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A sub-stoichiometric tungsten-mediated Pauson–Khand reaction: Scope and limitations

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ABSTRACT

Terminal alkynes do not partake in sequential [2+2+1]/benzoannulation reactions with Fischer carbene complexes and highly reactive and sterically hindered olefins; instead, they undergo a Fischer carbene complex-catalyzed Pauson–Khand reaction (PKR). This result has allowed the development, for the first time, of a tungsten-catalyzed PKR, although of limited scope.

1. Introduction

The Pauson–Khand reaction (PKR), a formal [2+2+1]-cycloaddition reaction involving an olefin, an alkyne, and carbon monoxide, has become one of the most powerful methods for cyclopentenone syntheses [1]. Although the original conditions required heating a mixture of stoichiometric amounts of dicobalt octacarbonyl, an alkyne and an alkene [2], further development of new reaction conditions have greatly expanded the scope and synthetic utility of the PKR. These improvements have been based on the use of additives and/or other transition metals. In this regard, titanium, nickel, iron, rhodium, ruthenium, zirconium, iridium, or molybdenum species have been employed [3]. Particularly, Hoye has reported the so far unique example of the employment of tungsten carbonyl complexes as catalysts in PKR; he pointed out that stoichiometric amounts of $W(CO)_5THF$ are required to promote the intramolecular PKR reaction of 1,6-enynes [4]. However, nowadays, a major goal is the development of enantioselective and/or truly catalytic approaches to the PKR [5].

We have recently reported a novel multicomponent reaction (MCR) [6] involving chromium alkoxy alkynyl carbene complexes **1** [7] and sterically hindered olefins, such as naphthalene oxide **2a**, which resulted in the formation of [2+2+1]/[2+1] cycloaddition adducts **3** (Scheme 1) [8]. The sequence was assumed to proceed through a non-stabilized carbene complex **I**, which could be trapped with another unit of the same olefin or even with a unit of a different olefin. We hypothesized that intermediate **I** (R = Ph) should also be able to insert an alkyne unit to form **II** which, in principle, should evolve either by a cyclopentannulation or by a Dötz-like benzannulation processes [9] to generate new and highly functionalized indenes **4** or naphthols **5** (Scheme 1). However, when such possibility was explored using terminal alkynes **6** as the fourth partner for the MCR, a sub-stoichiometric tungsten-mediated [2+2+1]-Pauson–Khand reaction occurred. In this manuscript we present our results in the development of this process as well as its scope and limitations.

2. Results and discussion

The reaction between Fischer carbene complex (FCC) **1a**, 1,4-epoxynaphthalene **2a**, and 1-hexyne **6a** as alkyne unit under the general reaction conditions employed for the [2+2+1]/[2+1] cycloaddition sequence [8] (ratio **1a**:**2a**:**6a** = 1:3:15, toluene, at 80–100 °C), resulted in the isolation of cyclopentenone **7a** as the major product (Scheme 2). Performing the reaction with half of the amount of **1a**, caused the doubling of the isolated chemical yield of **7a** (45% vs. 94%, based on **1a**, while the yield based on reacted olefin **2a** was similar), which suggests that **1a** is able to transfer more than one carbonyl ligand from its coordination sphere. The

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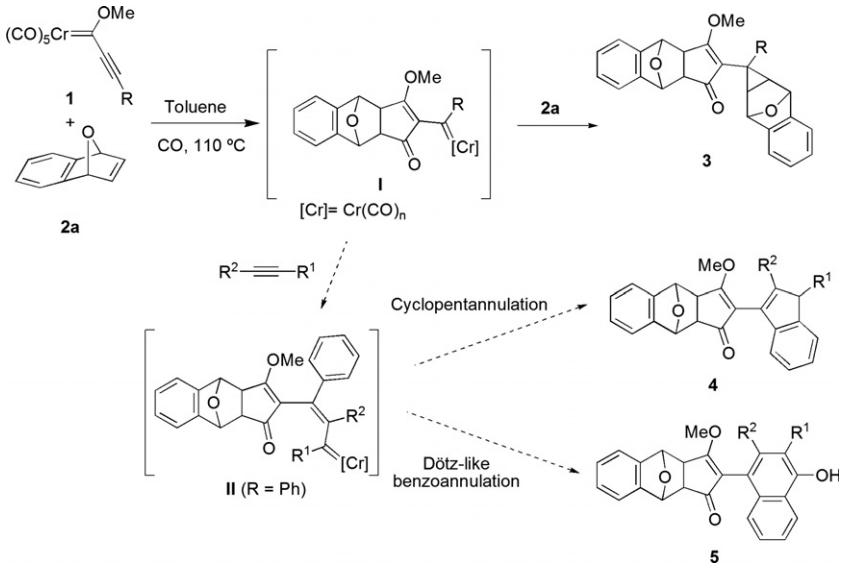
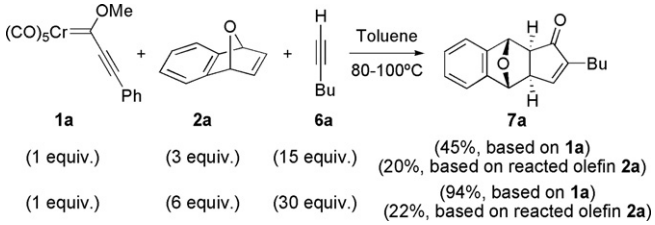


Scheme 1. [2+2+1]/[2+1] Reaction sequence and possible evolution patterns following alkyne insertion in intermediate **I**.



Scheme 2. Pauson–Khand reaction with FCC **1a**, bicyclic olefin **2a** and 1-hexyne **6a.**

formation of cyclopentenone **7a** is perfectly explained in terms of a PKR [10]. Interestingly, Hoye had previously reported that bicyclic cyclopentenones are obtained as minor byproducts for the reaction of FCCs with enynes [11].

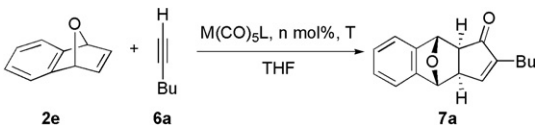
In the view that the carbene ligand is not transferred to the final product (Scheme 2), and that catalytic and/or intermolecular approaches to the PKR employing chromium or tungsten complexes have not been reported, we decided to explore the ability of other group VI metal carbonyl complexes to catalyze the intermolecular PKR. The results are displayed in Table 1.

The initial essays were carried out with several different chromium and tungsten complexes in both stoichiometric (entries 4 and 5) and sub-stoichiometric (entries 1–3, 6) amounts. From these tests, tungsten proved to have more possibility than chromium as potential catalyst; notably, the result presented in entry 6, where a 63% of PKR adduct **7a** was isolated employing just 50 mol% of catalyst loading, indicates that *more than one CO ligand has been transferred into the final product*. However, when the catalysts loading was diminished to a 20 mol% (entry 7), the isolated yield of adduct dropped considerably. Nonetheless, the true catalytic nature of the process was demonstrated in entry 8. A 62% yield could be reached with 20 mol% catalysts loading by performing the reaction under CO atmosphere. However, a further decrease in the amount of catalyst resulted in low-yielding reactions (entries 9 and 10). Therefore, the conditions displayed in entry 8 were chosen to analyze the scope of the tungsten-catalyzed PKR.

Regarding the screening of the alkyne partner, olefin **2a** provided moderate to good yields of PKR adducts **7a–c** when treated with 1-butyne **6a**, 1-decyne **6b** or phenylacetylene **6c** (Table 2, entries 1–3). The reaction failed for trimethylsilylacetylene and for an internal alkyne, 3-hexyne. We turned then to examine the hindered olefin component to find that the optimized reaction conditions only worked for hindered and highly reactive olefins, as neither norbornene nor norbornadiene produced the desired PKR adducts. Therefore, electron-donating and electron-withdrawing substituted 1,4-dihydro-1,4-epoxynaphthalenes **2b** and **2c** did provide the expected cyclopentenones **7d** and **7e** when reacted with 1-hexyne (entries 4 and 5), although with lower yields than **2a**, which indicates that the reaction is quite sensitive to electronic effects on the aromatic ring. On the other hand, neither the more hindered olefin **2d** nor **2e**, which presents a *t*-BOC protected nitrogen atom instead of the oxygen atom, underwent the PKR under such conditions (entries 6 and 7), thus evidencing a strong steric effect.

In all cases (entries 1–5), only one regio- and diastereomer was detected; in fact, the reaction products displayed both an excellent regioselectivity, with the bulky substituent of the alkyne located at

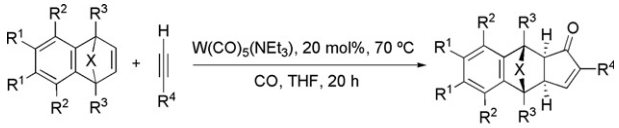
Table 1
Optimization of the group VI metal-promoted intermolecular PKR conditions



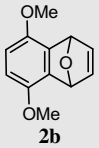
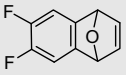
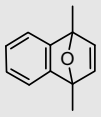
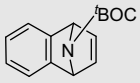
Entry[a]	$M(CO)_5L$	mol%	T[b] (°C)	CO atm[c]	Yield[d] (%)
1	$Cr(CO)_6$	33	80		–
2	$Cr(CO)_5(NEt_3)$	33	70[e]		9
3	$Cr(CO)_5(THF)$	50	80		14
4	$Cr(CO)_5(THF)$	100	rt		–
5	$W(CO)_5(THF)$	100	rt		53
6	$W(CO)_5(NEt_3)$	50	70[e]		63
7	$W(CO)_5(NEt_3)$	20	70[e]		27
8	$W(CO)_5(NEt_3)$	20	70[e]	Yes	62
9	$W(CO)_5(NEt_3)$	10	70[e]	Yes	33[f]
10	$W(CO)_5(NEt_3)$	5	70[e]	Yes	9[f]

[a] Ratio **2a**:**6a** = 1:7.5, except for entry 3 (ratio **2a**:**6a** = 1:5).
[b] External temperature, unless otherwise stated.
[c] Reaction performed under CO pressure in a sealed tube (initially 1 atm, reaction pressure not quantified).
[d] Isolated yield based on reacted olefin **2a**, unless otherwise stated.
[e] Temperature reached when the reaction mixture was heated with a 400 W medium pressure Hg lamp for the formation of the catalytic complex.
[f] Estimated ^1H NMR-yield from the crude reaction mixture.

Table 2
Sub-stoichiometric tungsten-catalyzed intermolecular PKR



2 6 7

Entry	2	6	R^4	7	Yield[a] (%)
1	**2a**	**6a**	Bu	**7a**	62
2	**2a**	**6b**	Octyl	**7b**	64
3	**2a**	**6c**	Ph	**7c**	50
4	 **2b**	**6a**	Bu	**7d**	38
5	 **2c**	**6a**	Bu	**7e**	38
6	 **2d**	**6a**	Bu		
7	 **2e**	**6a**	Bu		

[a] Isolated yields based on starting olefins **2**.

the α-position to the ketone in the reaction product, and an excellent *exo* diastereoselectivity, as established by comparison with previous syntheses of such compounds [10].

3. Conclusions

In summary, the presence of terminal alkynes inhibits the [2+2+1]/[2+1] cascade reaction between alkoxy alkynyl Fischer carbene complexes and strained and hindered olefins by promoting a Pauson–Khand reaction leading to cyclopentenones. Therefore, a *sub-stoichiometric tungsten-catalyzed intermolecular* PKR has been developed, although of limited scope regarding both the olefin (only works for 1,4-dihydro-1,4-epoxynaphthalene derivatives) and the alkyne (restricted to terminal alkynes).

4. Experimental

4.1. General considerations

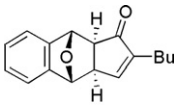
All reactions were carried out under a N_2 atmosphere (99.99%). All glassware was oven-dried (120 °C), evacuated and purged with nitrogen. All common reagents and solvents were obtained from commercial suppliers and used without any further purification unless otherwise indicated. FCC **1a** [12] and non-commercial bicyclic olefins **2b** [13], **2c** [14], **2d** [15], and **2e** [16] were prepared following established procedures. Triethylamine was distilled over KOH. Toluene and THF were dried by standard methods. Hexane and ethyl acetate were distilled before use. TLC was performed on aluminum-backed plates coated with Silica Gel 60 with F_{254} indicator and were visualized under ultraviolet light and/or by staining with a Ce/Mo reagent, or anisaldehyde or phosphomolybdic acid solutions and subsequent heating. R_f values are reported on silica gel. Flash column chromatography was carried out on Silica Gel 60, 230–240 mesh, using hexane/ethyl acetate mixtures as eluents. NMR measurements were recorded on Bruker DPX-300 or AV-400 spectrometers. ^{1}H NMR: splitting pattern abbreviations are: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{13}C NMR: multiplicities were determined by DEPT, abbreviations are: q, CH_3; t, CH_2; d, CH; s, quaternary carbons. In the case of compound **7e** which bears F, the abbreviation refers to the splitting pattern due to C–F coupling (the corresponding coupling constant is also reported); for this compound, the number of hydrogen atoms linked to a carbon atom is indicated in the form: CH_3, CH_2, CH, C. ^{19}F NMR chemical shifts are referred to $CFCl_3$. Standard pulse sequences were employed for the DEPT experiments. FT-IR was performed with a Mattson 3000 FT-IR spectrometer. Mass spectra were determined by Universidad de Oviedo, Universidad de Vigo (CACTI) and Universidad de Zaragoza services, with a Finnigan Mat95, a VG AutoSpec M, and a PFK AutoSpec E Mass Spectrometers respectively for high resolution mass spectra (HRMS); low resolution mass spectra were obtained with a Hewlett–Packard 5880 A Spectrometer. Electron impact (70 eV) or fast atom bombardment (FAB) techniques were employed. Melting points were determined on a Büchi-Tottoli apparatus and are uncorrected. Elemental analyses were carried out with a Perkin–Elmer 240 B microanalyzer.

4.2. General procedure for the synthesis of cyclopentenones ***7***

The corresponding olefin **2** (1 mmol) and alkyne **6** (7.5 mmol) were sequentially added, followed by NEt_3 (0.7 mmol, 98 μL), to a solution of $W(CO)_6$ (0.2 mmol, 70 mg) in dry THF (2 mL), at room temperature, in a sealed tube under CO atmosphere. The reaction mixture was irradiated under a medium pressure 400 W mercury arch lamp for 20 h. Solvents were evaporated under vacuum and the crude residue was purified by column chromatography to give cylopentenones **7**, in the yields reported in Tables 1 and 2.

4.3. Cyclopentenone ***7a*** *[10a,c]*

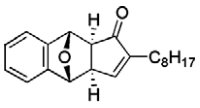
Yield: 63%. White solid. M.p.: 54–56 °C. R_f = 0.32 (hexane/AcOEt: 5/1). IR ν (cm^{-1}) 1701. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.15 (5H, m), 5.41 (1H, s), 5.11 (1H, s), 2.96 (1H, m), 2.54 (1H, d, J = 5.1 Hz), 2.21 (2H, t, J = 7.7 Hz), 1.55–1.45 (2H, m), 1.41–1.32 (2H, m), 0.92 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 207.0 (s), 155.4 (d), 150.7 (s), 145.2 (s), 144.0 (s), 126.9 (d), 126.8 (d), 119.4 (d), 119.3 (d), 80.8 (d), 79.5 (d), 52.8 (d), 48.2 (d), 29.4 (t), 24.6 (t), 22.3 (t), 13.7 (q). MS (*m/z*) 255 (100, $[M+1]^+$), 254 (92, M^+), 237 (68), 211 (39). HRMS (FAB, $[M+1]^+$) calc. for $C_{17}H_{19}O_2$, 255.1385. Found: 255.1387.



7a

4.4. Cyclopentenone ***7b***

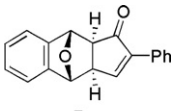
Yield: 64%. Yellow solid. M.p.: 67–69 °C. R_f = 0.51 (hexane/AcOEt: 5/1). IR ν (cm^{-1}) 1700. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.02–7.92 (3 H, m), 7.87–7.81 (2H, m), 6.06 (1H, s), 5.77 (1H, s), 3.64–3.60 (1H, m), 3.19 (1H, d, J = 6.8 Hz), 2.90–2.83 (2H, m), 2.20–2.14 (2H, m), 2.07–1.82 (10H, m), 1.58–1.51 (3H, t, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 207.0 (s), 155.4 (d), 150.9 (s), 145.3 (s), 144.2 (s), 127.0 (d), 126.9 (d), 119.5 (d), 119.4 (d), 80.9 (d), 79.7 (d), 52.9 (d), 48.3 (d), 31.7 (t), 29.3 (t), 29.2 (t), 29.1 (t), 27.4 (t), 25.0 (t), 22.5 (t), 14.0 (q). MS (*m/z*) 310 (35, M^+), 293 (25), 211 (42), 118 (71), 84 (100). HRMS (EI, M^+) calc. for $C_{21}H_{26}O_2$, 310.1933. Found: 310.1931.



7b

4.5. Cyclopentenone ***7c*** *[10a,c]*

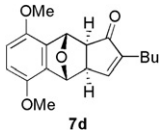
Yield: 50%. Yellow solid. M.p.: 108–110 °C. R_f = 0.20 (hexane/AcOEt: 5/1). IR ν (cm^{-1}) 1706. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.82 (1 H, d, J = 2.9 Hz), 7.76 (2H, d, J = 7.0 Hz), 7.44–7.32 (5H, m), 7.27–7.20 (2H, m), 5.56 (1H, s), 5.26 (1H, s), 3.14–3.10 (1H, m), 2.76 (1H, d, J = 5.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 205.0 (s), 156.6 (d), 147.1 (s), 145.3 (s), 144.0 (s), 131.0 (s), 128.7 (d), 128.3 (d, 2 CH), 127.2 (d), 127.1 (d, 2 CH), 127.0 (d), 119.7 (d), 119.5 (d), 81.3 (d), 79.8 (d), 54.0 (d), 47.9 (d). MS (*m/z*) 274 (100, M^+), 273 (40), 257 (49), 118 (77). HRMS (EI, M^+) calc. for $C_{19}H_{14}O_2$, 274.0988. Found: 274.0982.



7c

4.6. Cyclopentenone ***7d***

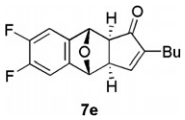
Yield: 38%. White solid. M.p.: 78–80 °C. R_f = 0.15 (hexane/AcOEt: 5/1). IR ν (cm^{-1}) 1703. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.27 (1H, s), 6.67 (2H, s), 5.56 (1H, s), 5.27 (1H, s), 3.82 (3H, s), 3.80 (3H, s), 2.98 (1H, bs), 2.56 (1H, d, J = 5.1 Hz), 2.21 (2H, t, J = 7.3 Hz), 1.53–1.45 (2H, m), 1.40–1.30 (2H, m), 0.92 (3H, t, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 206.9 (s), 155.3 (d), 150.9 (s), 146.9 (s), 146.7 (s), 134.5 (s), 133.2 (s), 111.7 (d), 111.3 (d), 79.1 (d), 77.7 (d), 55.9 (q, 2 CH_3), 52.5 (d), 47.9 (d), 29.5 (t), 24.7 (t), 22.4 (t), 13.7 (q). MS (*m/z*) 314 (6, M^+), 243 (9), 178 (100), 163 (41). HRMS (EI, M^+) calc. for $C_{19}H_{22}O_4$, 314.1518. Found: 314.1518.



7d

4.7. Cyclopentenone ***7e***

Yield: 38%. Yellow solid. M.p.: 80–83 °C. R_f = 0.31 (hexane/AcOEt: 5/1). IR ν (cm^{-1}) 1703. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.18–7.13 (1 H, m), 7.08–6.98 (2H, m), 5.27 (1H, s), 4.99 (1H, s), 2.87–2.83 (1H, m), 2.42 (1H, d, J = 5.1 Hz), 2.11 (2H, t, J = 7.2 Hz), 1.44–1.33 (2H, m), 1.31–1.15 (2H, m), 0.82 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 206.3 (C), 154.9 (CH), 151.3 (C), 149.4 (dd, $^1J_{CF}$ = 231.7 Hz, $^2J_{CF}$ = 15.4 Hz, C), 149.2 (dd, $^1J_{CF}$ = 250.8 Hz, $^2J_{CF}$ = 16.5 Hz, C), 141.3 (dd, $^3J_{CF}$ = 6.0 Hz, $^4J_{CF}$ = 3.3 Hz, C), 140.2 (dd, $^3J_{CF}$ = 6.6 Hz, $^4J_{CF}$ = 3.3 Hz, C), 109.6 (dd, $^2J_{CF}$ = 19.8 Hz, $^3J_{CF}$ = 11.5 Hz, 2 CH), 80.6 (CH), 79.5 (CH), 52.7 (CH), 48.2 (CH), 29.5 (CH_2), 24.7 (CH_2), 22.3 (CH_2), 13.7 (CH_3). ^{19}F NMR ($CDCl_3$, 282 MHz) δ −258.1 (d, J = 18.5 Hz), −258.4 (d, J = 18.6 Hz). MS (*m/z*) 290 (40, M^+), 273 (30), 247 (36), 219 (46), 154 (100). HRMS (EI, M^+) calc. for $C_{17}H_{16}F_2O_2$, 290.1113. Found: 290.1114. Elemental Anal. Calc. (%) for $C_{17}H_{16}F_2O_2$ (290.30): C, 70.33; H, 5.56. Found: C, 70.11; H, 6.45%.



7e

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