Bimetallic Phase Transfer Catalysis

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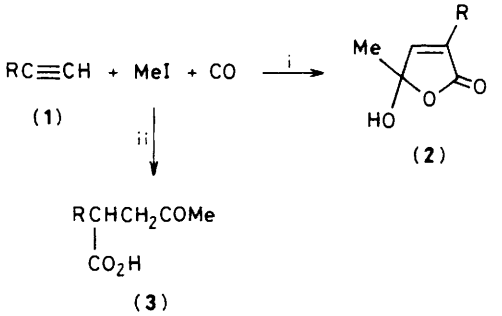
γ-Keto acids are obtained by the phase transfer catalysed reaction of alkynes with carbon monoxide and methyl iodide in the presence of catalytic amounts of cobalt and ruthenium carbonyl complexes.

Recent investigations have demonstrated the value of effecting metal catalysed reactions by means of phase transfer catalysis.[1] Although most of the chemistry involves reactions which are carried out under basic conditions, an example of organometallic phase transfer catalysis under acidic conditions has been disclosed.[2] We now report the first example of bimetallic phase transfer catalysis whereby a reaction, observed with two metal carbonyl complexes as catalysts, does not occur with either metal complex alone.

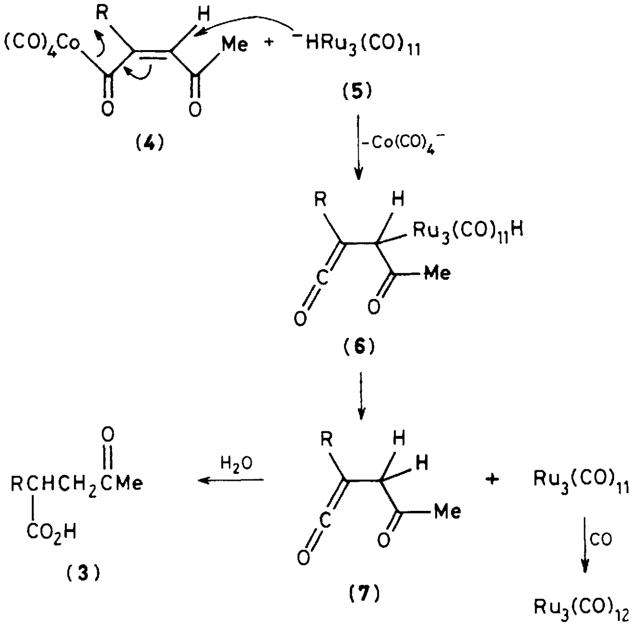
In 1978, one of us[3] described the phase transfer and cobalt carbonyl complex catalysed reaction of alkynes (**1**) with carbon monoxide and methyl iodide to give but-2-enolides



Scheme 1. i, $Co_2(CO)_8$, CTAB, 5 M NaOH, C_6H_6, room temp., 1 atm; ii, $Co_2(CO)_8$, $Ru_3(CO)_{12}$, DTAC, 5 M NaOH, C_6H_6, room temp., 1 atm.

(**2**). If a ruthenium carbonyl complex is substituted for the cobalt carbonyl complex, then no carbonyl containing products are formed (a minute amount of 1,2,4-triphenylbenzene was obtained). However, if one uses a 1 : 1 mixture of cobalt and ruthenium carbonyl complexes as catalysts [33 : 1 : 1 ratio of (**1**) : $Co_2(CO)_8$: $Ru_3(CO)_{12}$] then the γ-keto acid (**3**) is formed (Scheme 1). This transformation occurs for a series of aryl acetylenes [(**1**), R = Ph, *p*-tolyl, *p*-$MeOC_6H_4$, *p*-$EtOC_6H_4$] and for cyclohexylacetylene [(**1**), R = C_6H_{11}]. The γ-keto acids (**3**) were identified on the basis of analytical and spectral data [*e.g.* (**3**), R = Ph: chemical ionization mass spectrum *m/z* 193 ($M + 1$); ^{13}C n.m.r. ($CDCl_3$) δ 178.74, 206.04 p.p.m. (carbonyl carbons); ^1H ($CDCl_3$) δ 2.13 (s, 3H, $COCH_3$), 2.66, 3.22 (m, 2H, CH_2–diastereoisotopic being adjacent to a chiral centre), 4.10 (dd, 1H, PhCH), 7.33 (s, 5H, Ph), 11.00 (br. s, 1H, CO_2H)]. Note that dodecyltrimethylammonium chloride (DTAC) was used as the phase transfer catalyst in place of cetyltrimethylammonium bromide (CTAB). This substitution is done for convenience only as emulsions are formed using CTAB but not DTAC. But-2-enolides (**2**) are not converted into the γ-keto acids (**3**) using $Ru_3(CO)_{12}$. In addition, chalcone, an α,β-unsaturated ketone, is inert under the bimetallic catalysis conditions.

A key intermediate in the conversion of alkynes (**1**) into but-2-enolides (**2**) may be the acylcobalt carbonyl complex (**4**) (Scheme 2).[3] Nucleophilic addition by the *in situ* generated ruthenium hydride, $HRu_3(CO)_{11}^-$ (**5**),[4] would give (**6**) and regenerate $Co(CO)_4^-$. Reductive elimination of (**6**) to (**7**) [and subsequent regeneration of $Ru_3(CO)_{12}$] followed by hydration of the ketene would afford the γ-keto acid. Of course, hydration of the ketene function of (**6**) may occur prior to, or concurrent with, reductive elimination.



Scheme 2

The following general procedure was used: to a mixture (degassed) of benzene (25 ml), 5 M NaOH (20 ml), and DTAC (0.3 mmol) was added $Co_2(CO)_8$ (0.3 mmol). Carbon monoxide was bubbled through the solution for 4 h and methyl iodide was added, followed 30 min later, by $Ru_3(CO)_{12}$ (0.3 mmol) and then (**1**) (10.0 mmol). The reaction mixture was stirred under carbon monoxide for 24 h at room temperature and one atmosphere pressure. Standard work-up [separation of the phases, extraction of (**3**) from the aqueous phase, and chromatography] gave pure (**3**).

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