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Twofold Pauson–Khand reaction of acyclic and cyclic diynes with ethylene

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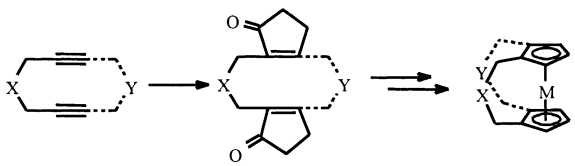
Abstract—The twofold DMSO promoted Pauson–Khand reaction of acyclic heptadiynes **1**–**3**, acyclic functionalized nonadiynediol derivatives **7**–**9** and cyclic diynes **13**–**15** with ethylene is reported.

The Pauson–Khand reaction has become a widely used procedure in organic synthesis for preparing cyclopentenones from triple bonds, olefins and a CO source.[1] Its use is often limited to reactions of terminal alkynes and strained olefins. Lately, reactions with ethylene have also been reported.[2–5] To the best of our knowledge, twofold Pauson–Khand reactions of diynes with ethylene have not been reported. To further investigate the intermolecular cobalt mediated cyclisation, we heated a solution of various heptadiyne derivatives and cyclic diynes, respectively, in toluene with 2.2 equivalents of $Co_2(CO)_8$ and ethylene (50 bar at 25°C) at 110°C for 4 days using DMSO as promotor.[6] We were interested in this reaction for preparing singly and doubly tethered cyclopentenones as starting materials for *ansa*-metallocenes,[7] as indicated in Scheme 1.

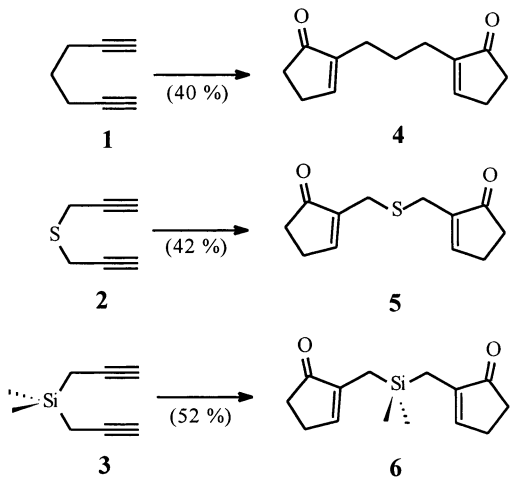
The reaction of 1,6-heptadiyne (**1**),[8] 4-thiahepta-1,6-diyne (**2**)[9] and 4,4-dimethyl-4-silahepta-1,6-diyne (**3**)[10] affords in a highly stereospecific reaction the corresponding biscyclopentenone derivatives **4**–**6** (Scheme 2) in yields between 40 and 52%.[11] It is interesting to note that the corresponding ethers and azacompounds, 5-oxahepta-1,6-diyne[12] and 5-isopropyl-5-azahepta-1,6-diyne,[13] did not yield Pauson–Khand products.



Scheme 1.

Because propargylic alcohols tend to show instability under Pauson–Khand conditions,[14] we tested several protecting groups[15] such as tetrahydropyranyl (thp), *tert*-butyldiphenylsilyl (tbdps) and *tert*-butyldimethylsilyl (tbdms), respectively, and found that the tbdms group is superior (Scheme 3). The yields obtained in this highly stereospecific synthesis varied between 22% (**12**) and 40% (**10**).[16]

Applying the Pauson–Khand protocol to cyclic diynes such as cyclotetradeca-1,8-diyne (**13**),[17] 1-thiacyclotetradeca-4,11-diyne (**14**)[18] and cyclotetradeca-4,11-diynone (**15**)[19] (Scheme 4) led to a mixture of the isomeric twofold bridged biscyclopentenones **16**–**18**.[20] The yields for this reaction varied considerably.



Scheme 2.

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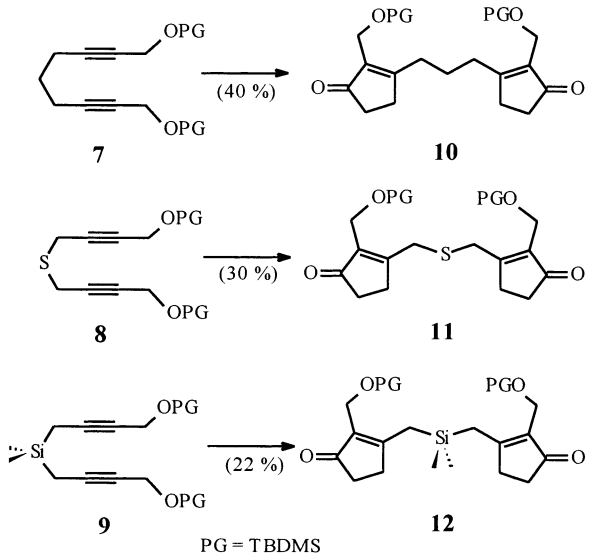
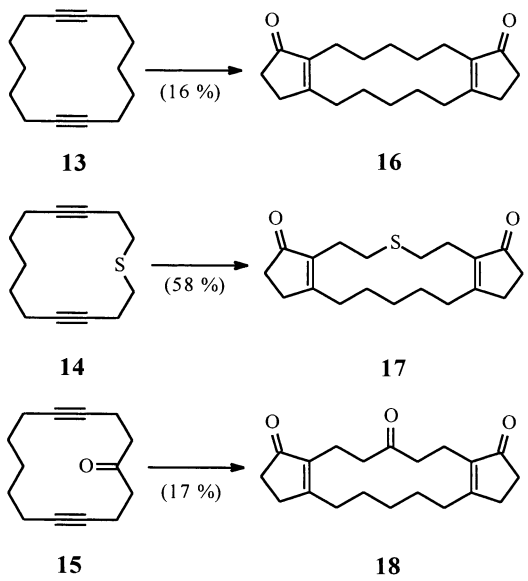


Scheme 3.



Scheme 4.

In summary we successfully established the twofold Pauson–Khand reaction of terminal and internal alkynes with ethylene. By this we managed to create promising precursors for the synthesis of twofold bridged *ansa*-metallocenes.

Acknowledgements

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11. **4**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.68$ (2H, CH_2), 2.18 (4H, CH_2) 2.37 (4H, CH_2), 2.55 (4H, CH_2), 7.33 (2H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=25.1$, 26.3, 27.2, 35.3 (CH_2), 146.4, 158.5 (C_{olef}), 210.7 (CO). Anal. calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.26; H, 7.78. **5**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=2.43$ (4H, CH_2), 2.61 (4H, CH_2), 3.22 (4H, CH_2), 7.55 (2H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=25.2$, 26.5, 34.6 (CH_2), 142.5, 159.9 (C_{olef}), 208.3 (CO). Anal. calcd for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35; S, 14.42. Found: C, 64.76; H, 6.39; S, 14.39. **6**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-0.09$ (6H, CH_3), 1.61 (4H, CH_2), 2.33 (4H, CH_2), 2.51 (4H, CH_2), 7.15 (2H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-2.7$ (CH_3), 13.4, 27.0, 34.6 (CH_2), 143.9, 155.8 (C_{olef}), 210.4 (CO). Anal. calcd for $C_{14}H_{20}O_2Si$: C, 67.69; H, 8.12. Found: C, 67.48; H, 8.12.
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16. **10**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.06$ (12H, CH_3), 0.88 (18H, CH_3), 1.32–1.40 (2H, CH_2), 2.09–2.14 (4H, CH_2), 2.30–2.33 (4H, CH_2), 2.55 (4H, CH_2), 4.49 (4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-5.4$ (CH_3), 18.3 (C), 23.1 (CH_2), 25.9 (CH_3), 26.9, 27.0, 34.0, 61.1 (CH_2), 138.7, 172.1 (C_{olef}), 210.7 (CO). HRMS (FAB): 493.3198 (+2.8 mmu). **11**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.10$ (12H, CH_3), 0.91 (18H, CH_3), 2.38–2.41 (4H, CH_2), 2.63 (4H, CH_2), 3.33 (4H, CH_2), 4.63 (4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-5.3$ (CH_3), 18.4 (C), 23.9 (CH_2), 26.0 (CH_3), 27.3, 34.0, 61.6 (CH_2), 135.8, 174.6 (C_{olef}), 208.2 (CO). HRMS (FAB): 511.2762 (+2.8 mmu). **12**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-0.11$ (6H, CH_3), 0.08 (12H, CH_3), 1.65 (4H, CH_2), 2.33–2.36 (4H, CH_2), 2.58 (4H, CH_2), 4.45 (4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-5.3$, -2.4 (CH_3), 12.7 (CH_2), 18.4 (C), 26.0 (CH_3), 27.0, 33.9, 61.5 (CH_2), 137.0, 167.8 (C_{olef}), 209.6 (CO). HRMS (FAB): 537.3263 (+1.1 mmu).

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18. **14**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.43$–1.54 (4H, CH_2), 1.81–1.89 (2H, CH_2), 2.18–2.24 (4H, CH_2), 2.46–2.52 (4H, CH_2), 2.74 (4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.7$, 18.9, 26.7, 28.1, 31.4 (CH_2), 79.3, 82.4 (C). HRMS (EI): 206.1129 (+1.8 mmu).
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20. **16**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.24$ (4H, CH_2), 1.46 (4H, CH_2), 1.63 (4H, CH_2), 2.14 (4H, CH_2), 2.35 (4H, CH_2), 2.40 (4H, CH_2), 2.46 (4H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 23.9$, 26.5, 27.2, 28.4, 29.3, 30.3, 34.9 (CH_2), 141.3, 174.2 (C_{olef}), 211.1 (CO). HRMS (EI): 300.2089 (±0 mmu). **17**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.23$–1.30 (2H, CH_2), 1.45–1.50 (2H, CH_2), 1.60–1.68 (2H, CH_2), 2.14–2.19 (2H, CH_2), 2.35–2.51 (12H, CH_2), 2.61–2.65 (6H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 23.1$, 24.2, 26.4, 27.1, 28.1, 28.6, 28.9, 29.0, 29.2, 30.2, 31.2, 34.3, 34.5 (CH_2), 139.3, 141.0, 171.0, 174.4 (C_{olef}), 209.8, 210.0 (CO). HRMS (EI): 318.1653 (−0.1 mmu). **18**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.02$–1.19 (2H, CH_2), 1.27–1.31 (2H, CH_2), 1.57–1.63 (2H, CH_2), 2.10–2.15 (2H, CH_2), 2.32–2.49 (12H, CH_2), 2.61–2.66 (6H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 17.5, 23.3, 25.7, 26.2, 26.7, 27.5, 28.3, 28.4, 28.5, 29.5, 33.9, 39.6, 40.1 (CH_2), 139.5, 140.4, 170.3, 173.8 (C_{olef}), 208.1, 209.7, 209.9 (CO). HRMS (EI): 314.1879 (+0.3 mmu).