Polymer-supported Chain Homologation

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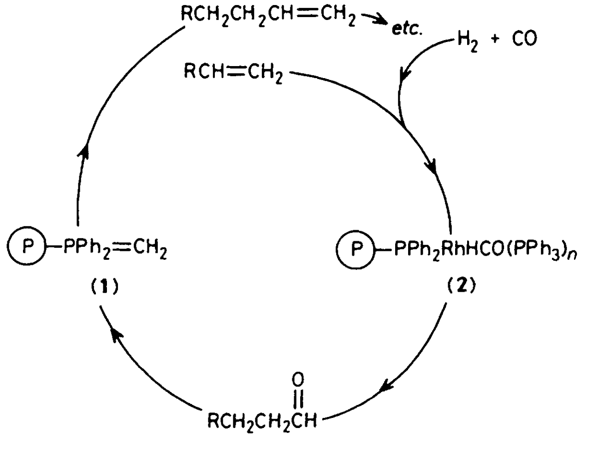
Addition of hept-1-ene to a suspension of polystyrene-bound forms of hydridocarbonyltris(triphenylphosphine)rhodium(I) and methylenetriphenylphosphorane in tetrahydrofuran, under a hydrogen/carbon monoxide atmosphere (60 °C; 120 lb in^{-2}), produces 2-methylheptanal (10%), n-octanal (45%), n-decanal (12%), n-dodecanal (2%), and n-tetradecanal (0.3%) as major products.

The use of synthesis gas (H_2 + CO) in combination with Fischer–Tropsch catalysts provides a practical synthetic route to a homologous series of n-aliphatic alcohols.[1] Major limitations of this method are that product mixtures are complex (generally obeying a Schultz–Flory distribution[2]) and that high reaction temperatures (>200 °C) are required. Here we report the coupling of a polymer-based hydroformylation process with a polymeric Wittig reaction, resulting in a non-Schultz–Flory distribution of aldehydes, under mild conditions (60 °C; 120 lb in^{-2}).

The method involves co-suspension of a resinous Wittig reagent (**1**) with an immobilized hydroformylation catalyst (**2**) in an organic solvent. A suitable alkene is introduced into the system, and the mixture is heated under an atmosphere of H_2 + CO. Diffusion of alkene into and aldehyde product out of



Scheme 1

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the catalyst (**2**), followed by alkene regeneration *via* methylene transfer from the Wittig reagent (**1**), completes one cycle and extends the chain by two carbon atoms.

A stainless steel reaction vessel (75 ml) equipped with a Teflon-coated magnetic stirring bar, was charged with the Wittig reagent (**1**) (0.81 g, 1.0 mmol; generated by treatment of a 2% cross-linked, 53% ring-substituted polymeric phosphonium salt with n-butyl-lithium in hexane[3]), the catalyst (**2**) (0.840 g, 0.30 mmol Rh; produced from a 2% cross-linked, 53% ring-substituted phosphine polymer, 0.36 mmol Rh per g),[4]) tetrahydrofuran (10 ml; distilled from sodium benzophenone ketyl), and hept-1-ene (0.049 g, 0.5 mmol) under nitrogen. A 1 : 1 mixture of H_2 and CO was introduced (120 lb in^{-2}) at room temperature. The system was heated to 60 °C, stirred for 16 h, cooled to *ca.* 5 °C, vented, and analysed by g.l.c. Major products identified by g.l.c.–mass spectrometric comparisons with authentic samples were 2-methylheptanal (10%), n-octanal (45%), n-decanal (12%), n-dodecanal (2%), and n-tetradecanal (0.3%). Control experiments carried out with the Wittig reagent (**1**) plus soluble hydridocarbonyltris(triphenylphosphine)rhodium(I) yielded only unchanged hept-1-ene.

Although the required use of stoicheiometric quantities of Wittig reagent (**1**) precludes any practical development of this system, these results demonstrate that mild, non-Schulz–Flory chain homologation based on synthesis gas is possible. Efforts are being directed toward the development of a fully catalytic chain homologation employing synthesis gas.

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