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ACTIVATION OF C-H BONDS IN SATURATED HYDROCARBONS. THE FORMATION OF BIS-(TRIPHENYLPHOSPHINE)(η-ALKADIENE)RHENIUM TRIHYDRIDES FROM n-ALKANES, AND THEIR SELECTIVE CONVERSION INTO THE CORRESPONDING 1-ALKENES

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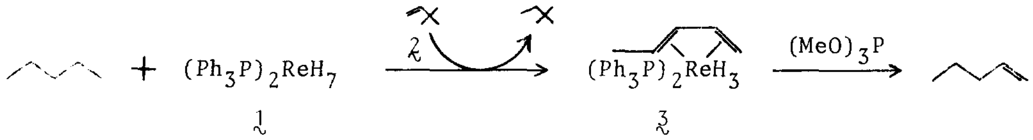
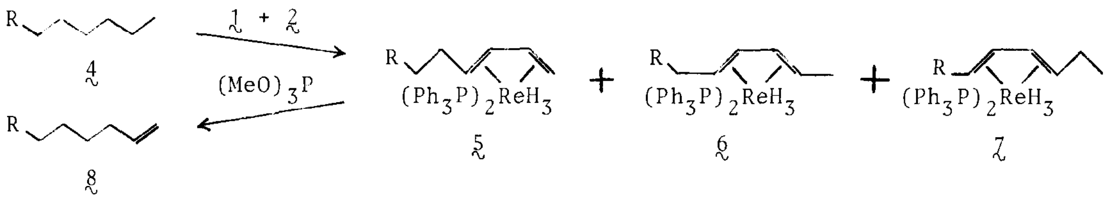
Summary.- n-Alkanes (C_6-C_8) react at 70°C with bis(triphenylphosphine)-rhenium heptahydride and 3,3-dimethylbutene to afford equilibrium mixtures of the corresponding bis(triphenylphosphine)(η-conjugated-diene)-rhenium trihydrides; treatment of these mixtures with trimethylphosphite at 60°C converts them, in >95% yield and with >98% selectivity, into the corresponding 1-alkenes.

The chemistry of n-alkanes is limited, and the few reactions they undergo (with radical reagents and electrophiles) are generally rather unselective. n-Pentane has, however, recently been converted into the (η-pentadiene)rhenium trihydride **3**, and the reaction of this with trimethylphosphite affords 1-pentene in 95% yield (Scheme 1).[1] Here we report the functionalisation of the higher n-alkane homologues **4a**-**c**.



Scheme 1. The selective functionalisation of n-pentane.

Whereas **3** is the only (η-conjugated-trans-diene)rhenium trihydride which can be formed from n-pentane, n-hexane **4a** and n-heptane **4b** can each give two isomers [**5a** (≡ **7a**) and **6a**, and **5b** and **6b** (≡ **7b**)], and n-octane **4c** can give three (**5c**, **6c**, **7c**). In the event, this is exactly what occurred (Scheme 2). When the heptahydride **1**[3] (50 mg) and 3,3-dimethylbutene **2** (90 μl) were heated at 70°C in n-hexane (16 ml) for 40 minutes under nitrogen, the heptahydride **1** gradually dissolved to afford an amber solution; evaporation of the excess n-hexane left a residue containing a ca 2:1 mixture of the (η-hexadiene)rhenium trihydrides **5a** and **6a** (55-60% yield by nmr).[4] Similar mixtures of **5a** and **6a** were formed when **1** was refluxed in THF with a variety of isomeric hexadienes.[5,6] In the same way, n-heptane, **1** and **2** at 70°C gave a *ca* 1:1 mixture of **5b** and **6b** (65-70% yield by nmr)[4,7] and n-octane gave a *ca* 2:2:1 mixture of **5c**, **6c** and **7c** (70-80% yield by nmr); the same mixture of **5c**, **6c** and **7c** was obtained (75% yield) from 1,7-octadiene and **1** in THF.[4,6] The n-alkanes **4** thus lead in all cases to mixtures, in approximatively statistical proportions, of all the possible (η-conjugated-*trans*-diene)rhenium trihydride isomers **5**, **6** and **7**.

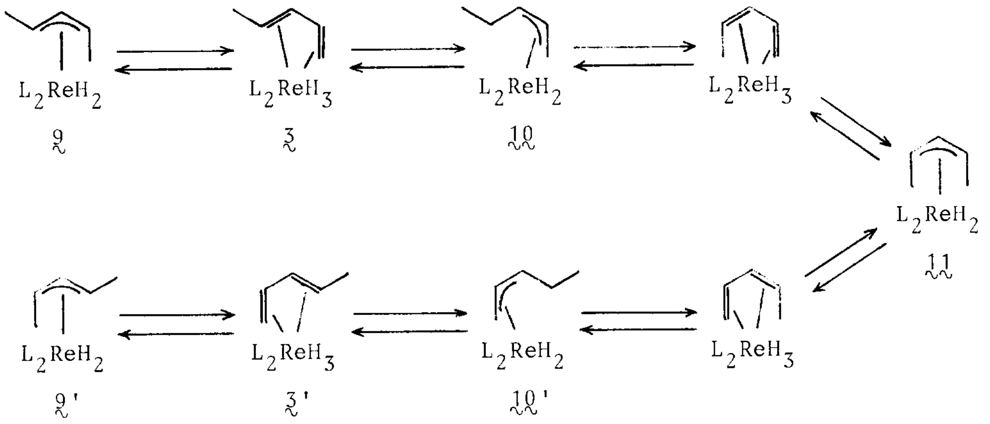


Scheme 2. (η-Diene)rhenium trihydrides formed from n-alkanes, and their conversion into 1-alkenes. R = **a**, H; **b**, Me; **c**, Et

These mixtures of (η-diene)rhenium trihydrides were converted in high yield, and with high selectivity, into the corresponding 1-alkenes. Thus, when the 2:1 mixture of **5a** and **6a** (98 mg) was heated at 60°C for 1 hour with trimethylphosphite (0.5 ml), 1-hexene **8a** was formed in >95% yield and >98% selectivity (by g.c.). The crude mixture of **5a** and **6a** obtained from n-hexane also gave 1-hexene[8] (>95% pure by g.c.). 1-Heptene **8b** was the major product (*ca* 95%)[9] formed from the crude mixture (1:1) of **5b** and **6b**, and the 2:2:1 mixture of **5c**, **6c** and **7c** gave 1-octene **8c** in >95% yield (by g.c.) and >98% selectivity (by nmr).[10] We do not understand the reasons for this remarkably regioselective formation of 1-alkenes by treatment of **3** and the mixtures of **5**, **6** and **7** with trimethylphosphite;[11] **3** also reacted with other phosphites [$(EtO)_3P$, $(PhO)_3P$] to give a mixture of n-pentane and 1-pentene, and the reaction of **3** with CO or $(CH_3)_2CHCN$ led to the formation of mixtures of pentane and all the pentenes.

The virtually quantitative formation of 1-alkenes from the mixtures of isomers **5**, **6** and **7** suggested, however, that these isomers are interconverting in solution. We have confirmed, by ^{1}H nmr spin saturation transfer (SST), that this rearrangement does indeed occur in the case of the (η-hexadiene)rhenium trihydrides **5a** and **6a**,[12] and we have studied it in more detail in the case of the (η-pentadiene)rhenium trihydride **3**, where it is degenerate (**3** ≡ **3'**, Scheme 3). This trihydride is in mobile equilibrium at 40°C with the (η-allyl)rhenium dihydrides **9** and **10**, and **3** and **3'** are rapidly interconverted at 80°C. A possible mechanism for this rearrangement, *via* the symmetrical η-allyl intermediate **11**, is shown in Scheme 3.

Because of this equilibrium between the (η-diene)rhenium trihydrides **3**, **6** and **7**, we cannot tell where in the n-alkane the initial activation of a C-H



Scheme 3. Possible mechanism for the degenerate rearrangement of the (η-pentadiene)rhenium trihydride **3** (≡ **3**'). L = Ph_3P.

bond takes place. We imagine, however, that it occurs preferentially on a methyl group,[13] and that it involves the carbene-like insertion of a coordinatively unsaturated complex [possibly the 14e trihydride $(Ph_3P)_2ReH_3$].[14] We think the (n-alkyl)rhenium intermediate thus formed undergoes β-elimination to afford an 18e (η-1-alkene)rhenium pentahydride, which can either lose olefin or suffer further dehydrogenation to lead ultimately to the (η-diene)rhenium trihydride.

Whereas loss of olefin seems to be the major pathway in the case of cycloalkanes[2,15] (except cyclopentane),[14] leading to their catalytic dehydrogenation,[13] it is only a very minor reaction in the case of n-alkanes. We assume that steric compression destabilises intermediates incorporating the bulkier cycloalkenes, and that these therefore dissociate rapidly before further dehydrogenation can occur.[15]

Although a number of soluble transition metal systems are now known which activate C-H bonds in saturated hydrocarbons,[1b] the one described above is, to our knowledge, the first which leads to the functionalisation of the terminal carbon of n-alkanes in fair yield (60-80% based on rhenium) and with high (> 98%) regioselectivity.

References and Footnotes

1. (a) D. Baudry, M. Ephritikhine, H. Felkin, and J. Zakrzewski, J.Chem.Soc., Chem.Commun., 1982, 1235; (b) For references to other recent work on the activation of C-H bonds in saturated hydrocarbons by soluble transition metal systems, see accompanying communication.[2]

2. Accompanying communication: H. Felkin, T. Fillebeen-Khan, Y. Gault, R. Holmes-Smith, and J. Zakrzewski, *Tetrahedron Letters*, 1984, *25*,
3. J. Chatt and R.S. Coffey, *J.Chem.Soc.A*, 1969, 1963.
4. 400 MHz ^{1}H nmr spectra in C_6D_6, δ from TMS. All the (η-diene)rhenium trihydrides **5**-**7** show phenyl resonances between 7 and 8.5, and two broad hydride resonances at about -3 and -7. Diene ligands (all the signals are multiplets; the methyl signals are doublets or triplets, J = 6-7 Hz): **5a**, -0.80 (H1 *anti*), 2.25 (H1 *syn*), 3.92 (H2), 3.45 (H3), -0.40 (H4), 1.99 and 1.56 (H5 and H5'), 0.75 t (H6); **6a**, 1.74 d (H1 and H6), -0.30 (H2 and H5), 3.58 (H3 and H4); **5b**, -0.74 (H1 *anti*), 2.30 (H1 *syn*), 3.98 (H2), 3.45 (H3), -0.39 (H4), 2.03 and 1.52 (H5 and H5'), 1.11 (H6), 0.74 t (H7); **6b**, 1.75 d (H1), -0.23 (H2), 3.58 (H3 and H4), -0.39 (H5), 2.03 and 1.64 (H6 and H6'), 0.81 t (H7); the spectrum of the mixture of **5c**, **6c** and **7c** resembles that of the lower homologues, but is more complex, with overlapping signals; the spectrum in CD_2Cl_2, however, clearly shows four methyl signals of approximatively equal intensities at 1.36 d (H1 in **6c**), 0.67 t (H1 and H8 in **7c**) and 0.57 t and 0.56 t (H8 in **5c** and H8 in **6c**).
5. *cis*-1,4-, *trans*,*trans*-2,4-, *cis*-*trans*-2,4- and 1,5-hexadiene; the latter gave the best isolated yield (75%).
6. For the preparation of (η-diene)rhenium trihydrides by this route, see D. Baudry, M. Ephritikhine, and H. Felkin, *J.Organometal.Chem.*, 1982, *224*, 363.
7. The mixture of **5b** and **6b** was not isolated and purified.
8. Identified by g.c-m.s. We thank Mr. J.M. Dedieu (Orsay) for this analysis.
9. 1-Heptene was identified by its g.c. retention time only (SE30 silicone column); the only visible contaminant had the retention time of n-heptane.
10. The presence of >2% of any of the isomeric octenes would have been easily detected in the 400 MHz ^{1}H nmr spectrum.
11. Similar, but much less pronounced, selectivity in favour of 1-alkene formation from (η-allyl)-copper and -nickel precursors has been observed previously, and explained by the greater stability, and hence rate of formation, of (η-1-alkene)metal intermediates. J.K. Kochi and H.E. Mains, *J.Org.Chem.*, 1965, *30*, 1862; C. Chuit, H. Felkin, C. Frajerman, G. Roussi, and G. Swierczewski, *J.Organometal.Chem.*, 1977, *127*, 371.
12. Irradiation of the signal corresponding to the methyl groups of **6a** in the 250 MHz spectrum of a 2:1 mixture of **5a** and **6a** in deuteriotoluene at 90°C led to a 30% decrease in the intensity of the methyl group signal of **5a**.
13. D. Baudry, M. Ephritikhine, H. Felkin, and R. Holmes-Smith, *J.Chem.Soc., Chem.Commun.*, 1983, 788.
14. D. Baudry, M. Ephritikhine, and H. Felkin, *J.Chem.Soc.,Chem.Commun.*, 1980, 1243.
15. D. Baudry, M. Ephritikhine, and H. Felkin, *J.Chem.Soc.,Chem.Commun.*, 1982, 606.

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