Synthesis of Aryl Methyl Ketones mediated by Cobalt Tetracarbonyl Anion

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The reaction of aryl halides with excess of methyl iodide in the presence of cobalt tetracarbonyl anion (generated under phase-transfer conditions), gave aryl methyl ketones along with aromatic carboxylic acids.

Cobalt tetracarbonyl anion, $[Co(CO)_4]^-$, acts as a nucleophile in the displacement reaction of active organic halides to give alkylcobalt carbonyl complexes, which are transformed into acylcobalt carbonyl complexes by the successive migratory insertion of the carbon monoxide ligand.[1—4] These species react with hydroxide ion and alkoxides to produce carboxylic acids and esters, respectively, and with 1,3-dienes, alkynes, and allenes to give the corresponding acylated products.[1—8]

We report the first example, to the best of our knowledge, of the synthesis of unsymmetrical ketones from aryl halides and methyl iodide mediated by cobalt carbonyl.† The reactions of the aromatic (**1a**—**d**) and heteroaromatic halides (**1e**—**f**) with excess of methyl iodide in the presence of $[Co(CO)_4]^-$ [generated from 0.3 equiv. of $Co_2(CO)_8$ under phase-transfer conditions],[9] gave the corresponding aryl methyl ketones (**2a**—**f**) along with aromatic carboxylic acids (**3a**—**d**) [equation (1) and Table 1].

$$\mathrm{ArX + MeI \xrightarrow{i} ArCOMe + ArCO_2H} \qquad (1)$$

i, $Co_2(CO)_8$, CTAB, aq. $NaOH–C_6H_6$

The following example is representative. To a solution of octacarbonyldicobalt (0.3 mmol) in benzene (15 ml) was added a solution of cetyltrimethylammonium bromide (CTAB; 0.2 mmol) and sodium hydroxide (25 mmol) in water (25 ml) under carbon monoxide (1 atm) and the mixture was stirred at 20 °C for 2 h. A solution of 1-bromonaphthalene (**1d**) (1 mmol) and methyl iodide (10 mmol) in benzene (10 ml) was then added and the resulting mixture was stirred for a further 20 h. The organic layer was found to contain 1-acetylnaphthalene (**2d**) (54%) together with 1-naphthal-

Table 1. Reaction of aromatic halides with methyl iodide in the presence of $[Co(CO)_4]^-$ under phase-transfer conditions.[a]

Aromatic halide	Yield (%)[b] Aryl methyl ketone	 Carboxylic acid	 Recovery
(**1a**)	(**2a**) (4)[c]	(**3a**) (15)	(**1a**) (69)[c]
(**1b**)	(**2b**) (19)	(**3b**) (10)	(**1b**) (52)[c]
(**1c**)	(**2c**) (34)	(**3c**) (23)	(**1c**) (21)
(**1d**)	(**2d**) (54)	(**3d**) (20)	—[d]
(**1e**)	(**2e**) (38)	—[e]	—
(**1f**)	(**2f**) (15)	—[e]	—[f]

[a] The reaction was carried out at 20 °C for 20 h under CO (1 atm). $[ArX]:[MeI]:[Co_2(CO)_8]:[CTAB] = 1:10:0.3:0.2$. [b] Isolated yield unless otherwise noted. [c] Determined by g.l.c. analysis. [d] 1-Naphthaldehyde (3%) and bis(1-naphthyl) ketone (2%) were also formed. [e] Products in the aqueous phase were not investigated. [f] 2-Methylquinoline was isolated in 30% yield.

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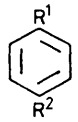
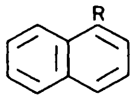
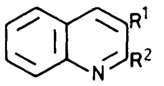
† The following relevant work has been published. (a) Iodobenzene reacts with octacarbonyldicobalt in tetrahydrofuran at 70 °C to give benzophenone: I. Ree, M. Ryang, S. Murai, and N. Sonoda, *Chem. Lett.*, 1978, 909. (b) Photostimulated reaction of aryl halides with octacarbonyldicobalt under phase transfer conditions gives aromatic carboxylic acids: J. J. Brunet, C. Sidot, and P. Caubere, *J. Org. Chem.*, 1983, **48**, 1166. (c) Alkylcobalt carbonyl complexes can catalyse alkoxycarbonylation of aromatic halides in aliphatic alcohols containing base: M. Foa, F. Francalanci, E. Bencini, and A. Gardano, *J. Organomet. Chem.*, 1985, **285**, 293.



(1a) ; R^1 = Br, R^2 = H
(1b) ; R^1 = Br, R^2 = Cl
(1c) ; R^1 = Br, R^2 = Ph
(2a) ; R^1 = Ac, R^2 = H
(2b) ; R^1 = Ac, R^2 = Cl
(2c) ; R^1 = Ac, R^2 = Ph
(3a) ; R^1 = CO_2H, R^2 = H
(3b) ; R^1 = CO_2H, R^2 = Cl
(3c) ; R^1 = CO_2H, R^2 = Ph



(1d) ; R = Br
(2d) ; R = Ac
(3d) ; R = CO_2H



(1e) ; R^1 = Br, R^2 = H
(1f) ; R^1 = H, R^2 = Cl
(2e) ; R^1 = Ac, R^2 = H
(2f) ; R^1 = H, R^2 = Ac

dehyde (3%) and bis(1-naphthyl) ketone (2%). From the aqueous layer 1-naphthoic acid (**3d**) (20%) was isolated.

Benzyl bromide can also be used in place of methyl iodide; the reaction of (**1d**) (1 mmol) with benzyl bromide under the same conditions afforded benzyl 1-naphthyl ketone (15%) and (**3d**) (5%) together with phenylacetic acid (18%), 1,2-diphenylethane (15%), and dibenzyl ketone (1%).[10] The starting material (**1d**) was also recovered (56%).

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