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The Selective Conversion of n-Pentane into Pent-1-ene *via* Trihydrido(*trans*-penta-1,3-diene)bis(triarylphosphine)rhenium

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Treatment of n-pentane with heptahydridobis(triarylphosphine)rhenium and 3,3-dimethylbutene gives trihydrido(*trans*-penta-1,3-diene)bis(triarylphosphine)rhenium; trimethyl phosphite converts this, with high selectivity, into pent-1-ene.

Cycloalkanes have recently been found to react under mild conditions (50-80 °C, 1 h) with $(Ar_3P)_2ReH_7$ (1) in the presence of 3,3-dimethylbutene (2) as a hydrogen acceptor. Cyclopentane gives $(\eta^5-C_5H_5)(Ar_3P)_2ReH_2$,^{1,2} and the larger

cycloalkanes (C_6 , C_7 , and C_8) give the corresponding cycloalkenes.^{2,3} Here we report that n-pentane is also activated by this system, and can be converted with high selectivity into pent-1-ene. When $[(p-MeC_6H_4)_3P]_2ReH_7^4$ (1a) (55 mg) was stirred with (2) (0.09 ml) and n-pentane† (8 ml) at 80 °C (evacuated sealed tube) it dissolved to give a clear pale brown solution. After being heated at 80 °C for 30 min, this was evaporated to dryness to afford trihydrido(*trans*-penta-1,3-diene)bis(tri-*p*tolylphosphine)rhenium (3a) (45% yield by n.m.r. spectroscopy; 20% isolated yield), identical with an authentic sample.‡ Similarly, (Ph₃P)₂ReH₇⁶ (1b) (50 mg) and (2) (0.09 ml) in pentane (16 ml) (80 °C, 1 h) gave (3b)⁵ (20% yield by n.m.r. spectroscopy).§

Treatment of the diene trihydride (3a) (32 mg) with trimethylphosphite (0.5 ml) (90 °C, 1 h, sealed tube) led selectively and almost quantitatively to pent-1-ene (90% yield by g.c.). Pent-1-ene was also formed (95% yield by g.c.) from (3b) under similar conditions (Scheme 1).

The crude products (3) obtained in the reaction of pentane with the heptahydrides (1) and 3,3-dimethylbutene (2) could

[‡] The diene trihydride (**3a**) was prepared by the reaction⁵ between (**1a**) and *trans*-penta-1,3-diene [¹H n.m.r. τ (CD₂Cl₂): 6.6 (1H, m), 7.05 (1H, m), 7.65 (18H, s), 8.35 (1H, m), 8.7 (3H, d, *J* 6 Hz), 11.0 (1H, m), 11.6 (1H, m), 15.5 (2H, br.), and 17.9 (1H, br.)].

§ Less dilute solutions of (1a) and (1b) in pentane (ca. 200 mg in 10 ml) gave lower yields of (3a) and (3b), and the ¹H n.m.r. spectra of the crude products suggested that dihydrido(η^5 -pentadienyl)bis(triarylphosphine)rhenium may have been formed concurrently under these conditions.

¶ The pent-1-ene was identified by its g.c. retention times and by its mass spectrum (g.c.-m.s.); it was accompanied by traces (<5% in all) of five C₅ impurities (pentane, pent-2-enes, and penta-1,3-dienes).



Scheme 1. a: $Ar = p-MeC_6H_4$; b: Ar = Ph.

be treated directly with trimethylphosphite to give essentially pure pent-1-ene, which can thus be obtained from pentane in a 'one-pot' reaction [45% and 20% yield by g.c., based on (1a) and (1b) respectively].

As found in the activation of cycloalkanes with this system,² the yields are better with the heptahydride (1a) containing the more electron-releasing phosphine. Here again, as with the cycloalkanes, we assume that the actual activation step involves the insertion of a reactive intermediate (possibly L_2ReH_3) into a C-H bond of the saturated hydrocarbon.

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[†] It is essential that the n-pentane should be entirely free of alkenes; it has been pointed out by a referee that as little as 400 p.p.m. (2 mg) of pentenes, present as impurities in the 8 ml of n-pentane used, would have been sufficient to account for the formation of (3a) in 45% yield based on (1a), without involvement of n-pentane. To remove the alkenes, commercial n-pentane (containing ca. 2% of 2-methylbutane) was stirred with two portions of conc. H₂SO₄ (the second portion remaining colourless), washed (Na₂CO₃), distilled, and percolated through alumina (activity 1) just before use. The resulting n-pentane was shown by g.c. to be devoid of pent-1-ene (silicone SE 30 column) and of cis- and trans-pent-2-enes ($\beta\beta'$ -oxydipropionitrile column), under conditions such that 5 p.p.m. of these alkenes in n-pentane would have been easily detected.