Visible light driven room temperature Pauson–Khand reaction†

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Received 11th June 2009, Accepted 12th August 2009

First published as an Advance Article on the web 24th August 2009
DOI: 10.1039/b911228f

Visible light driven decarbonylation of [(μ₂-alkyne)Co₂(CO)₈] complexes enables the formation of cyclopentenones in good yields at ambient temperatures.

The Pauson–Khand reaction (PKR),¹ ² the [2+2+1] co-cyclisation of an alkene, an alkyne and CO, is a powerful transformation in the construction of cyclopentenones,³ ⁴ not least because of the high levels of regio-⁵ stereo-selectivity (using chiral ligands)⁶ ⁷ that can be achieved. Its versatility is manifested in its frequent application in the synthesis of natural products⁸ and pharmaceutically active compounds,⁹ ¹0 ¹1 e.g. prostaglandins.⁶ ¹0 ¹1

The PKR is typically stoichiometric in terms of the metal carbonyl complex (e.g. [Co₂(CO)₈]),¹ which provides both a coordinative framework for formation of the cyclopentenone ring and the CO that is inserted in the ring. The reaction can proceed catalytically at high CO pressures, however the initial step, CO loss from the [(μ₂-alkyne)Co₂(CO)₈] complex, necessitates elevated temperatures, microwave radiation¹² or ultrasound.¹³ Decarbonylation can be accelerated using stoichiometric reagents, e.g. N-oxides, amines etc.,¹⁴ allowing the catalysed reaction to proceed at reduced temperatures. The benefit of this is often negated by the subsequent need to remove the additive, although this can be circumvented by immobilising the additive on a polymer support.¹⁵ The key challenge therefore is to achieve decarbonylation at ambient temperatures without the use of chemical additives.

Photochemical activation is an especially attractive alternative to the use of chemical additives to promote the catalysed PKR. That this is possible was demonstrated two decades ago by Brown and co-workers,¹⁶ albeit with UV light (300 nm) and elevated temperatures. Subsequent efforts to use light activated decarbonylation to drive the PKR have required the concomitant use of additives and/or high temperatures.¹⁷ ¹⁸ Pagenkopf and Livinghouse¹⁷ have demonstrated the potential viability of a photochemically driven intramolecular version of the PKR using 1 atm of CO, albeit still requiring elevated temperatures (50–55 °C).

Here we report the first example of an intermolecular PKR driven solely by visible light at ambient temperatures, and in the absence of additives. The alkynes trimethylsilylacylene and ethynylferrocene complexed to dicobalt hexacarbonyl were converted to their corresponding functionalised cyclopentenone products under visible irradiation at room temperature. In sharp contrast to earlier studies,⁹ ¹⁶ the present system does not require increased temperatures and/or high photon flux to achieve efficient formation of the desired cyclopentenone product. Furthermore, as in the thermal or additive promoted reactions, the bulky substituents on the alkyne dictate the regiochemistry of the reaction and in the case of 1b (Scheme 1) allows for subsequent functionalisation.

Scheme 1 Photochemically assisted intermolecular Pauson–Khand [2+2+1] cycladdition of norbornene to [(μ₂-alkyne)Co₂(CO)₈] complexes (1a and 2a) to form derivatised cyclopentenones 1b and 2b.

The reaction of the [(μ₂-alkyne)Co₂(CO)₈] complexes 1a¹⁶ and 2a to the cyclopentenones 1b and 2b (trimethylsilyl- and ferrocenyltricyclo[5.2.1.0²⁸]deca-4,8-dien-3-one, respectively) were carried out in toluene and in hexane under CO (1 atm) and with excess norbornene (Table 1). Conversion was accompanied by a marked colour change from deep green to brown and deep red to pale yellow for the ferrocenyl and TMS derivatives, respectively. Full conversion of the hexacarbonyl alkyne complex was observed within 45 h.¹⁹

The products 1b and 2b were purified by column chromatography and characterised by standard methods and, in the case of 1b, by X-ray crystallography (see ESI†). The moderate yield of the cyclopentenone products is not unexpected as, as reported previously by Horn and Senge²⁰ and Tam and co-workers,²¹ large substituents on the reacting alkyne, although enhancing regioselectivity, retard the volume demanding PKR.

<table>
<thead>
<tr>
<th>Table 1 Reaction of 1a and 1b to form the TMS (1b) and ferrocenyldicyclo[5.2.1.0²⁸]deca-4,8-dien-3-one derivatives in toluene</th>
<th>Isolated yield (%)</th>
<th>endo/exo ratio</th>
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<tbody>
<tr>
<td>1b</td>
<td>78 (59)</td>
<td>3 : 97 (2 : 98)</td>
</tr>
<tr>
<td>2b</td>
<td>78 (23)</td>
<td>2 : 98 (2 : 98)</td>
</tr>
</tbody>
</table>

† Electronic supplementary information (ESI) available: Experimental methods and syntheses, spectoscopic data for photosubstitution reactions. CCDC reference number 699252. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b911228f

References

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3. a. A. Livinghouse. 
4. b. A. Coleman et al. 
5. c. A. Coleman et al.
The molecular structure of the 2b was determined by single crystal X-ray diffraction from a crystal grown from a pentane-CH₂Cl₂ solution (Fig. 1). As expected for the PKR the exo-isomer is formed, which has been ascribed to the preferential electrophilic addition to norbornene from the exo direction, and to other factors including steric and torsional strain. The molecular structure of the trimethylsilyl functionalised cyclopentenone 1b was reported previously.  

Matrix isolation studies have demonstrated that UV and near UV irradiation of [(μ-alkyne)Co₂(CO)₆] complexes can provide access to two distinct photochemical pathways: Co–Co bond homolysis and reversible CO loss (in an argon matrix, τ_CO = 390 nm). Although the former process, Co–Co bond homolysis, is considered to be an energy wasting process due to the rapid rate of Co–Co recombination, the latter process, that of CO loss, is widely accepted to be the key initial step in the PKR, as proposed originally by Magnus and co-workers. In addition theoretical studies by Platts and co-workers suggest that in terms of Co–Co bond cleavage these systems may be viewed electronically as possessing singlet diradical character while computational studies of these systems with various substituents on the acetylene have indicated that the substituents attached may have an important impact on the regiochemistry observed. From a photochemical perspective, although the promotion of the PKR with visible light is unexpected, earlier matrix isolation studies by Gordon and co-workers at <20 K indicated that such photochemical promotion of the PKR may be feasible.

In the present study verification that irradiation with visible light results in decarbonylation of the cobalt complexes was obtained using triphenylphosphine as a trapping ligand (see ESIF). Heating of 1a/2a in the presence of PPh₃ results in formation of the monosubstituted complex followed by disubstitution. Similarly, irradiation with visible light lead to initial generation of the monosubstituted complex [(μ-alkyne)Co₂(PPh₃)₂(CO)₄] and subsequently the disubstituted species [(μ,ο-alkyne)Co₂(PPh₃)₃(CO)₃]. However, in the case of 2a irradiation at λ > 500 nm provided the monosubstituted pentacarbonyl species only and not the tetracarbonyl complex (see ESIF).

In summary, we report the first example of visible light-driven highly-regioselective formation of cyclopentenones, i.e. 1b and 2b, at ambient temperatures and without the addition of decarbonylation agents. Importantly the TMS group of the product 1b allows for subsequent modification at the α-position of the cyclopentenone formed allowing for further generation of biologically active systems, while, as shown by, Dong and co-workers, the electrochemical and photochromic properties of ferrocenyl-cyclopentenone and cyclopentenediones show considerable potential in developing complex biologically active molecules. Furthermore the recent report by Fairlamb and coworkers on the potential application of these complexes as in vivo CO delivery agents together with the present results open the possibility of application to photodynamic therapies. Future studies will be directed towards developing a photochemically driven catalytic variant of the PKR reaction.

Acknowledgements

We thank Dublin City University, the Netherlands Science Organisation (NWO, ‘VIDI’ WRB), NanoNed (ACC, BLF), NRSCC (BLF) for financial support.

Notes and references

† Crystallographic data for 2b: (a) C₂₀H₂₀FeO (M_r = 332.22), triclinic, space group P1, a = 8.7216 (12), b = 10.2643 (14), c = 10.3445 (14) Å, α = 60.6714 (14)°, β = 88.8587 (16)°, γ = 69.6825 (15)°, V = 743.79 (15) Å³, Z = 2, D_x = 1.483 g cm⁻³, μ = 10.12 cm⁻¹, T = 100 K, GOF = 1.107, wR(F) = 0.0874 for 3536 unique reflections from 6709 measured reflections, R(F) = 0.0344 for 3182 reflections, R_p = 0.0215, crystal size = 0.47 × 0.39 × 0.33 mm; (b) CCDC 699252 contains the supplementary crystallographic data for this paper. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b911228f


For the samples irradiated using sunlight, complete conversion was observed to the cyclopentenone after 1 month and 2 months for the ferrocenyl and TMS-derivatives, respectively.

20 Source: Kodak Ektapro 3000 Slide Projector with a 82 V/300 W/35 h halogen lamp.


