Manganese Carbonyl and Phase Transfer catalysed, Stereospecific Hydroacylation of Allenes to α,β-Unsaturated Ketones

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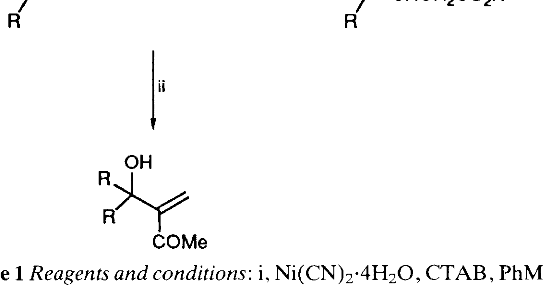
Phase transfer (5 mmol dm^{-3} NaOH, CH_2Cl_2, cetyltrimethylammonium bromide) catalysed reaction of allenes with carbon monoxide, decacarbonyldimanganese and methyl iodide affords α,β-unsaturated ketones in a stereospecific process.

Few reports have appeared on the application of manganese complexes in phase transfer catalysed reactions. Examples include the conversion of bromopentacarbonylmanganese to $Mn_2(CO)_9Br^-$,[1,2] and the synthesis of γ-butyrolactones by treatment of terminal alkynes with carbon monoxide and methyl iodide, using 5 mol dm^{-3} NaOH as the aqueous phase, methylene chloride as the organic phase, $Mn(CO)_5Br$ or $Mn_2(CO)_{10}$, and either benzyltriethylammonium chloride or polyethylene glycol (PEG-400) as phase transfer agents.[3]

Several interesting metal catalysed reactions of allenes have been effected under homogeneous[4] or phase transfer conditions. Regarding the latter, nickel cyanide catalyses the regiospecific carbonylation of allenes to β,γ-unsaturated acids[5] while hydroxyketones are usually the main products obtained using cobalt carbonyl and methyl iodide (Scheme 1).[6] We now report that allenes undergo net hydroacylation to α,β-unsaturated ketones by treatment with carbon monoxide, methyl iodide, and decacarbonyldimanganese under phase conditions (Scheme 2).

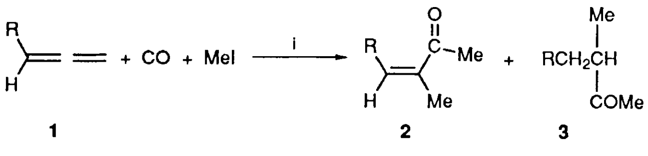
Reaction of decacarbonyldimanganese in methylene chloride with 5 mol dm^{-3} NaOH and cetyltrimethylammonium bromide (CTAB) as the phase transfer agent, followed by treatment with carbon monoxide, methyl iodide and octa-1,2-diene **1** (R = C_5H_{11}) for one day at 40 °C and one atmosphere afforded (*Z*)-3-methylnon-3-en-2-one **2** (R = C_5H_{11}) in 40% yield of isolated material. Spectral results (IR, mass, NMR) for **2** are in accord with literature data.[7] A by-product of the reaction was the saturated ketone **3** (R = C_5H_{11}), formed in 7% yield. This hydroacylation reaction is applicable to other monosubstituted allenes including undeca-1,2-diene **1** (R = n-C_8H_{17}) which gave the (*Z*) ketone **2** (R = n-C_8H_{17}) in 80% yield with **3** (R = C_8H_{17}) obtained in 8% yield. Also, (*Z*)-3-methylhex-3-en-2-one[8,9] was produced in 32% yield from penta-1,2-diene. None of the (*E*)-isomer of **2** was detected in these reactions.



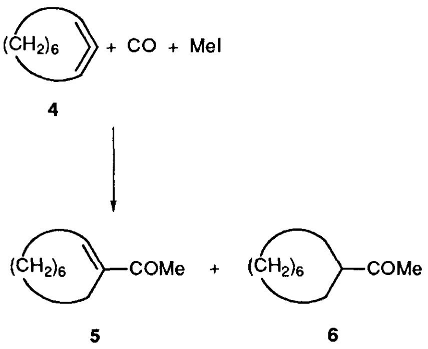
Scheme 1 *Reagents and conditions*: i, $Ni(CN)_2\cdot4H_2O$, CTAB, PhMe, 5 mol dm^{-3} NaOH, 90 °C, 1 atm; ii, $Co_2(CO)_8$, C_6H_6, 5 mol dm^{-3} NaOH, MeI, room temp., CTAB

The phase transfer reaction also proceeds with 1,3-disubstituted allenes, cyclonona-1,2-diene **4** reacting to give the unsaturated ketone **5** in 49% yield, with 3% of **6** formed as a by-product. However, trisubstituted allenes do not react with $Mn_2(CO)_{10}$ and carbon monoxide under phase transfer conditions. Also, it is noteworthy that **2** (R = C_5H_{11}) was not formed on treatment of octa-1,2-diene with either methyl-[10] or acetyl-pentacarbonylmanganese[11] under phase transfer conditions (CO, CTAB, 5 mol dm^{-3} NaOH, CH_2Cl_2).

The following general procedure was used: a mixture of CH_2Cl_2 (35 cm^3), 5 mol dm^{-3} NaOH (20 cm^3) and CTAB (0.20 mmol) was degassed with nitrogen for 30 min at 40 °C (oil bath temperature). $Mn_2(CO)_{10}$ (1.0 mmol) was added, and the mixture was stirred under nitrogen for 30 min during which time the colour of the organic phase changed from yellow to orange. The flask was removed from the oil bath, nitrogen was replaced by carbon monoxide, and methyl iodide (0.75 cm^3 per 2 cm^3 of CH_2Cl_2) was added, followed 15 min later by the substrate (2.0 mmol). The mixture was stirred at 40 °C for 18–24 h, the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 cm^3). The combined CH_2Cl_2 portion was evaporated, and the resulting oil was treated with ether (30 cm^3). 30% Hydrogen peroxide (5 cm^3) was slowly added to the ether solution at 0 °C and the mixture was stirred for 10 min and then concentrated to give the crude product which was purified by preparative TLC (9 : 1 hexane–ethyl acetate) or by distillation.



Scheme 2 *Reagents and conditions*: $Mn_2(CO)_{10}$, CTAB, 5 mol dm^{-3} NaOH, CH_2Cl_2, 40 °C, 1 atm



In conclusion, allenes react with $Mn_2(CO)_{10}$, methyl iodide, and carbon monoxide, under mild phase transfer conditions, to give (*Z*)-isomers of α,β-unsaturated carbonyls. This process is simple in execution and work-up, as well as providing a stereospecific route to trisubstituted alkenes.

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