A New Catalyst for Olefin Metathesis†

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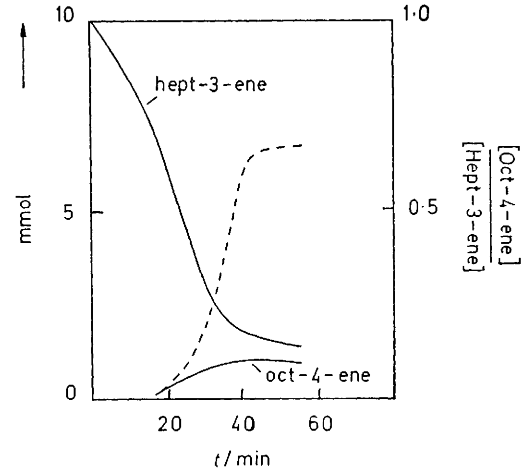
Summary Lithium aluminium hydride has been found to be an effective co-catalyst with tungsten hexachloride for the homogeneous disproportionation of olefins.

Olefin metathesis has previously been catalysed with tungsten hexachloride (WCl_6) in the presence of either $EtAlCl_2$–EtOH[1] or BuLi[2] as co-catalysts. We have found that $LiAlH_4$ is an effective alternative catalyst which has the merit of relative availability and stability to air. In a series of reactions the metathesis of hept-3-ene with WCl_6 and $LiAlH_4$ in chlorobenzene was followed by quantitative g.l.c. Typical results are illustrated in the Figure for a WCl_6–olefin mol. ratio of 1 : 20 and WCl_6–$LiAlH_4$ ratio of 1 : 4 (olefin concentration 2M). The reaction approaches equilibrium (1), and *cis–trans*-ratios were not determined.

$$2\text{ hept-3-ene} \rightleftharpoons \text{oct-4-ene} + \text{hex-3-ene} \qquad (1)$$

With this system an induction period was observed (see Figure) and the reaction reached a maximum rate at an Al–W ratio of 4 : 1. Calderon *et al.*[1] have also found this



Figure

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ratio to be the most effective with $EtAlCl_2$–EtOH as co-catalyst. Aluminium hydrides are known to react with olefins by addition giving alanes. The reaction is not normally marked, except with terminal olefin,[3] but is catalysed by salts of transition metals.[4] It is proposed, therefore, that during the induction period of the metathesis reaction when hept-3-ene is being consumed but no oct-4-ene appears (Figure) a lithium alanate species is produced which reacts with the WCl_6 to form the active catalyst.

At the high catalyst levels described above the absolute yield of oct-4-ene is poor and decreases after reaching a maximum value. The yield is increased by using higher olefin–WCl_6 ratios and more concentrated olefin solutions. A typical run was as follows. To WCl_6 (5×10^{-4} mol) and $LiAlH_4$ (2×10^{-3} mol) under nitrogen was added a dry solution of hept-3-ene (4×10^{-2} mol) in chlorobenzene (5·0 ml). The mixture was stirred for 2 h, the reaction was then terminated with methanol (0·5 ml), and the mixture was analysed. The yields of hex-3-ene, hept-3-ene, and oct-4-ene were 18·5, 39, and 23% respectively. Three other products (10% total) were also formed, shown by g.l.c. to be nonene, pentene, and butene. $LiAlH_4$ is known to isomerise internal to terminal olefins in forming alanes[5] and the by-products therefore appear to arise from a small amount of isomerisation.

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