## 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,<sup>1</sup> however, little is known of their chemical properties owing to the difficulties of their preparation.<sup>2</sup> Acylcobalt tetracarbonyls have been prepared previously by a low yielding reaction sequence starting from alkenes and HCo(CO)<sub>4</sub>,<sup>3</sup> or from acyl halides,<sup>4</sup> or carboxylic anhydrides<sup>5</sup> and NaCo(CO)<sub>4</sub>.

We found that ketenes react rapidly at -79 °C with HCo(CO)<sub>4</sub> in a 1:1 molar ratio forming quantitatively the corresponding acylcobalt tetracarbonyls which can be isolated in excellent yields.

Typically, a cold  $(-60 \,^{\circ}\text{C})$  solution of HCo(CO)<sub>4</sub> (15 mmol) in n-pentane (20 ml) was added with stirring to a solution of dimethyl ketene<sup>6</sup> (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<sup>7</sup> reacted similarly to give pure (1b) in 95% yield.<sup>†</sup> 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.

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<sup>†</sup> The acylcobalt tetracarbonyls were identified and their purities checked by their i.r. and n.m.r. spectra:  $v_{CO}$  (n-heptane) (1a): 2104s, 2046s, 2023vs, 2003vs, 1968vw, 1737m, and 1669m; (1b): 2105s, 2046s, 2024vs, 2004vs, 1969vw, 1735w, sh, and 1717m cm<sup>-1</sup>; <sup>1</sup>H n.m.r.  $(C_6D_6)$  (1a):  $\delta$  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.