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

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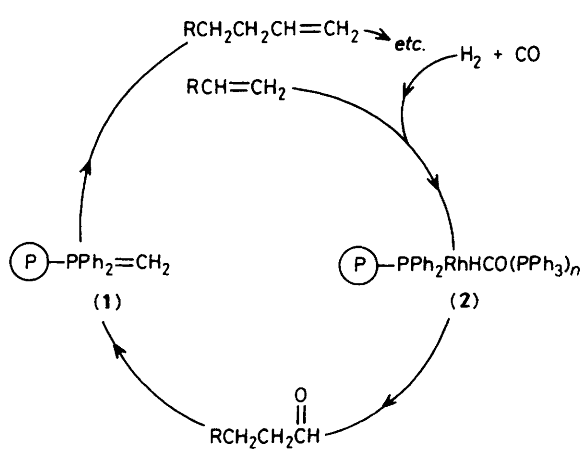

Scheme 1

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.

We are grateful to the Division of Basic Energy Sciences of the U.S. Department of Energy for financial support of this work.

Received, 22nd April 1987; Com. 539

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