Homogeneous Catalysts for Olefin Disproportionation

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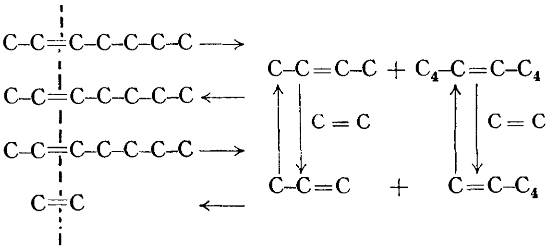
A recent unique reaction is the disproportionation† of olefins over heterogeneous catalysts.[1,2] A series of lower and higher olefins is formed when an acyclic olefin interacts with a supported molybdenum or tungsten system at elevated temperatures. For example, the disproportionation of propene has given ethylene and but-2-ene in quantities which correspond to the thermodynamic equilibrium.[2] We report the preparation of homogeneous catalysts which will effect olefin disproportionation.‡

Treatment of the green nitrosyl complexes, $L_2Cl_2(NO)_2M$ [M = Mo or W; $L = Ph_3P$, C_5H_5N, Ph_3PO, *etc.*],[3] with a variety of alkylaluminium halides in chlorobenzene yields brown, homogeneous solutions, which are very active catalysts for disproportionation at low temperatures (0—50°).

The catalyst from $[Ph_3P]_2Cl_2(NO)_2Mo$ (0·0005 mole) and methylaluminium sesquichloride (MASC, 0·1 ml.) in chlorobenzene (10 ml.) reacted at 0—5° with pent-1-ene (10 ml.); ethylene was allowed to bubble off at atmospheric pressure. The mixture was hydrolyzed after 50 min. to give oct-4-ene (48%). Oct-1-ene was similarly converted into tetradec-7-ene. The corresponding pyridine derivative ($L = C_5H_5N$) (0·0001 mole) when treated with MASC in chlorobenzene gave a system which reacted after 25 min., with oct-1-ene (10 ml.) at 50 ± 3° to give a mixture containing 60 weight per cent of tetradec-7-ene. After 1 hr. under comparable conditions the tungsten analogue, $(C_5H_5N)_2Cl_2(NO)_2W$, also effected disproportionation of oct-1-ene to give tetradec-7-ene (29 wt. %).

Systems employing ethylaluminium dichloride as the co-catalyst effect isomerization together with disproportionation. In a reaction with $[Ph_3P]_2Cl_2(NO)_2Mo$ and pent-1-ene at ambient temperature for 16 hr. the products, excluding ethylene and propene, were butenes (18 wt. %), pentenes (25%), hexenes (28%), heptenes (11%), and octenes (16%). In a similar reaction with hept-2-ene, every olefin from ethylene to dodecene was readily discernible. Therefore, we suggest the interaction of a combination of α- and internal olefins to account for the products.

The versatility of these catalysts can be further demonstrated by the reactions of an internal olefin with itself and reaction of the olefin in the presence of ethylene. After 1 hr. at ambient temperature, the system $[Ph_3P]_2Cl_2(NO)_2Mo$ (0·0001 mole), MASC (0·1 ml.), and hept-2-ene (10 ml.) gave a product containing but-2-ene (12%), hept-2-ene (61%), and dec-5-ene (27%). When a comparable reaction was conducted under 20 lb. in.$^{-2}$ of ethylene, the product was composed of propene (6%), but-2-ene (3%), hex-1-ene (19%), hept-2-ene (66%), and dec-5-ene (7%). These results are consistent with the double bonds undergoing an alignment on the catalyst to form a four-centre intermediate, perhaps in a pseudo-cyclobutane arrangement. Thus, the reaction of ethylene and hept-2-ene can be pictured as follows:



The reaction of two molecules of hept-2-ene in the designated orientation would produce but-2-ene and dec-5-ene, but should one of the hept-2-ene molecules be in the opposite orientation no new olefins would be formed. Cleavage of hept-2-ene with ethylene would give propene and hex-1-ene, but these products can also arise from the ethylene cleavage of but-2-ene and dec-5-ene. These disproportionation reactions have been demonstrated to be reversible and, therefore, the products are readily interconvertible.

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† The terms "dismutation" and "metathesis" have also been employed.

‡ Olefin interactions with the system WCl_6, ethanol, and ethylaluminium dichloride are described in a recent paper by N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Letters*, 1967, 3327.

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