

reduced carbon surface can be oxidized by molecular oxygen. Similar catalytic role of carbon surface has been postulated for the reduction of cobaltous ion by molecular hydrogen (13). The lower activity of the cobalt ion on the top layer may be attributed to the difficulty of such regeneration. In the plateau region, the dependence of the rate on the acidity of carbon is quite different from that at the beginning of the reaction as shown in Table I. The direct interaction between cobalt ion and the acidic sites on carbon surface seems to be unimportant for the catalytic activity. The detailed mechanism in this region, however, remains to be elucidated.

In conclusion, the catalytic action of the cobalt-carbon catalysts for liquid-phase oxidation was demonstrated. This is a kind of solidified homogeneous catalyst, the advantage of which was emphasized by Acres (14, 15). The effect of carbon carrier was also investigated quantitatively, and it was found that the catalytic activity at the beginning of the reaction depends on the surface acidity of the carrier. The cooperative action of cobalt ions and the acidic oxides on carbon was suggested.

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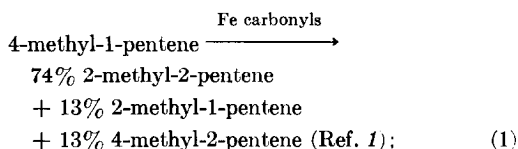
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Isomerization of 1-Olefins Using 1,5-Cyclooctadienetungsten Tetracarbonyl

There are many catalysts for the isomerization of alk-1-enes to nonterminal olefins; however, some, if not all, of these reactions produce results and/or side effects which are often undesirable. For instance, some tend to promote polymerization and/or degradation of either the reactant or the product of the isomerization. Other of these processes

suffer from low conversions. A few examples of these are illustrated here:



2-methyl-1-pentene $\xrightarrow{\text{Al}_2\text{O}_3, 80^\circ\text{C}}$
 62% 2-methyl-2-pentene, 4-methyl-1-pentene \rightarrow
 4% 4-methyl-2-pentene, and 1-hexene \rightarrow
 no reaction (Ref. 2); (2)
 and

3-methyl-1-pentene $\xrightarrow{\text{Ca}(\text{NH}_2)_2, 80^\circ\text{C}}$
 22% *trans*-3-methyl-2-pentene
 + 28% *cis*-3-methyl-2-pentene, and
 4-methyl-1-pentene \rightarrow 60% 4-methyl-2-pentene
 + 13% 2-methyl-2-pentene (Ref. 3). (3)

In our laboratory we have discovered a new catalytic reaction for isomerization of terminal to internal olefins. The catalyst is 1,5-cyclooctadienetungsten tetracarbonyl (4). A mixture of 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B),* and 1-pentene alone were isomerized by this catalyst to 2M2B and 2-pentene, respectively, in high conversion. Selectivities to the internal olefins varied from 90 to 100% in the temperature range 115–265°C at olefin/W = 50. To the best of our knowledge, this tungsten zero complex is practically the best of the organometallic catalysts thus far tested in the study of the migrations of olefinic double bonds.

All experiments were carried out in a reaction system composed of two stainless-steel pressure vessels (30 ml each), connected by means of a section of stainless-steel tubing. One pressure vessel (A) was employed as a reaction chamber and the other (B) as a mixing chamber. While vessel (A) was heated to reaction temperature, vessel (B) was charged with 1.54 cm³ of a mixture of 1.3 M 2M1B and 1.3 M 2M2B in *n*-pentane and 4.0 cm³ of 0.01 M 1,5-cyclooctadienetungsten tetracarbonyl in benzene. This mixture was then transferred by nitrogen pressure to the reaction vessel.

All reactions were carried out for 15 min, cooled, and analyzed for isomerization products on a gas-liquid chromatograph using *n*-pentane as internal standard. Results are given in Table 1.

* We first expected the mixture of 2M1B and 2M2B to be metathesized by this tungsten (0) catalyst to *cis*-3-methyl-2-pentene and 2-methyl-2-pentene; instead, isomerization of 2M1B to 2M2B took place.

TABLE 1
ISOMERIZATION OF 2-METHYL-1-BUTENE

Temp (°C)	Conversion of 2M1B (%)	2M2B Formed (%)	Higher hydrocarbons (%)
25	0	0	0
115	62	100	0
160	68	96	4
175	72	90	10
200	65	90	10

A blank, run at 160°C, showed a thermal conversion of only 5% of 2-methyl-1-butene. Of the converted olefin, 53% was 2M2B and 47% was higher olefins.

A series of experiments were also performed with 1-pentene, in which 4.5 cm³ of 0.01 M 1,5-cyclooctadienetungsten tetracarbonyl catalyst and 0.5 cm³ of 4.5 M 1-pentene were used and all experiments were run for 15 min. Table 2 shows pertinent data.

TABLE 2
ISOMERIZATION OF PENTENE-1

Temp (°C)	Conversion of pentene-1 (%)	Pentene-2 formed (%)	Higher hydrocarbons (%)
115	28	95	5
160	51	99	1
215	63	98	2
240	62	100	0
265	55	99	1

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