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An efficient catalytic protocol for the Pauson–Khand reaction

Jaime Blanco-Urgoiti[†], Delbrin Abdi, Gema Domínguez, Javier Pérez-Castells*

Departamento de Química, Facultad de Farmacia, Universidad San Pablo-CEU, Urb. Montepríncipe, Boadilla del Monte, 28668 Madrid, Spain

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Abstract

New experimental conditions have been developed for an efficient catalytic Pauson–Khand reaction. These are based on the use of a mixture of molecular sieves and *tert*-butanol as inducers of the process. This mixture, with the appearance of a paste, is able to adsorb CO, thus improving the conversion and making it possible to effect the reactions in the absence of a CO atmosphere. The protocol is applied to known and unknown substrates and compared to previously described conditions, showing good results with intra- and intermolecular examples.

Keywords: Pauson–Khand; Catalysis; Cyclization

1. Introduction

The establishment of an efficient catalytic protocol for the Pauson–Khand[1] reaction has received great attention in the past years.[2] The only possibility of fulfilling the principles of green chemistry in this reaction would be the use of efficient and reusable metal catalysts. The first reports[3] used severe reaction conditions with high CO pressures, or chemical additives like phosphites to induce the reaction.[4] The situation changed after the contributions of Livinghouse[5] and Krafft.[6] These groups made extensive studies with reactions carried out at 1 atm of CO. Thus, Livinghouse determined the best temperature for a catalytic Pauson–Khand reaction, which was situated in the narrow gap of 65–75 °C. Krafft reported good results with commercial non-purified $Co_2(CO)_8$, and indicated a generally favorable effect of the addition of cyclohexylamine in the reaction. Both groups used alternatively as catalyst a preformed and purified cobalthexacarbonyl–alkyne complex.[7] Other cobalt sources like $Co_2(CO)_7PPh_3$,[8] $Co_4(CO)_{12}$,[9] or alkylidene-$Co_3(CO)_9$[10] have been used generally with high CO pressures. Cobalt on mesoporous silica,[11] charcoal,[12] Raney cobalt,[13] colloidal[14] cobalt particles or heterogeneous bimetallic catalyst[15] have also been used to catalyze the reaction with high yields although using severe conditions. Still, most of these studies lack generality and are made only with a few substrates *gem*-disubstituted or bearing heteroatoms that act as soft ligands.

Other metals give an interesting alternative for the catalysis of this reaction. Ruthenium,[16] iridium[17] or molybdenum[18] have been used, although the most promising complexes are actually those of rhodium.[19] The main problems to be solved in catalytic PKR are the finding of an efficient procedure that avoids or minimizes the use of CO and that is applicable to a wide variety of substrates including intermolecular reactions.

In the past years, new reaction protocols and promoters have increased the use of the reaction to new substrates.[20] In particular we have shown that molecular sieves can act as new efficient promoters for Pauson–Khand reactions.[21] This zeolites improve the conversion of known and new substrates and have allowed new applications of this reaction in benzenic enynes[22] and enynoindoles.[23] The aim of the present work is to develop a new protocol for a catalytic version of the Pauson–Khand reaction based on the use of molecular sieves.[24] As zeolites are able to adsorb small molecules such as CO, we believe this will help in the recovery of active cobalt

* Corresponding author.
E-mail address: jpercas@ceu.es (J. Pérez-Castells).
† Present address: Centro de investigación Lilly, S. A., Avda. de la industria, 30, 28108 Alcobendas, Madrid, Spain.

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species thus improving the catalytic cycle, and allowing milder conditions.

Performing a catalytic PKR implies the use of a CO atmosphere. This discourages many potential users of this powerful synthetic process. A couple of groups have developed a new way to produce CO in situ by using aldehydes as a source of this gas via a decarbonylation process induced by the same rhodium complex that catalyses the PKR.[25] We believed that it was worth trying to tune up a procedure in which the use of CO gas could be minimized, being experimentally easy and efficient.

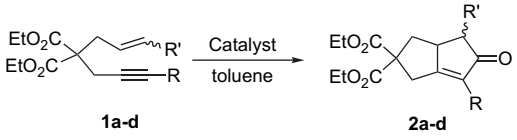
2. Results and discussion

We investigated a catalytic Pauson–Khand reaction in the absence of a CO atmosphere, to see if molecular sieves could favor the recovery of active species giving rise to catalytic cycles. The beneficial effect of the zeolites in the PKR may be due to surface interaction with the enyne that would stabilize the pre-transition state, as suggested for the DSAC conditions (Dry State Adsorption Conditions), described in early times by Smit and Caple.[26] Adsorption of CO by the sieves and regeneration of active cobalt species is probably responsible for their favorable effect. With the aim to develop a new catalytic protocol, we submitted compound **1a** to three reactions in air atmosphere with 10% cobalt octacarbonyl (entries 1–3, Table 1): blank reaction, addition of molecular sieves, and addition of molecular sieves heated to 200 °C and cooled under carbon monoxide.

The results showed an important increase in conversion with sieves, reaching 65% with the pre-treated zeolite. This result was comparable with standard catalytic conditions under 1 atm of CO (entry 4). In view of the result of entry 3, we prepared a suspension of powdered 4 Å molecular sieves in *tert*-butanol. This mixture was submitted to three cycles of vacuum/CO, and then it was kept in the fridge producing a pale brown paste. The use of *tert*-butanol was intended to slow the diffusion of the CO, being this solvent easily eliminated after the reaction in vacuo, and able to solidify in the fridge so that it could be kept for long time without losing efficiency. The mixture of molecular sieves and *tert*-butanol treated with CO (1 g per mmol of substrate) was added to a flask with substrate **1a** and 10% of $Co_2(CO)_8$ dissolved in toluene, and after 16 h the PKR had finished and the product was obtained in 60% yield. The activity of this paste along time was checked, repeating the reaction after 2 days and 2 weeks, using the same batch of paste. Yields were kept in these experiments in the same range (entry 5, note d). Next, the procedure was used with substrates **1b–d**. The use of the paste gives similar results (entries 6, 11, 13, and 15) than with standard conditions under CO atmosphere (entries 8, 12, 14, and 16). With non-terminal alkyne **1b**, a reaction at higher temperature was tested showing an important decrease in yield (entry 7). In addition, this substrate was submitted to a rhodium catalyzed reaction and gave similar results with the standard conditions (entry 10) and with the use of the paste (entry 9).

Next we extended this methodology to other substrates. In particular we selected aromatic enynes **3**. Compound **3a** was used as a model and the stoichiometric PKRs that we described previously[27] are indicated in Table 2 for comparative reasons. These conditions are: combination of trimethylamine *N*-oxide (TMANO) with molecular sieves in toluene at room

Table 1
Tuning up of catalytic PKR conditions with substrates **1**



1a-d **2a-d**

Entry	Catalyst/loading	Additive	CO	R	R′	Product	Temp (°C)	Time (h)	Method	Yield (%)
1	$Co_2(CO)_8$/10%	No	No	H	H	**2a**	65	18	A	15
2	$Co_2(CO)_8$/10%	M.S.[a]	No	H	H	**2a**	65	18	B	30
3	$Co_2(CO)_8$/10%	Pre-CO M.S.[b]	No	H	H	**2a**	65	18	C	65
4	$Co_2(CO)_8$/10%	No	1 atm	H	H	**2a**	65	24	D	58
5	$Co_2(CO)_8$/10%	Paste[c]	No	H	H	**2a**	65	16	E	60[d]
6	$Co_2(CO)_8$/10%	Paste[c]	No	Me	H	**2b**	65	24	E	62
7	$Co_2(CO)_8$/10%	Paste[c]	No	Me	H	**2b**	100	24	E	15
8	$Co_2(CO)_8$/10%	No	1 atm	Me	H	**2b**	65	24	D	60
9	$[Rh(CO)_2Cl]_2$/2.5%	Paste[c]	No	Me	H	**2b**	100	36	F	68
10	$[Rh(CO)_2Cl]_2$/2.5%	No	1 atm	Me	H	**2b**	100	31	G	70
11	$Co_2(CO)_8$/10%	Paste[c]	No	H	*Z*-OMe	***cis*-2c**	65	48	E	62
12	$Co_2(CO)_8$/10%	No	1 atm	H	*Z*-OMe	***cis*-2c**	65	20	D	65
13	$Co_2(CO)_8$/10%	Paste	No	H	*E*-OMe	***trans*-2c**	65	48	E	71
14	$Co_2(CO)_8$/10%	No	1 atm	H	*E*-OMe	***trans*-2c**	65	24	D	73
15	$Co_2(CO)_8$/10%	Paste[c]	No	Me	*E*-OMe	***trans*-2d**	65	40	E	67
16	$Co_2(CO)_8$/10%	No	1 atm	Me	*E*-OMe	***trans*-2d**	65	24	D	63

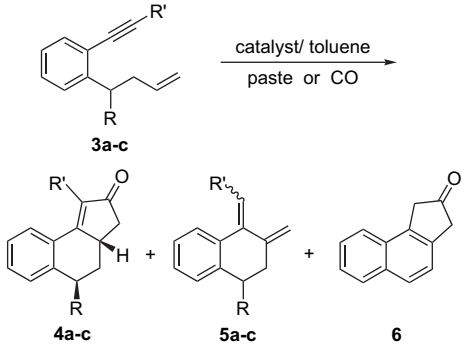
[a] M.S.: powdered 4 Å molecular sieves.
[b] Pre-CO M.S.: powdered 4 Å molecular sieves heated at 200 °C and cooled under CO in a separate flask.
[c] Paste: mixture of powdered 4 Å molecular sieves/*tert*-butanol treated with CO (see Section 4) 1 g/mmol of substrate.
[d] This reaction was repeated 2 days and 2 weeks after preparation of the paste with the following yields: 58% and 61%, respectively.

temperature (method H, entry 1) and only with molecular sieves as promoters in refluxing toluene (method I, entry 2).[21] The catalytic reactions were performed using methods D and E (with cobalt, entries 3 and 4, Table 1). The results are summarized in Table 2.

The first two entries, corresponding to the stoichiometric versions show that different reaction products were obtained depending on the reaction conditions. Thus, the hydroxy-tetraline **4a** was obtained at room temperature, while in refluxing toluene, dehydration and isomerization lead to naphthalene **6** with good yields. Compound **4a** was obtained as a single stereoisomer, which resulted to be trans-fused as shown by the NOE experiments. Entries 3 and 4 show that there are no significant differences when using our procedure and a standard catalytic method. Compound **3b** gave under catalytic conditions D and E similar yields of an only stereoisomer of **4b** (entries 5 and 6), in contrast with what we had observed in previous stoichiometric reactions where a mixture of diastereoisomers was obtained.[27] For compound **3c** elevation of the reaction temperature gave better results (entries 7–9). This compound was also reacted using rhodium catalysis, giving similar results with both methods (entries 10 and 11), although worse than with cobalt catalysis. The reaction with rhodium proceeded only at 100 °C, not observing any conversion at lower temperatures. In these aromatic compounds our procedure gives, in general, comparable although slightly lower yields than with standard conditions.

Finally we selected a bunch of substrates, including some intermolecular examples, and compared the results of our protocol (conditions E) with standard catalytic conditions D and stoichiometric conditions I (Table 3). The results show that our procedure works well with different structures and gives similar results than other catalytic protocols under CO atmosphere. In some examples (entries 2, 3, 5, and 7) stoichiometric reactions give significant better yields than both catalytic protocols. The intermolecular PKR is still limited in scope to certain strained alkenes and some allenes. We tested the reaction of norbornene with 1-hexyne and phenylacetylene (entries 5 and 6) with moderate to good results. In addition, the catalytic reaction of ethyl 2,3-butadienoate with 3-hexyne gave the desired cyclopentenone in low yield although not far from the result with stoichiometric conditions (entry 7). This latter reaction was performed in sealed tube to avoid evaporation of the starting materials.

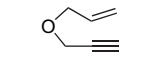
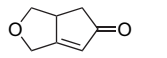
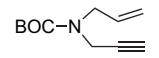
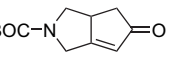
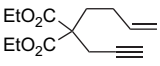
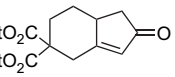
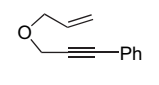
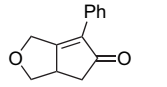
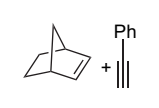
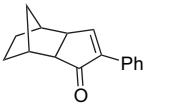
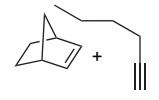
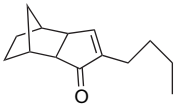
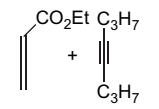
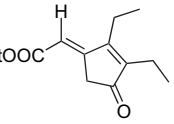
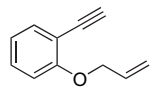
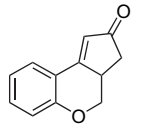
Table 2
PKR of compounds **3** in different conditions



Entry	Subs.	Method	R	R′	Temp (°C)	Yield (%)		
						4	**5**	**6**
1	**3a**	H	OH	H	rt	77	—	—
2	**3a**	I	OH	H	110	—	—	75
3	**3a**	D	OH	H	65	40	—	<5
4	**3a**	E	OH	H	65	55	—	<5
5	**3b**	D	OTBS	H	65	40	—	—
6	**3b**	E	OTBS	H	65	57	—	—
7	**3c**	D	OTBS	Me	65	24	38[a]	—
8	**3c**	D	OTBS	Me	110	65	—	—
9	**3c**	E	OTBS	Me	110	75	—	—
10	**3c**	F	OTBS	Me	100	38	—	—
11	**3c**	G	OTBS	Me	100	40	8	—

[a] Obtained as a 1:1 mixture of *Z*/*E* isomers.

Table 3
PKR of different substrates comparing our protocol with paste (conditions E) with standard conditions D and stoichiometric conditions I

Entry	Starting material	Product	Yield (%)		
			Method D	Method E	Method I
1			48	52	55
2			45	40	60
3			50	50	61
4			51	49	54
5			41	55	60
6			78	68	75
7			10	25[a]	40[a]
8			62	60	60

[a] This reaction was carried out in sealed tube.

3. Conclusion

A new easy procedure for catalytic PKR is shown. The protocol diminishes the use of CO gas in the lab and gives similar results as other procedures described in the literature. The

preparation of the paste still needs the usual safety conditions to operate with CO gas, but this mixture can be used in a different lab with only standard working conditions and the procedure allows carrying out a set of reactions at the same time. Although not reusable, one batch of this paste can be used for several reactions along, at least, 2 weeks. Different substrates including intermolecular examples can be used and the conditions work both with cobalt catalysis and rhodium complexes. The possible applications of the paste described herein to other reactions are underway.

4. Experimental

4.1. General methods

General methods have been published before.[28] The synthesis of **1a**[29] and **1b**[29] have been done according to literature procedures. Starting materials and products shown in Table 3 are also known (except that of entry 7).

4.2. Starting materials

4.2.1. (Z,E)-Diethyl 2-(3-methoxyallyl)-2-(prop-2-ynyl)-malonate, *1c*

To a suspension of 7.43 g (21.7 mmol) of methoxymethyltriphenylphosphonium chloride in THF (30 mL), 36.40 mL (18.2 mmol) of KHMDS 0.5 M was added. The mixture was stirred 30 min and was cannulated to a solution of 2.08 g (8.7 mmol) of diethyl 2-(2,2-diethoxyethyl)-2-(2-propynyl)-malonate in THF (30 mL). The mixture was stirred at room temperature for 30 min and then was poured to a mixture of diethylether–water 1:1. The organic layer was extracted, washed with water (2×60 mL) and brine (2×60 mL), dried over anhydrous $MgSO_4$ and concentrated in vacuo. Purification by flash chromatography with hexane–EtOAc 20:1 as eluent. The product was obtained (1.07 g ***E*-1c**, 0.65 g ***Z*-1c**, 82% yield) as colorless oils. *Z-isomer*: ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 6H, J=7.1 Hz), 1.99 (t, 1H, J=2.7 Hz), 2.78 (d, 2H, J=2.7 Hz), 2.83 (dd, 2H, J_1=7.7 Hz, J_2=1.1 Hz), 3.56 (d, 3H, J=2.2 Hz), 4.16–4.24 (m, 5H), 6.00 (dd, 1H, J_1=4.9 Hz, J_2=1.1 Hz). ^{13}C NMR ($CDCl_3$) δ 13.9, 22.5, 26.7, 56.7, 59.4, 61.4, 70.8, 79.1, 98.9, 149.3, 169.9. Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.51; H, 7.66. *E-isomer*: ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3H, J=7.1 Hz), 1.26 (t, 3H, J=7.1 Hz), 2.02 (t, 1H, J=2.7 Hz), 2.68 (d, 2H, J=7.7 Hz), 2.79 (d, 2H, J=2.7 Hz), 3.50 (d, 3H, J=1.6 Hz), 4.21 (q, 2H, J=7.1 Hz), 4.22 (q, 2H, J=7.1 Hz), 4.49 (dtd, 1H, J_1=12.6 Hz, J_2=7.7 Hz, J_3=1.6 Hz), 6.40 (d, 1H, J=12.6 Hz). ^{13}C NMR ($CDCl_3$) δ 13.9, 22.1, 30.3, 55.6, 57.0, 61.3, 71.2, 78.8, 94.8, 150.2, 169.6. IR (film) ν 3280, 2980, 2940, 2840, 2120, 1740, 1660 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.39; H, 7.46.

4.2.2. 1-(2-Ethynylphenyl)but-3-en-1-ol, *3a*

To a solution of 2.00 g (9.8 mmol) of 2-trimethylsilylethynylbenzaldehyde in anhydrous THF (50 mL) at −78 °C, 11.8 mL (11.8 mmol) of 1 N allylmagnesium bromide was added. The mixture was stirred 2 h at −78 °C, and the reaction was quenched with saturated NH_4Cl. The mixture was extracted with EtOAc, washed with water (2×100 mL) and brine (2×100 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under vacuo. Purification by flash chromatography with hexane–EtOAc 10:1 as eluent gave a product (1.64 g, 70% yield) as colorless oil. This product (0.31 g, 1.3 mmol) was dissolved in anhydrous THF (50 mL) at 0 °C, and 19.6 mL (19.6 mmol) of 1 N TBAF was added. The mixture was stirred at this temperature for 2.5 h and quenched with water, hexane, and diethylether. The organic layer was washed with water (2×100 mL) and brine (2×100 mL), dried over anhydrous $MgSO_4$ and concentrated under vacuo. Purification by flash chromatography with hexane–EtOAc 10:1 as eluent gave **3a** (0.18 g, 83% yield) as colorless oil. ^{1}H NMR ($CDCl_3$) δ 2.37–2.47 (m, 1H), 2.56–2.65 (m, 1H), 2.90 (br s, 1H), 3.33 (s, 1H), 5.10–5.21 (m, 3H), 5.78–5.91 (m, 1H), 7.20 (td, 1H, J_1=7.1 Hz, J_2=1.1 Hz), 7.34 (td, 1H, J_1=7.7 Hz, J_2=1.1 Hz), 7.45 (dd, 1H, J_1=7.7 Hz, J_2=1.1 Hz), 7.50 (d, 1H, J=7.7 Hz). ^{13}C NMR ($CDCl_3$) δ 42.5, 70.8, 81.3, 82.2, 117.9, 119.1, 125.2, 126.8, 129.0, 132.6, 134.4, 146.3. IR (film) ν 3400, 3295, 2940, 2100 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.40; H, 7.26.

4.2.3. tert-Butyl(1-(2-ethynylphenyl)but-3-enyloxy)dimethyl silane, *3b*

To a solution of 1.51 g (8.7 mmol) of **3a** in DMF (50 mL) at room temperature, 1.38 g (21.8 mmol) of imidazole and 2.60 g (17.4 mmol) of *tert*-butyldimethylsilyl chloride were added. The mixture was stirred 2 h and the mixture was extracted with diethylether. The organic layer was washed with water (4×50 mL) and brine (4×50 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under vacuo. Purification by flash chromatography with hexane–EtOAc 5:1 as eluent gave **3b** (2.17 g, 87% yield) as colorless oil. ^{1}H NMR ($CDCl_3$) δ −0.13 (s, 3H), 0.03 (s, 3H), 0.88 (s, 9H), 2.34–2.51 (m, 2H), 3.29 (s, 1H), 4.98 (s, 1H), 5.02 (d, 1H, J=4.4 Hz), 5.21 (dd, 1H, J_1=7.1 Hz, J_2=4.4 Hz), 5.78–5.92 (m, 1H), 7.17 (td, 1H, J_1=7.7 Hz, J_2=1.1 Hz), 7.34 (td, 1H, J_1=7.7 Hz, J_2=1.1 Hz), 7.42 (dd, 1H, J_1=7.7 Hz, J_2=1.1 Hz), 7.53 (d, 1H, J=7.7 Hz). ^{13}C NMR ($CDCl_3$) δ −5.0, −4.8, 18.2, 25.8, 44.2, 72.2, 81.5, 81.8, 116.8, 118.8, 126.1, 126.5, 128.9, 132.3, 135.2, 147.7. IR (film) ν 3300, 3060, 3950, 3920, 3850, 2100 cm^{-1}. Anal. Calcd for $C_{18}H_{26}OSi$: C, 75.46; H, 9.15. Found: C, 75.72; H, 8.99.

4.2.4. tert-Butyldimethyl(1-(2-(prop-1-ynyl)phenyl)-but-3-enyl oxy)silane, *3c*

To a solution of 0.10 g (0.42 mmol) of **3b** in anhydrous THF (4 mL) at −78 °C, 0.3 mL (0.46 mmol) of 1.6 M BuLi was added. The mixture was stirred 10 min at −78 °C, and 0.03 mL (0.46 mmmol) of iodomethane was added. The mixture was stirred 22 h at room temperature, and the reaction was quenched with saturated NH_4Cl. The mixture was extracted with diethylether (3×2.5 mL) and washed with brine (2.5 mL). The organic layer was dried over anhydrous

$MgSO_4$, filtered and concentrated under vacuo. Purification by flash chromatography with hexane as eluent gave a product (0.096 g, 80% yield) as colorless oil. ^{1}H NMR ($CDCl_3$) δ −0.13 (s, 3H), 0.03 (s, 3H), 0.89 (s, 9H), 2.09 (s, 3H), 2.33–2.51 (m, 2H), 4.99–5.05 (m, 2H) 5.17 (dd, 1H, J_1=7.7 Hz, J_2=4.4 Hz), 5.80–5.95 (m, 1H), 7.14 (t, 1H, J=7.2 Hz), 7.24–7.34 (m, 2H), 7.50 (d, 1H, J=8.2 Hz). ^{13}C NMR ($CDCl_3$) δ −5.0, −4.7, 4.4, 18.2, 25.8, 44.1, 72.4, 77.5, 90.4, 116.6, 120.7, 125.8, 126.4, 127.6, 131.5, 135.7. IR (film) ν 3060, 2950, 2920, 2850, 1640 cm^{-1}. Anal. Calcd for $C_{19}H_{28}OSi$: C, 75.94; H, 9.39. Found: C, 75.69; H, 9.16.

4.3. General procedures for the Pauson–Khand reaction

4.3.1. Method A

To a solution of 1.00 mmol of the enyne in toluene (12 mL), 0.1 mmol of $Co_2(CO)_8$ was added and the mixture was stirred at 65 °C. After filtration and solvent elimination the crude was purified and/or separated by flash chromatography (hexane–EtOAc mixtures).

4.3.2. Method B

Enyne of 1.00 mmol was dissolved in toluene (12 mL), in a flask containing two times the mass of the enyne of powdered 4 Å molecular sieves. To this solution, 0.1 mmol of $Co_2(CO)_8$ was added and the resulting mixture was submitted to three Ar-vacuo cycles and three vacuo-CO cycles. The reaction was carried out at 65 °C, under a 1 atm of CO. After filtration and solvent elimination the crude was purified and/or separated by flash chromatography (hexane–EtOAc mixtures).

4.3.3. Method C

Enyne of 1.00 mmol was dissolved in toluene (12 mL), in a flask containing two times the mass of the enyne of powdered 4 Å molecular sieves. To this solution, 0.1 mmol of $Co_2(CO)_8$ was added and the mixture was stirred at 65 °C. After filtration and solvent elimination the crude was purified and/or separated by flash chromatography (hexane–EtOAc mixtures).

4.3.4. Method D

To a solution of 1.00 mmol of the enyne in toluene (12 mL) or 1.5 mmol of alkyne, 1.00 mmol of alkene or allene, 0.10 mmol of $Co_2(CO)_8$ was added and the resulting mixture was submitted to three Ar-vacuo cycles and three vacuo-CO cycles. The reaction was carried out at 65 or 100 °C, under a 1 atm of CO. After filtration and solvent elimination the crude was purified and/or separated by flash chromatography (hexane–EtOAc mixtures).

4.3.5. Method E

Enyne of 1.00 mmol or alkyne of 1.5 mmol and alkene or allene of 1.00 mmol was dissolved in toluene (12 mL). To this solution, 0.1 mmol of $Co_2(CO)_8$ and 1 g of paste (vide infra), was added and the mixture was stirred at 65 or 100 °C. In the case of the reaction of entry 7 (Table 3), the reaction was heated in a sealed tube. After filtration and solvent elimination the crude was purified and/or separated by flash chromatography (hexane–EtOAc mixtures).

4.3.6. Method F

Enyne of 1.00 mmol was dissolved in toluene (12 mL). To this solution, 0.1 mmol of $[Rh(CO)_2Cl]_2$ and 1 g of paste (vide infra) was added and the resulting mixture stirred at 110 °C. After filtration and solvent elimination the crude was purified and/or separated by flash chromatography (hexane–EtOAc mixtures).

4.3.7. Method G

To a solution of 1.00 mmol of the enyne in toluene (12 mL), 0.1 mmol of $[Rh(CO)_2Cl]_2$ was added and the resulting mixture was submitted to three Ar-vacuo cycles and three vacuo-CO cycles. The reaction was carried out at 110 °C, under a 1 atm of CO. After filtration and solvent elimination the crude was purified and/or separated by flash chromatography (hexane–EtOAc mixtures).

4.3.8. Method H

Enyne of 1.00 mmol was dissolved in dry toluene (40 mL) at room temperature under argon, in a flask containing eight times the mass of the enyne of powdered 4 Å molecular sieves. To this solution, 1.20 mmol of $Co_2(CO)_8$ was added and the resulting mixture was stirred for 2 h until total complexation of the enyne (TLC). The reaction was then cooled to −10 °C with an ice/salt bath, and a suspension of Me_3NO (9.00 mmol) in toluene at 0 °C was added drop wise. Stirring was continued at room temperature until completion. The mixture was filtrated, the solvent was evaporated under vacuum and the crude was purified and/or separated by flash chromatography (hexane–EtOAc mixtures).

4.3.9. Method I

Enyne of 1.00 mmol was dissolved in dry toluene (40 mL) at room temperature under argon, in a flask containing eight times the mass of the enyne of powdered 4 Å molecular sieves. To this solution, 1.20 mmol of $Co_2(CO)_8$ was added and the resulting mixture was stirred for 2 h until total complexation of the enyne (TLC). The reaction was refluxed until completion. After filtration and solvent elimination the crude was purified and/or separated by flash chromatography (hexane–EtOAc mixtures).

4.3.10. Preparation of the PASTE

In a 250 mL flask, 20 g of powdered 4 Å molecular sieves was placed and 25 mL of *tert*-butanol was added. The flask was stoppered and submitted to three vacuo-CO cycles. The resulting mixture was stirred for 30 min under CO atmosphere. The flask was then kept in the fridge until used.

4.3.11. Preparation of diethyl 5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate, **2a**[29]

From 1 mmol of **1a**, yield of **2a** is as follows. Method A: 15%, method B: 30%, method C: 65%, method D: 58%,

method E: 60%. Yellow oil (hexane–EtOAc 9:1). ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 3H, J=7.1 Hz), 1.29 (t, 3H, J=7.1 Hz), 1.75 (t, 1H, J=12.6 Hz), 2.14 (dd, 1H, J_1=18.1 Hz, J_2=3.3 Hz), 2.63 (dd, 1H, J_1=18.1 Hz, J_2=6.6 Hz), 2.80 (dd, 1H, J_1=12.6 Hz, J_2=7.7 Hz), 3.10–3.15 (m, 1H), 3.26 (d, 1H, J=18.6 Hz), 3.36 (d, 1H, J=18.6), 4.21 (q, 2H, J=7.1 Hz), 4.26 (q, 2H, J=7.1 Hz), 5.94 (s, 1H). IR (film) ν 2985, 2910, 1725 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.04; H, 6.96.

4.3.12. Preparation of diethyl 6-methyl-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate, ***2b***

From 1 mmol of **1b,** yield of **2b** is as follows. Method E: at 65 °C, 62%; at 100 °C, 15%, method D: 60%, method F: 68%, method G: 70%. Yellow oil (hexane–EtOAc 7:1). ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 3H, J=7.14 Hz), 1.24 (t, 3H, J=7.14 Hz), 1.61 (t, 1H, J=12.7 Hz), 1.68 (s, 3H), 2.05 (dd, 1H, J_1=18.1 Hz, J_2=3.0 Hz), 2.61 (dd, 1H, J_1=18.2 Hz, J_2=6.6 Hz), 2.74 (dd, 1H, J_1=12.7 Hz, J_2=7.1 Hz), 2.93 (br s, 1H), 3.13 (d, 1H, J=18.6 Hz), 3.21 (d, 1H, J=19.2 Hz), 4.14–4.25 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 8.6, 14.0, 14.1, 34.0, 39.1, 41.4, 42.7, 60.9, 61.9, 62.1, 133.0, 171.0, 171.6, 117.9, 209.5. IR (film) ν 2980, 2920, 1725, 1665 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.45; H, 7.22.

4.3.13. Preparation of (3aS,4S*)-diethyl 4-methoxy-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate,* ***cis-2c***

From 1 mmol of ***Z*-1c**, yield of ***cis*-2b** is as follows. Method E: at 65 °C, 62%, method D: 65%. Colorless oil (hexane–EtOAc 7:1). ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 3H, J=7.1 Hz), 1.24 (t, 3H, J=7.1 Hz), 1.88 (dd, 1H, J_1=13.2 Hz, J_2=12.6 Hz), 2.52 (dd, 1H, J_1=12.6 Hz, J_2=7.7 Hz), 3.10–3.23 (m, 1H), 3.20 (d, 1H, J=19.2 Hz), 3.29 (dd, 1H, J_1=18.2 Hz, J_2=1.1 Hz), 3.46 (d, 3H, J=1.1 Hz), 3.72 (dd, 1H, J_1=6.1 Hz, J_2=1.6 Hz), 4.13–4.23 (m, 4H), 5.84 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 13.9, 32.0, 35.4, 48.8, 58.4, 60.1, 61.9, 62.0, 80.1, 122.7, 170.5, 171.6, 184.8, 206.7. IR (film) ν 2980, 2940, 1730, 1640 cm^{-1}. NOE: $H_{3a\beta}\rightarrow H_{4\beta}$ (11%), $H_{3\beta}\rightarrow H_{3a\beta}$ (8%). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.63; H, 6.65.

4.3.14. Preparation of (3aS,4R*)-diethyl 4-methoxy-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate,* ***trans-2c***

From 1 mmol of ***E*-1c**, yield of ***trans*-2c** is as follows. Method E: at 65 °C, 71%, method D: 73%. Colorless oil (hexane–EtOAc 7:1). ^{1}H NMR ($CDCl_3$) δ 1.15 (t, 3H, J=7.1 Hz), 1.17 (t, 3H, J=7.1 Hz), 1.88 (dd, 1H, J_1=12.6 Hz, J_2=12.1 Hz), 2.77 (dd, 1H, J_1=12.6 Hz, J_2=8.2 Hz), 2.92–2.98 (m, 1H), 3.10 (d, 1H, J=19.2 Hz), 3.24 (d, 1H, J=19.2 Hz), 3.43 (s, 3H), 3.63 (d, 1H, J=3.3 Hz), 4.10 (q, 2H, J=7.1 Hz), 4.14 (d, 2H, J=7.1 Hz), 5.86 (d, 1H, J=1.6 Hz). ^{13}C NMR ($CDCl_3$) δ 13.7, 35.2, 37.6, 50.4, 58.2, 60.4, 61.9, 62.0, 88.3, 123.6, 170.3, 170.8, 179.9, 205.4. IR (film) ν 2980, 2940, 1730, 1640 cm^{-1}. NOE: $H_{4\alpha}\rightarrow H_{3a\beta}$ (0%), $H_{3\beta}\rightarrow H_{3a\beta}$ (6%). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.67; H, 6.71.

4.3.15. Preparation of (3aS,4R*)-diethyl 4-methoxy-6-methyl-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate,* ***trans-2d***

From 1 mmol of ***E*-1d**, yield of ***trans*-2d** is as follows. Method E: at 65 °C, 67%, method D: 63%. Colorless oil (hexane–EtOAc 7:1). ^{1}H NMR ($CDCl_3$) δ 1.24 (t, 3H, J=7.14 Hz), 1.26 (t, 3H, J=7.14 Hz), 1.71 (s, 3H), 1.88 (dd, 1H, J_1=12.1 Hz, J_2=11.0 Hz), 2.82–2.94 (m, 2H), 3.11 (d, 1H, J=19.2 Hz), 3.22 (d, 1H, J=19.2 Hz), 3.52 (s, 3H), 3.65 (d, 1H, J=2.8 Hz), 4.15–4.26 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 205.7, 172.5, 171.2, 170.8, 131.8, 88.0, 62.2, 62.1, 60.8, 58.3, 49.1, 38.3, 34.1, 14.0, 8.8. IR (film) ν 2980, 2925, 1725, 1670 cm^{-1}. NOE: $H_{3a\beta}\rightarrow H_{3\beta}$ (7%), $H_{4\alpha}\rightarrow H_{3\alpha}$ (4%), $H_{4\alpha}\rightarrow OCH_3$ (2%). Anal. Calcd for $C_{16}H_{22}O_6$: C, 91.92; H, 7.15. Found: C, 91.84; H, 7.06.

4.3.16. PKR of compound ***3a***

From 1 mmol of **3a**, yield of **4a** and **6** are as follows. Method D: 40% of **4a** and **6** detected in crude, method E: 55% of **4a** and **6** detected in crude, method H: 77% of **4a**, method I: 75% of **6**.

4.3.16.1. (3aS,5R*)-5-Hydroxy-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalen-2-one,* ***4a***. Yellow oil (hexane–EtOAc 1:1). ^{1}H NMR ($CDCl_3$) δ 1.79 (td, 1H, J_1=13.7 Hz, J_2=3.3 Hz), 2.16 (dd, 1H, J_1=18.1 Hz, J_2=3.3 Hz), 2.38–2.44 (m, 1H), 2.73 (dd, 1H, J_1=18.1 Hz, J_2=6.6 Hz), 3.17 (br s, 1H), 3.52–3.58 (m, 1H), 4.92–4.93 (m, 1H), 6.36 (d, 1H, J=2.2 Hz), 7.36–7.40 (m, 1H), 7.44–7.46 (m, 2H), 7.64 (d, 1H, J=7.7 Hz). ^{13}C NMR ($CDCl_3$) δ 208.5, 174.9, 139.1, 131.6, 130.5, 129.1, 128.5, 126.6, 124.0, 66.9, 41.9, 37.1, 33.7. IR (film) ν 3390, 2910, 1690, 1665, 1595 cm^{-1}. NOE: $H_{3\beta}\rightarrow H_{3a\beta}$ (5%), $H_{5\alpha}\rightarrow H_{4\alpha}$ (4%). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.79; H, 5.89.

4.3.16.2. 1H-Cyclopenta[a]naphthalen-2(3H)-one, ***6***. Yellow solid (mp 113–116 °C) ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 2H), 3.84 (s, 2H), 7.42 (d, 1H, J=7.7 Hz), 7.46–7.57 (m, 2H), 7.68 (d, 1H, J=7.7 Hz), 7.79 (d, 1H, J=7.7 Hz), 7.88 (d, 1H, J=7.7 Hz). ^{13}C NMR ($CDCl_3$) δ 42.3, 44.8, 122.6, 124.0, 125.6, 126.6, 127.7, 128.7, 129.7, 132.5, 133.7, 134.8, 209.6. IR (KBr) ν 3060, 3940, 2250, 2050, 1750 cm^{-1}. Anal. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.45; H, 5.37.

4.3.17. PKR of compound ***3b***

From 1 mmol of **3b**, yield of **4b** is as follows. Method D: 40%, method E. 57%.

4.3.17.1. (3aS,5R*)-5-(tert-Butyldimethylsilyloxy)-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalen-2-one,* ***4b***. Yellow oil (hexane–EtOAc 19:1). ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 3H), 0.19 (s, 3H), 0.87 (s, 9H), 1.80 (td, 1H, J_1=13.2 Hz, J_2=2.7 Hz), 2.20 (dd, 1H, J_1=18.7 Hz, J_2=3.8 Hz), 2.29 (dt, 1H,

J_1=13.2 Hz, J_2=3.3 Hz), 2.79 (dd, 1H, J_1=18.7 Hz, J_2=6.0 Hz), 3.62–3.67 (m, 1H), 4.92 (t, 1H, J=2.7 Hz), 6.41 (d, 1H, J=2.2 Hz), 7.32 (d, 1H, J=7.7 Hz), 7.34–7.45 (m, 2H), 7.68 (dd, 1H, J_1=7.7 Hz, J_2=1.1 Hz). ^{13}C NMR ($CDCl_3$) δ −4.4, −4.3, 17.9, 25.7, 33.9, 38.4, 42.2, 68.1, 124.2, 126.8, 128.3, 129.3, 130.4, 131.3, 139.6, 174.9, 208.1. IR (film) ν 2950, 2920, 2880, 2850, 1690, 1595 cm^{-1}. NOE: $H_{3a\beta} \rightarrow H_{5\alpha}$ (0%). Anal. Calcd for $C_{19}H_{26}O_2Si$: C, 72.56; H, 8.33. Found: C, 72.84; H, 8.40.

*4.3.18. PKR of compound **3c***

From 1 mmol of **3c**, yield of **4c** and **5c** are as follows. Method D: at 65 °C 24% of **4c** and 38% of **5c**; at 110 °C 65% of **4c**, method E: 75% of **4c**, method F: 38% of **4c**, method G: 40% of **4c** and 8% of **5c**.

4.3.18.1. (3aS,5R*)-5-(tert-Butyldimethylsilyloxy)-1-methyl-3,3a,4,5-tetrahydro-2H-cyclopenta[a]naphthalen-2-one, **4c**.* White solid (mp 126–129 °C). ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 3H), 0.17 (s, 3H), 0.85 (s, 9H), 1.73 (td, 1H, J_1=12.6 Hz, J_2=3.5 Hz), 2.05 (s, 3H), 2.10 (dd, 1H, J_1=18.7 Hz, J_2=3.3 Hz), 2.27 (dt, 1H, J_1=13.2 Hz, J_2=2.2 Hz), 2.76 (dd, 1H, J_1=18.7 Hz, J_2=6.6 Hz), 3.41–3.49 (m, 1H), 4.89 (t, 1H, J=2.8 Hz), 7.32–7.41 (m, 3H), 7.71–7.75 (m, 1H). ^{13}C NMR ($CDCl_3$) δ −4.3, −4.2, 10.0, 18.0, 25.7, 32.5, 39.3, 40.4, 68.3, 127.8, 128.2, 130.0, 130.6, 131.2, 133.3, 140.1, 165.8, 208.8. IR (KBr) ν 2950, 2920, 2880, 2845, 1790, 1600 cm^{-1}. NOE: $H_{3a\beta} \rightarrow H_{5\alpha}$ (0%). Anal. Calcd for $C_{20}H_{28}O_2Si$: C, 73.12; H, 8.59. Found: C, 73.23; H, 8.68.

*4.3.18.2. tert-Butyl-(4-ethyliden-3-methylen-1,2,3,4-tetrahydronaphthalen-1-yloxy)dimethylsilane, **5c**. E-isomer*: yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 3H), 0.14 (s, 3H), 0.94 (s, 9H), 1.97 (d, 3H, J=7.1 Hz), 2.51 (dd, 1H, J_1=13.2 Hz, J_2=9.9 Hz), 2.74 (dd, 1H, J_1=13.2 Hz, J_2=5.5 Hz), 4.79 (dd, 1H, J_1=9.9 Hz, J_2=5.5 Hz), 5.04 (s, 1H), 5.24 (s, 1H), 6.19 (q, 1H, J=7.1 Hz), 7.20 (dd, 2H, J_1=6.1 Hz, J_2=3.3 Hz), 7.39 (dd, 1H, J_1=5.5 Hz, J_2=3.3 Hz), 7.46 (dd, 1H, J_1=5.5 Hz, J_2=3.8 Hz). ^{13}C NMR ($CDCl_3$) δ −4.7, −4.3, 16.0, 18.2, 25.9, 43.1, 70.5, 114.2, 122.0, 122.9, 126.1, 126.7, 127.4, 136.0, 136.1, 139.3, 140.1. IR (film) ν 2950, 2920, 2850 cm^{-1}. NOE: $H_{CHethyliden} \rightarrow H_5$ (23%). Anal. Calcd for $C_{19}H_{28}OSi$: C, 75.94; H, 9.39. Found: C, 75.74; H, 9.11. *Z-isomer*: yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 3H), 0.12 (s, 3H), 0.94 (s, 9H), 1.91 (d, 3H, J=7.7 Hz), 2.35–2.45 (m, 1H), 2.78 (dd, 1H, J_1=15.4 Hz, J_2=5.0 Hz), 4.67 (dd, 1H, J_1=10.5 Hz, J_2=5.0 Hz), 4.75 (s, 1H), 5.28 (s, 1H) 6.16 (q, 1 h, J=7.1 Hz), 7.25–7.26 (m, 3H), 7.47–7.50 (m, 1H). ^{13}C NMR ($CDCl_3$) δ −4.6, 15.4, 18.3, 25.9, 40.4, 68.7, 106.7, 121.5, 123.4, 125.8, 126.1, 126.4, 126.7, 127.7, 129.5, 131.5. IR (film) ν 2950, 2920, 2850 cm^{-1}. Anal. Calcd for $C_{19}H_{28}OSi$: C, 75.94; H, 9.39. Found: C, 75.68; H, 9.18.

4.3.19. Preparation of ethyl (2E)-(2,3-diethyl-4-oxocyclopent-2-en-1-ylidene)ethanoate

The yield of the compound is as follows. Method D: 10%, method E: at 110 °C in sealed tube, 25%, method I: 40%. Colorless oil (hexane–EtOAc 20:1). ^{1}H NMR ($CDCl_3$) δ 1.07 (t, 3H, J=7.3 Hz), 1.17 (t, 3H, J=7.9 Hz), 1.33 (t, 3H, J=7.3 Hz), 2.36 (q, 2H, J=7.3 Hz), 2.56 (q, 2H, J=7.9 Hz), 3.38 (d, 2H), 4.23 (q, 2H, J=7.3 Hz), 5.98 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 13.0, 13.4, 14.2, 17.0, 19.1, 39.3, 60.3, 111.0, 149.8, 152.3, 165.6, 166.2, 202.8. IR (film) ν 2980, 2940, 1710, 1640, 1600 cm^{-1}. NOE: $H_2 \rightarrow H_{CH_2Et}$ (6%), $H_2 \rightarrow H_{CH_3Et}$ (3%). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.51; H, 7.95.

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