Tetrahedron Letters No.34, pp. 3327-3329, 1967. Pergamon Press Ltd. Printed in Great Britain.

OLEFIN METATHESIS - A NOVEL REACTION FOR SKELETAL TRANSFORMATIONS OF UNSATURATED HYDROCARBONS

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(Received 29 May 1967)

It has been discovered that when an internal olefin is exposed to a catalyst comprised of tungsten hexachloride, ethanol and ethylaluminum dichloride, the following metathesis reaction occurs:

$$2\ R_1-CH = CH-R_2 \rightleftharpoons R_1-CH = CH-R_1 + R_2-CH = CH-R_2$$

Thus, 2-pentene will undergo an interchange process resulting in the formation of a mixture containing at equilibrium 25, 50, and 25 mole percent of 2-butene, 2-pentene and 3-hexene, respectively.

TABLE 1

GLC Before and After the Metathesis of 2-Pentene Using an n-Pentane Internal Standard

Olefin / Standard	Area Olefin / Area Standard	Mole % of Total Olefins
	a. Before Reaction	
2-Pentene / n-Pentane	2.390	100.0
	b. After Reaction	
2-Butene / n-Pentane	0.474	24.9
2-Pentene / n-Pentane	1.190	50.1
3-Hexene / n-Pentane	0.713	25.0
	Total: 2.377	

$$\%\ \text{Selectivity}\ \frac{2.377}{2.390} = 99.6$$

The reaction proceeds rapidly at room temperature, with equilibrium being attained within a matter of seconds.

The reaction is extremely selective as indicated in Table 1. In the equilibrated mixture, 2-butene, 2-pentene, 3-hexene, and the internal standard, pentane, are the only compounds observed. Double bond migration within the olefin components of the mixture, leading to 1-butene, 1-pentene, 1-hexene, or 2-hexene, was not detected and a quantitative reaction selectivity was attained.

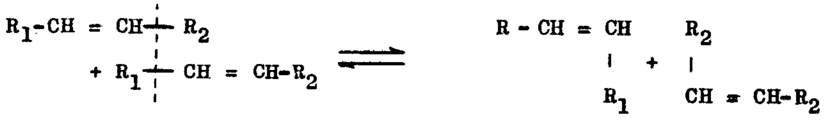
A typical olefin-metathesis reaction can be carried out by treating a solution of 0.1 mole 2-pentene in 15 ml. of benzene, which had been dried by silica gel treatment under a nitrogen atmosphere, with 0.2 ml. of a preformed 0.05M solution of WCl_6 and ethanol ($WCl_6/C_2H_5OH = 1/1$) in benzene, followed by 0.2 ml. of 0.2M ethylaluminum dichloride solution in benzene. The mixture is allowed to stand for about one to three minutes at room temperature before being terminated with a drop of methanol.

It has been found that equilibrium can be approached from either direction, i.e., an equimolar mixture of 2-butene and 3-hexene, after treatment with the above described catalyst, will lead to a mixture of 25, 50, and 25 mole per cent of 2-butene, 2-pentene and 3-hexene, respectively. In addition, by conducting the metathesis reaction under conditions whereby the lower boiling component is continuously removed from the system, it was found that the reaction can be driven considerably to one side.

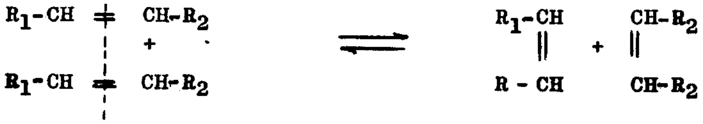
Mechanism

Two routes for the olefin-metathesis reaction are considered:

Transalkylation



Transalkylidenation



Transalkylation denotes an interchange of an alkyl group attached to a carbon of the double bond of one olefin molecule with a similarly disposed alkyl group of a second olefin molecule. Transalkylidenation is a route whereby an intermolecular interchange of alkylidene groups occurs. Experimental results with deuterated olefins are compatible with the transalkylidenation scheme.

Contribution No. 384 from the Research Laboratories, The Goodyear Tire and Rubber Company, Akron, Ohio.