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A novel chlorotris(triphenylphosphine)rhodium(I) mediated intramolecular C–C bond forming reaction

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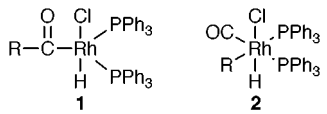
A novel Wilkinson's catalyst-mediated carbon–carbon bond forming reaction is described which is exemplified by the synthesis of the polycyclic compounds 14 and 18 from the keto aldehydes 13 and 17.

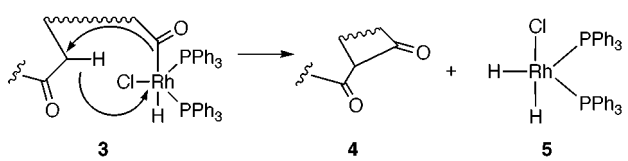
Transition metal mediated reactions leading to the formation or rupture of the C–H and C–C bonds of organic substrates constitute an area of research of wide importance.[1] In particular those involving C–H activation and decarbonylation of the CO(H) moiety of aldehydes are of considerable interest.[2] Chlorotris(triphenylphosphine)rhodium (I) (Wilkinson's catalyst) is a versatile catalyst for reactions such as hydrogenations,[3] hydrosilylations,[4] hydroformylations,[5] hydroborations,[6] isomerisations,[7] oxidations[8] and cross coupling reactions.[9] The stoichiometric homogeneous decarbonylation of aldehydes using Wilkinson's catalyst is a very useful synthetic transformation. It has been proved beyond doubt that decarbonylation of aldehydes by Wilkinson's catalyst proceeds *via* a stepwise mechanism[10] through an acyl rhodium hydride intermediate **1** and the alkyl rhodium hydride intermediate **2**.



1 **2**

The potential utility of the acyl rhodium hydride intermediate **1** in a variety of reactions, such as hydroacylations (addition to olefins) and the synthesis of organocarbonyl complexes,[11] is currently being intensely studied. We anticipated that the acyl-rhodium hydride intermediate **3** might undergo an intramolecular C–C bond formation (Scheme 1) with suitable substrates having weakly acidic C–H bonds (*e.g.* $CO–CH_2$ or similar systems) *via* an intramolecular hydride migration from the substrate to the Rh metal and the migration of the CO–Rh bond to generate the corresponding 1,3-diketone **4**. We report herein for the first time Wilkinson's catalyst mediated intramolecular carbon–carbon bond formation in the synthesis of polycyclic ring systems.

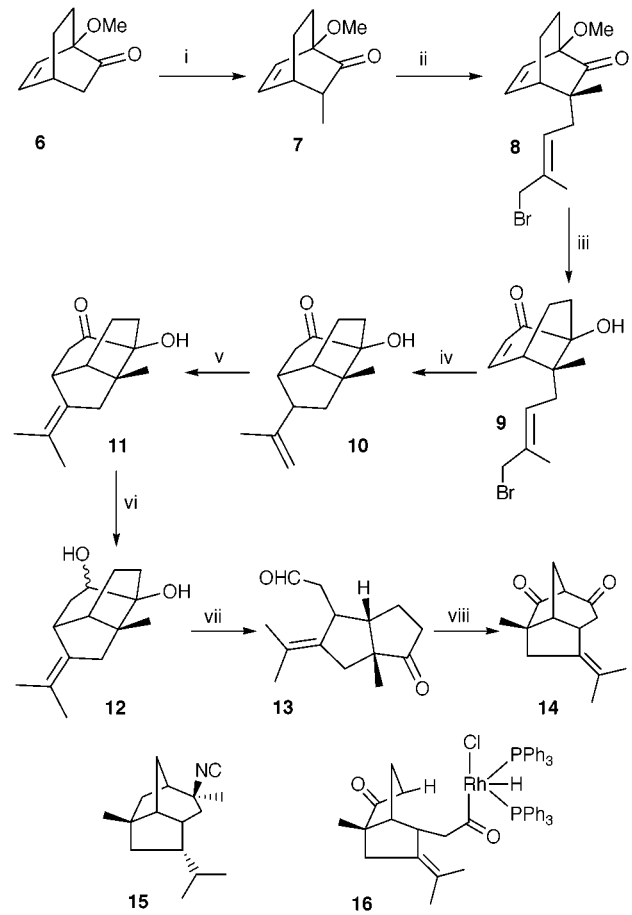
The synthesis of the requisite substrate, the keto aldehyde **13**, is shown in Scheme 2. Alkylation of the known[12] ketone **6** with LDA/MeI afforded exclusively the ketone **7**, which upon treatment with LDA and 1,4-dibromo-2-methylbut-2-ene afforded the product **8** in good yield. Treatment of **8** with a catalytic amount of perchloric acid (70%) in CH_2Cl_2 furnished the hydroxy enone **9**, which was converted into the tricyclic hydroxy olefin **10** through 5-*exo-trig* allyl radical cyclization[13] *via* treatment with Bu_3SnH. Isomerisation of the olefin **10** was carried out with TsOH in refluxing benzene to afford the hydroxy ketone **11**. $NaBH_4$ borohydride reduction of **11** furnished the 1,2-diol **12**, which was cleaved with periodic acid to the keto aldehyde **13** in quantitative yield.†



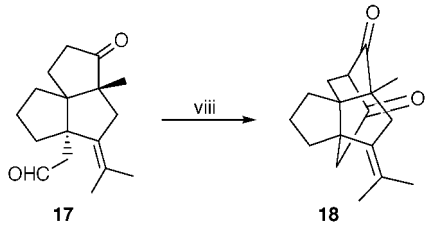
3 **4** **5**

Scheme 1

Treatment of the keto aldehyde **13** with a stoichiometric amount of chlorotris(triphenylphosphine)rhodium(I) in PhCN at 160 °C for 1.5 h afforded the expected 1,3-diketone **14** in 75% yield, whose structure was deduced from its spectral characteristics.† The formation of **14** can be only explained through the acyl rhodium hydride complex **16** of the keto aldehyde **13** (Scheme 3) through the intramolecular hydride transfer mechanism (Scheme 1). An alternative mechanism‡ involving a rhodium(I) catalyzed reversible aldol condensation, followed by the dehydrogenation of the resulting ketol leading to the formation of the product **14**, cannot be ruled out at this stage. This methodology constitutes, the first synthesis of a novel



Scheme 2 *Reagents and conditions*: i, LDA, THF, MeI, −78 °C (89%); ii, LDA, THF, HMPA, 1,4-dibromo-2-methylbut-2-ene, −78 °C (76%); iii, $HClO_4$ (cat), CH_2Cl_2, 0.5 h, (76%); iv, Bu_3SnH, AIBN, C_6H_6, reflux, 6 h (80%); v, TsOH, C_6H_6, reflux, 45 min (89%); vi, $NaBH_4$, MeOH, 0 °C (94%); vii, HIO_4, EtOH–H_2O (4:1) (100%); viii, Wilkinson's Catalyst (1 equiv.), PhCN, reflux, 1.5 h (75%).



Scheme 3

tricyclo[5.2.1.0^{4,8}]decane derivative, the norallopupukeanane-2,10-dione **14**, and can be used for the synthesis of the natural product 2-isocyanoallopupukeanane[14] **15**. Thus Wilkinson's catalyst can be used in catalytic amounts since the rhodium dihydride species **5** easily eliminates one molecule of hydrogen under the reaction conditions leading to the active catalyst species, the chlorobis(triphenylphosphine)rhodium(I) complex, which is recycled.

Similarly the angular triquinic keto aldehyde[15] **17** is transformed into the tetracyclic 1,3-diketone **18** by treatment with Wilkinson's catalyst under the same conditions in 72% yield.† This reaction is a novel and elegant methodology for the construction of complex polycyclic 1,3-diketones from the corresponding keto aldehydes. In both the examples the anticipated decarbonylation of the aldehyde group did not occur. The scope and limitations of this reaction in the synthesis of cyclic systems is currently under investigation.

Notes and references

† *Selected data* for **13**: ν_{max}/cm^{-1} 2930, 2720, 1730 and 1705; δ_H(300 MHz, $CDCl_3$) 1.16 (3H, s, Me), 1.65 (3H, s, Me), 1.66 (3H, s, Me), 1.70–2.50 (7H, m), 2.56 (1H, dd *J* 6.6, 15.0, C*H*CO), 2.86 (1H, d *J* 15.6, allylic), 3.11–3.19 (1H, m, H_2), 9.80 (1H, s, C*H*O); δ_C(75 MHz, $CDCl_3$) 20.6 (CH_3), 21.5 (CH_3), 22.0 (CH_3), 22.3 (CH_2), 36.1 (CH_2), 38.1 (CH_2), 39.1 (CH), 42.2 (CH_2), 47.4 (CH), 55.2 (C), 125.5 (C), 134.7 (C), 205.6 (CH) and 212.4 (C); *m/z* 220 (M^+, 46.5%), 202 (25), 192 (68), 177 (54), 149 (52), 133 (100), 119 (73), 105 (65) and 91 (70). For **14**: ν_{max}/cm^{-1}2950, 1740 and 1710; δ_H(300 MHz, $CDCl_3$) 1.15 (3H, s, Me), 1.48 (3H, s, Me), 1.55 (3H, s, Me), 2.13–2.33 (4H, m), 2.55 (1H, d, *J* 17.4, H_6), 2.72–2.78 (2H, m, H_6, H_3), 3.29–3.90 (2H, m, H_1, H_4); δ_C(75 MHz, $CDCl_3$) 20.8 (CH_3), 21.2 (CH_3), 21.4 (CH_3), 25.9 (CH_2), 38.5 (CH), 41.1 (CH_2), 42.9 (CH_2), 47.7 (CH), 55.9 (C), 66.4 (CH), 126.2 (C), 136.4 (C), 202.9 (C) and 214.8 (C); *m/z* 218 (M^+, 19%), 190 (28), 135 (29), 121 (55), 120 (100), 105 (25) and 55 (34). For **17**: ν_{max}/cm^{-1} 2910, 2700, 1735 and 1710; δ_H(300 MHz, $CDCl_3$) 1.18 (3H, s, Me), 1.65 (3H, s, Me), 1.72 (3H, s, Me), 1.50–2.30 (11H, m), 2.40 (1H, d *J* 15.3, allylic), 2.80 (1H, d *J* 15.3, allylic), 2.83 (1H, m, C*H*CO), 9.78 (1H, s, C*H*O); *m/z* 260 (M^+, 22%), 244 (54), 232 (55), 217 (29), 189 (60), 173 (62), 161 (100), 147 (66) and 105 (43). For **18**: ν_{max}/cm^{-1} 2960, 1740 and 1700; δ_H(300 MHz, $CDCl_3$) 1.11 (3H, s, Me), 1.52 (3H, s, Me), 1.66 (3H, s, Me), 1.70–1.85 (3H, m), 1.90–2.26 (5H, m), 2.26 (1H, d, *J* 12.9), 2.60 (1H, d, *J* 16.8, allylic), 2.63 (1H, d, *J* 16.8, C*H*CO), 2.93 (1H, d, *J* 16.8, allylic), 3.3 (1H, d, *J* 4.2, bridgehead *H*); δ_C(75, $CDCl_3$) 17.4 (CH_3), 20.7 (CH_3), 22.6 (CH_3), 26.2 (CH_2), 31.6 (CH_2), 32.7 (CH_2), 41.2 (CH_2), 44.4 (CH_2), 49.4 (CH_2), 54.2 (C), 55.6 (C), 62.6 (C), 65.7 (CH), 125.8 (C), 139.3 (C), 202.6 (C) and 214.5 (C); *m/z* 258 (M^+, 14%), 230 (16), 215 (5), 160 (100), 145 (23), 131 (8) and 105 (8).

‡ We thank the referee for this suggestion

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