

Note

Carbonylative dimerisation of norbornene by cobalt carbonyl: an overlooked by-product of the Pauson–Khand reaction

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Received 4 September 2003; accepted 20 November 2003

Abstract

Treatment of norbornene with either dicobaltoctacarbonyl or with preformed alkyne-dicobalthexacarbonyl complexes gives enol-lactone dimer **3**, derived from carbonylative coupling of two molecules of norbornene. This product which has not been recorded before under these conditions appears likely to be an overlooked by-product of many Pauson–Khand reactions.

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Keywords: Cobalt; Pauson–Khand; Alkene dimerisation; Carbonylation

1. Introduction

The Pauson–Khand (PK) reaction, or Khand cyclisation [1], the $\text{Co}_2(\text{CO})_8$ -mediated cyclisation of an alkyne and alkene and CO, is of interest due to easy carbon–carbon bond formation, often with high regio- and stereo-control. Many variations have been developed including the use of catalytic cobalt [1c], other cobalt sources [1d], other metals [1e], heterometallic clusters [1f] and asymmetric variations based on either chiral ligands on metals [1g,1h] or chiral auxiliaries on the substrates [1i].

2. Results and discussion

We are interested in axial chirality [2a] and PK reactions of unusual substrates [2b] and decided to investigate PK reactions of binaphthyls. The simplest approach seemed to be to synthesis the bi-propargyl ether of BINOL, **1** [3], which was easily realised by treatment of BINOL with propargyl bromide in acetone with potassium carbonate at reflux. The derived cobalt carbonyl complex **2** was simply synthesised by treatment of **1** with two equivalents of $\text{Co}_2(\text{CO})_8$, to give a red oil with the characteristic IR stretches associated with coordinated CO. It appeared that, both alkynes had reacted to give the

dicobalthexacarbonyl complexes as the signal assigned in the ^1H NMR to the alkynyl proton at 2.15 ppm had been replaced by one at 5.59 ppm, and this was further confirmed by mass spectrometry which showed a molecular ion peak at m/z 951 representing $(\text{M} + \text{NH}_4^+)$ under electrospray conditions. Under fast atom bombardment (FAB), although the molecular ion is not observed, a series of lower mass ions corresponding to the loss of carbonyls is observed starting at M-3CO and continuing with strong ions until the M-12CO ion, showing the loss of all the carbonyl ligands leaving the C_2Co_2 cluster intact, which we have not often seen in such complexes.

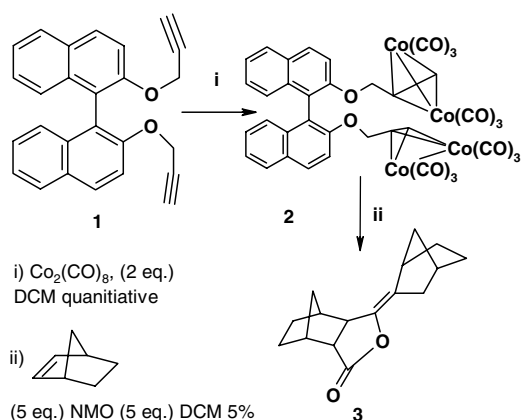
We attempted the PK reaction of **1** with norbornene, one of the commonest alkenes for the intermolecular PK reaction. Treatment of the derived dicobalthexacarbonyl complex **2**¹ with norbornene at room temperature, at 80°

¹ Red oil (R_f 0.80 DCM): δ_{H} (250 MHz; CDCl_3), 7.89 (d, $J = 8.7$ Hz, 1H Ar–H), 7.79 (d, $J = 7.4$ Hz, 1H, Ar–H), 7.39–7.08 (m, 4H, 4 × Ar–H), 5.59 (s, br, 1H, Co_2C_2 –H), 5.10 (d, $J = 13.0$ Hz, 1H, 1/2 × O–CH₂ AB), 4.94 (d, $J = 13$ Hz, 1H, 1/2 × O–CH₂ AB), δ_{C} (250 MHz CDCl_3), 197–199 (very broad, 6 × CO), 152.9, 133.1, 133.0, 128.9, 128.4, 126.8, 125.3, 124.3, 122.9, 120.1, 115.5, 70.8, 69.9. ν_{max} (thin film) 2092, 2051, 2011, 1624, 1589 cm^{-1} . m/z (%): (ES+) 951.8 ($\text{M} + \text{NH}_4^+$) (8), 803 (10), 798 (22), 770 (6), 748 (8), 666 (100). FAB 849 (M-3CO) (36), 737 (M-7CO) (52), 709 (M-8CO) (37), 681 (M-9CO) (54), 653 (M-10CO) (31), 625 (M-11CO) (48), 598 (M-12CO) (93), 539 (M-Co-12CO) (19), 480 (M-2Co-12CO) (30), 441 (M-2Co-12CO-C₃H₃) (42), 402 (M-2Co-12CO-2C₃H₃) (100). HRMS ES+ $\text{C}_{38}\text{H}_{22}\text{NO}_{14}\text{Co}_4$ ($\text{M} + \text{NH}_4^+$) requires 951.8363. Found: 951.8355; FAB $\text{C}_{35}\text{H}_{18}\text{O}_{11}\text{Co}_4$ (M-3CO) requires 849.8172. Found: 849.8182.

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or at reflux in toluene gave none of the expected cyclopentenone product, however, under NMO [1] promotion we recovered a small amount of a product (Scheme 1) previously assigned by several groups [4–6] as the enol-lactone **3**².

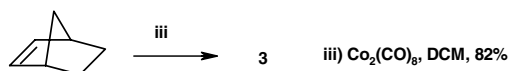
Formation of **3** from norbornene with high pressures of carbon monoxide and palladium or cobalt catalysts [4–6] is precedented, however, we believe that this is the first report of the formation of **3** from the reaction of norbornene with an alkyne dicobalthexacarbonyl complex. Further investigation showed that, the reaction³ of $\text{Co}_2(\text{CO})_8$ itself with norbornene in dichloromethane under an inert atmosphere at ambient temperature and pressure gave **3** in an isolated yield of 82% as a mixture



Scheme 1.

² **3** Colourless oil (R_f 0.58 DCM): δ_{H} (400 MHz; CDCl_3), 3.02 (s, br), 2.77 (s, br), 2.89 (approx. d, $J = 8.0$ Hz), 2.72 (m), 2.61 (s, br), 2.58 (approx. q, $J = 4.0$ Hz), 2.41 (s, br), 2.37 (approx. q, $J = 5.5$ Hz), 2.17 (approx. d, $J = 15$ Hz), 2.06 (approx. dd, $J = 15.0, 4.0$ Hz), 1.89 (approx. d, $J = 16.5$ Hz), 1.80 (approx. d, $J = 16.0$ Hz), 1.73 (approx. dd, $J = 15.0, 2.5$ Hz), 1.55 (m), 1.22 (m), 1.76 (approx. dq, $J = 7.5, 2.0$ Hz) (the already complex spectrum is further complicated by the presence of two double bond isomers. This led to incomplete proton assignments and supernumerary peaks in proton and carbon), δ ^{13}C (100 MHz, CDCl_3): 177.8, 142.7, 142.2, 121.1, 121.0, 49.3, 49.1, 45.5, 45.3, 43.2, 41.0, 40.9, 40.6, 40.3, 40.1, 39.8, 37.0, 36.7, 35.8, 35.7, 34.5, 34.4, 29.6, 29.5, 28.6, 28.4, 28.1, 27.7, 27.6. ν_{max} (thin film) 2955, 1781, 1714 cm^{-1} . m/z (%): (EI) 244 (19, M^+), 215 (100), 178 (9), 122 (12), 93 (64), HRMS (ES+). Found: 262.1807, expected 262.1810 for $\text{C}_{16}\text{H}_{24}\text{NO}_2$ ($\text{M} + \text{NH}_4$).

³ To DCM (20 ml) (freshly distilled from CaH_2 degassed by three freeze–pump–thaw cycles) under an atmosphere of dry Ar in a Schlenk type flask equipped with a magnetic stirring bar and attached to a double manifold line was added $\text{Co}_2(\text{CO})_8$ (382 mg, 1.12 mmol) stirred until dissolution was complete then treated with norbornene (528 mg, 5.62 mmol). The system was sealed and the flask wrapped in aluminium foil to exclude light and stirred for 20 h at ambient temperature. The volatiles were then removed under high vacuum and the residue dissolved in DCM (15 ml) treated with silica (3 g) opened to the atmosphere and stirred vigorously for 1 h, filtered through a pad of celite, washed with DCM (20 ml) and evaporated to dryness. Chromatography (60–80 ml of petroleum ether then DCM) gave **3** (224 mg, 82%).

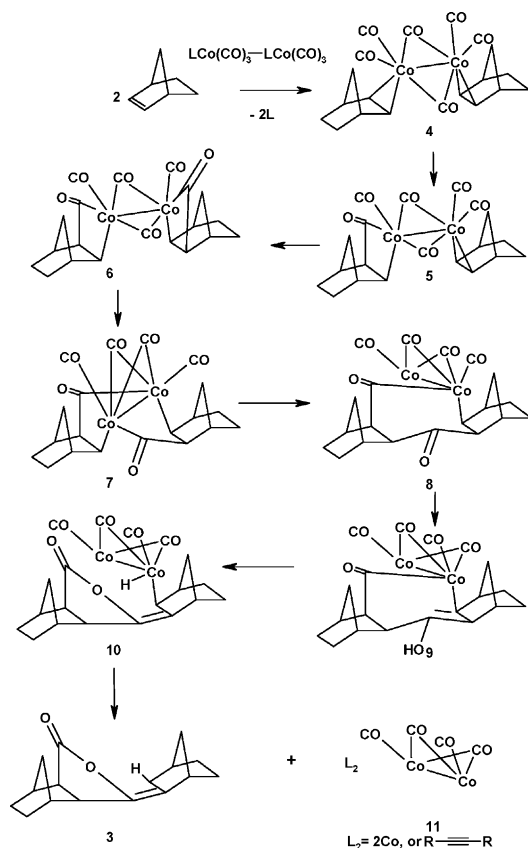


Scheme 2.

of olefin isomers, in line with the literature precedent [4,5] (Scheme 2).

2.1. Mechanism

The mechanism of the formation of enol-lactones from alkenes and CO under metal hydride catalysis is straightforward and a similar formation of enol-lactones (in the form of bifurandione) from the carbonylation of alkynes [7], at high pressure of CO has been reported, however, this reaction differs mechanistically from the present enol-lactone formation as no movement of hydrogen is involved. Similarly alkylidene lactones (as their metal complexes) are isolated from the addition of CO at high pressure to acetylene-dicobalthexacarbonyl complexes [8], again however, no hydrogen migration is involved. The formation of enol-lactone **3** however, both under high pressure of CO and with stoichiometric $\text{Co}_2(\text{CO})_8$ requires an additional mechanistic step in which an hydrogen, either as hydride or proton is transferred. Clearly this transfer is trivial in metal-hydride catalysed reactions, however, our reaction conditions were designed to avoid the formation of cobalt hydride, with the exclusion of light, moisture and any Lewis base strong enough to promote the disproportionation of $\text{Co}_2(\text{CO})_8$ which is known to generate anions [9] which in the presence of proton sources give cobalt hydrocarbonyl [10]. Although we attempted to prevent Co–H formation in itself this does not disprove such a mechanism. As cobalt hydrides are known to catalyse the formation of **3** from norbornene and CO, however, if such a species were involved we should see evidence for the super-stoichiometric formation of **3** w.r.t. $\text{Co}_2(\text{CO})_8$ if CO is present. To test this mechanism we repeated the reaction under conditions which if a free cobalt hydride was generated should have allowed the catalytic formation of **3** from norbornene. Repeating the reaction under either one atmosphere or a medium pressure (42 bar) of carbon monoxide gave no enhancement in the yield of **3** w.r.t. $\text{Co}_2(\text{CO})_8$ over 2 runs under each conditions, suggesting that $\text{Co}_2(\text{CO})_8$ is the reactive species rather than merely a source of CO for a reaction catalysed by, for example, a trace cobalt hydride impurity mimicking the precedented CoH catalysis [5]. A mechanism is, therefore, required which explains the formation of a product in which a hydrogen has moved without the formation of free cobalt hydrides. Our tentative mechanistic proposal (Scheme 3) is that two molecules of norbornene bind to the dicobalthexacarbonyl



Scheme 3.

fragment provided either by dicobaltoctacarbonyl or an alkyne dicobalthexacarbonyl complex to give a species **4** similar to the known and crystallographically characterised norbornadiene complex, in which each molecule of the alkene binds to a different cobalt, with two bridging carbonyls and the remaining coordination sites occupied by terminal carbonyls [11]. The complex then forms two new C–C bonds by two successive carbonyl insertions analogous to the accepted mechanism of the PK reaction [1] to give the bimetallo-cyclic species **6**. Each cobalt then inserts into the Co–C(O) bond which has been formed to the other cobalt to give the species **7** in which the two 4-membered rings of **6** have been expanded to 5-membered rings, with concomitant loss of ring-strain. Mechanistically this looks unusual but is a double example of a familiar process and links the two parent norbornene skeleta to the same metal centres. Reductive elimination of one of the cobalts forms the first new C–C bond, linking the norbornylenes via a ketone bridge **8**. Enolisation to **9** followed by alcoholysis of the cobalt acyl gives hydride **10** which we believe must rapidly undergo reductive elimination to give **3** and reform a cobalt carbonyl species possibly including the original ligands (L_2 i.e., alkyne or CO depending upon whether this reaction was performed with free $\text{Co}_2(\text{CO})_8$ or a cobalt carbonyl-alkyne complex). This mechanistic

hypothesis explains the formation of the enol-lactone, with a reasonable pathway for the transfer of a hydrogen from one carbon of the starting norbornylene to another and accounts for the fact that no catalytic activity is observed from the cobalt, as the cobalt hydride species is very short lived. Under very high pressures of CO it is reasonable that $\text{Co}_2(\text{CO})_8$ would be reformed from the cobalt by-product (as is known to be the case in the PK reaction [1]), and thus the reaction could become catalytic in Co [6].

3. Conclusion

Even though our results indicate that the yield of **3** from the reaction of norbornene with preformed dicobalthexacarbonyl alkyne complexes is very low, it is surprising that the formation of **3** in PK reactions has not been previously noted. It is common for a slight excess of $\text{Co}_2(\text{CO})_8$ to be used, and norbornene is commonly used in large excess [1], making it impossible but to conclude that **3**, at least in trace quantities, is routinely being overlooked even in successful PK reactions.

Acknowledgements

We thank Dr. Athanasia Dervisi (Cardiff University) for the high pressure work, the ERASMUS scheme for support (EN) and the EPSRC national mass spectrometry service at Swansea for accurate mass measurements and for the mass spectrometry on the particularly testing Co_4 species.

References

- [1] (a) P.L. Pauson, *Tetrahedron* 41 (1985) 5855;
- (b) A.J. Fletcher, S.D.R. Christie, *J. Chem. Soc., Perkin Trans. 1* (2000) 1657;
- (c) N. Jeong, S.H. Hwang, Y. Lee, Y.K. Chung, *J. Am. Chem. Soc.* 116 (1994) 3159;
- (d) S.-W. Kim, S.U. Son, S.S. Lee, T. Hyeon, Y.K. Chung, *Chem. Commun.* (2001) 2212;
- (e) T. Kobayashi, Y. Koga, K. Narasaka, *J. Organomet. Chem.* 624 (2001) 73;
- (f) D.T. Rutherford, S.D.R. Christie, *Tetrahedron Lett.* 39 (1998) 9805;
- (g) A.M. Hay, W.J. Kerr, G.G. Kirk, D. Middlemiss, *Organometallics* 14 (1995) 4986;
- (h) A.R. Kennedy, W.J. Kerr, D.M. Lindsay, J.S. Scott, S.P. Watson, *J. Chem. Soc., Perkin Trans. 1* (2000) 4366;
- (i) S. Fonquerna, A. Moyano, M. Pericas, A. Riera, *J. Am. Chem. Soc.* 119 (1997) 10225;
- (j) S. Shambayati, W.E. Crowe, S.L. Schreiber, *Tetrahedron Lett.* 31 (1990) 5289.

- [2] (a) M.P. Coogan, S. Passey, J. Chem. Soc., Perkin Trans. 1 (2000) 2060;
(b) M.P. Coogan, L.S. Stanton, T. Walther, J. Organomet. Chem. 677 (2003) 125.
- [3] S. Dhanalekshmi, K.K. Balasubramanian, C.S. Venkatachalam, Tetrahedron 50 (1994) 6387.
- [4] D. Roberto, M. Catellani, G.P. Chiusoli, Tetrahedron Lett. 29 (1988) 2115;
T. Kawaguchi, M. Kanno, T. Yanagihara, Y. Inoue, J. Mol. Catal. A 143 (1999) 253.
- [5] M. Lakshmi, N. Rao, M. Periasamy, J. Organomet. Chem. 553 (1998) 91.
- [6] Y. Colleuille, P. Perras, French Patent FR1,352,841, Chem. Abs. 1964, 35 593a.
- [7] J.C. Sauer, R.D. Cramer, V.A. Engelhardt, T.A. Ford, H.E. Holmquist, B.W. Houk, J. Am. Chem. Soc. 81 (1959) 3677.
- [8] H.W. Sternberg, J.G. Shukys, C.D. Donne, R. Markby, R.A. Friedel, I. Wender, J. Am. Chem. Soc. 81 (1959) 2339.
- [9] I. Wender, H.W. Sternberg, M. Orchin, J. Am. Chem. Soc. 74 (1952) 1216.
- [10] H.W. Sternberg, I. Wender, R.A. Friedel, M. Orchin, J. Am. Chem. Soc. 75 (1953) 2717.
- [11] S. Swaminathan, L. Lessinger, Cryst. Struct. Commun. 7 (1978) 621.