New Route for the Preparation of Acylcobalt Tetracarbonyls from Ketenes and $HCo(CO)_4$

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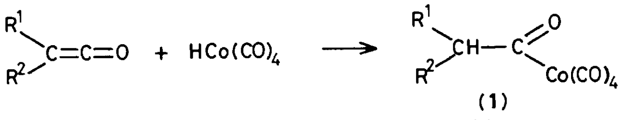
Hydridotetracarbonylcobalt reacts rapidly at −79 °C with dimethyl ketene and ethyl ketene to give quantitatively isobutyrylcobalt tetracarbonyl and n-butyrylcobalt tetracarbonyl, respectively.

Acylcobalt carbonyls are the key intermediates in the cobalt catalysed hydroformylation of olefins,[1] however, little is known of their chemical properties owing to the difficulties of their preparation.[2] Acylcobalt tetracarbonyls have been prepared previously by a low yielding reaction sequence starting from alkenes and $HCo(CO)_4$,[3] or from acyl halides,[4] or carboxylic anhydrides[5] and $NaCo(CO)_4$.

We found that ketenes react rapidly at −79 °C with $HCo(CO)_4$ in a 1:1 molar ratio forming quantitatively the corresponding acylcobalt tetracarbonyls which can be isolated in excellent yields.

Typically, a cold (−60 °C) solution of $HCo(CO)_4$ (15 mmol) in n-pentane (20 ml) was added with stirring to a solution of dimethyl ketene[6] (15 mmol) in diethyl ether (20 ml) at −79 °C. I.r. analysis after 5 min showed that the reaction product contained only (**1a**). The solvent could be removed at −30 °C *in vacuo* without decomposition of the pale yellow oily residue which was pure (**1a**) obtained in 90% yield. The missing 10% of the slightly volatile product was found in the cold trap together with the solvent. Ethyl ketene[7] reacted similarly to give pure (**1b**) in 95% yield.† Both (**1a**) and (**1b**) are moderately stable at room temperature under CO: solutions (0.1 M) in n-heptane could be stored under CO at 25 °C for 24 h without change.



(**1**)

	% Yield of (**1**)
a; $R^1 = Me$; $R^2 = Me$	90
b; $R^1 = Et$; $R^2 = H$	95

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† The acylcobalt tetracarbonyls were identified and their purities checked by their i.r. and n.m.r. spectra: ν_{CO} (n-heptane) (**1a**): 2104s, 2046s, 2023vs, 2003vs, 1968vw, 1737m, and 1669m; (**1b**): 2105s, 2046s, 2024vs, 2004vs, 1969vw, 1735w, sh, and 1717m cm^{-1}; ^1H n.m.r. (C_6D_6) (**1a**): δ 0.93 (d, *J* 6.5 Hz, 6H) and 3.03 (septet, *J* 6.5 Hz, 1H); (**1b**): 0.65 (t, *J* 7.2 Hz, 3H), 1.32 (sextet, *J* 7.1 Hz, 2H), and 2.74 (t, *J* 6.7 Hz, 2H). Both compounds gave satisfactory cobalt analyses.