase was extracted with ether (40 ml). Then it was washed successively with water (10 ml) and 10% $NaHCO_3$ solution. The organic extract thus obtained was dried over anhydrous $MgSO_4$ and concentrated. The crude product was subjected to column chromatography on silica gel. The corresponding cyclopentenone derivative (50%, 0.81 g) was isolated using 2% ethyl acetate in hexane as eluent. The product was identified by IR, ^1H, ^{13}C (DEPT experiments) NMR and by mass spectral data. The spectral data obtained for the product are given below.

3.2.1. Compound **1**

IR (neat) 1699 cm^{-1}; ^1H-NMR δ 0.84–0.91 (m, 2H), 1.15–1.21 (m, 2H), 1.49–1.56 (m, 2H), 1.69 (s, 3H), 2.07 (s, 2H), 2.29 (s, 1H), 2.47, (s, 1H), 7.06 (b, 1H); ^{13}C-NMR δ 9.9 ($-CH_3$), 28.3, 28.9 and 30.9 ($-CH_2$), 37.9, 38.8, 48.0 and 53.4 (–CH), 144.6 (quaternary), 159.4 (–CH, olefinic), 211.3 (CO); mass (*m*/*z*) 162 (M^+).

3.3. The reactions of other $(RC{\equiv}CCH_2OH)Co_2(CO)_6$ complexes were carried out following the above procedure

The spectral data of the products obtained (Table 1) are given below.

3.3.1. Compound **2**

Yield 40% (0.70 g); IR (neat) 1699 cm^{-1}; ^1H-NMR δ 0.80–0.83 (m, 2H), 1.19–1.23 (m, 2H), 1.35–1.59 (m, 2H), 1.60 (s, 3H), 1.94 (s, 3H), 2.05–2.18 (m, 2H), 2.29–2.35 (m, 2H); ^{13}C-NMR δ 7.8 and 15.6 ($-CH_3$), 28.6, 29.0 and 31.1 ($-CH_2$), 37.0, 38.6, 52.6 and 53.4 (–CH), 139.2 and 170.6 (quaternary), 210.6 (CO); mass (*m*/*z*) 176 (M^+).

3.3.2. Compound **3**

Yield 60% (0.71 g); m.p. 70°C (lit.[1b] m.p. 70–71°C); IR (KBr) 1695 cm^{-1}; ^1H-NMR δ 0.88–1.16 (m, 2H), 1.33–1.46 (m, 2H), 1.47–1.73 (m, 2H), 2.04 (s, 3H), 2.21–2.28 (m, 2H), 2.39–2.40 (m, 1H), 2.49–2.51 (d, 1H), 7.15–7.30 (m, 5H); ^{13}C-NMR δ 16.6 ($-CH_3$), 28.6, 29.1 and 31.3 ($-CH_2$), 37.6, 39.1, 52.7 and 53.9 (–CH), 127.5, 128.1, 129.0 and 131.9 (–CH), 143.1 and 172.2 (quaternary), 208.0 (CO); mass (*m*/*z*) 238 (M^+).

3.3.3. Compound **4**

Yield 56% (0.77 g); IR (neat) 1693 cm^{-1}; ^1H-NMR δ 0.84 (b, 5H), 1.19 (b, 11H), 1.54 (b, 5H), 1.94 (b, 3H), 2.07–2.17 (m, 4H), 2.34 (b, 2H); ^{13}C-NMR δ 13.9 ($-CH_3$), 15.4 ($-CH_3$), 22.5, 23.0, 28.3, 28.6, 29.1, 29.3, 29.5, 31.0, 31.7 and 34.5 ($-CH_2$), 37.1, 38.5, 52.5 and 53.4 (–CH), 143.8 and 170.2 (quaternary), 210.0 (CO); mass (*m*/*z*) 274 (M^+).

3.3.4. Compound **5**

Yield 55% (0.64 g); IR (neat) 1689 cm^{-1}; ^1H-NMR δ 0.78–0.84 (m, 6H), 1.19–1.57 (m, 9H), 1.94 (s, 3H), 2.03–2.37 (m, 6H); ^{13}C-NMR δ 13.8 ($-CH_3$), 15.4 ($-CH_3$), 22.3, 22.9, 27.9, 28.5, 29.0, 30.9 and 31.7 ($-CH_2$), 37.0, 38.5, 52.5 and 53.4 (–CH), 143.7 and 170.5 (quaternary), 210.1 (CO); mass (*m*/*z*) 232 (M^+).

3.3.5. Compound **6**

Yield 52% (0.60 g); IR (neat) 1693 cm^{-1}; ^1H-NMR δ 0.79 (m, 5H), 1.05–1.34 (m, 6H), 1.97 (s, 3H), 2.07 (m, 2H), 2.18 (m, 1H), 2.50 (s, 1H), 2.67 (s, 1H), 2.82 (s, 1H), 6.14 (s, 2H); ^{13}C-NMR δ 13.8 ($-CH_3$), 15.4 ($-CH_3$), 22.3, 23.0, 27.9, 31.7 and 41.1 ($-CH_2$), 41.9, 43.1, 51.8 and 52.0 (–CH), 137.3 and 137.8 (–CH), 144.9 and 170.3 (quaternary), 208.6 (CO); mass (*m*/*z*) 230 (M^+). Anal. Calc.: C 83.42%; H 9.62%. Found: C 83.55%; H 9.60%.

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