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# Isomerization of Olefin Catalyzed by Arenetricarbonylmolybdenum

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The catalytic properties of arenetricarbonylchromium toward isomerization of olefins have been investigated by Frankel and co-workers [1–3], but corresponding molybdenum complexes have been largely ignored. We have investigated the molybdenum derivatives and found them in general to be more active than their chromium analogues; furthermore, where mixtures of isomerized olefins are possible, the selectivities toward one isomer or another differ considerably between the two metals.

Table I shows the data on the isomerization of olefins using toluenetricarbonylmolybdenum, $(Tol)Mo(CO)_3$, as the catalyst; also included are $(Tol)W(CO)_3$, $(Mes)W(CO)_3$ (mes = mesitylene), and $(Tol)Cr(CO)_3$ catalysts for comparison.

As can be seen in the Table, both Mo and W are much more active catalysts toward isomerization of olefins than corresponding Cr compounds (compare data on methylenecyclohexane and allylbenzene). Even where weaker electron-donating arenes are used on $ArCr(CO)_3$ such as methyl benzoate, higher temperatures are required (160–175 °C) and generally lower conversions are realized [1, 3].

One example which illustrates differences in selectivities between $ArMo(CO)_3$ and $ArCr(CO)_3$ catalysts is in the isomerization of 1,5-cyclooctadiene. Whereas $(methylbenzoate)Cr(CO)_3$ promotes an 85% conversion of 1,5-COD to 1,4- and 1,3-COD in selectivities of 16 and 84%, respectively, in the same reaction catalyzed by $(Tol)Mo(CO)_3$, 65% conversion of 1,5-COD is accomplished leading to selectivities of 54%, 1,3-COD and 40%, 1,4-COD. After 120 hr, the final product mix contains 15% 1,5 55% 1,3 and 30% 1,4-COD. Apparently, equi-

TABLE I. Isomerization of Olefins Catalyzed by Arene Group VIB Tricarbonyls.

| Catalyst | Olefin (% Conversion) | Products (% Selectivity) | Conditions |
|---|---|---|---|
| $(Tol)Mo(CO)_3$ | 1-Pentene (72) | 2-Pentene (100)[a] | 100 °C, 24 hr |
| | 1-Hexene | 2-Hexene (26)[a]<br>3-Hexene (74)[a] | 120 °C, 24 hr |
| | 1,5-Cyclooctadiene (65) | 1,3-Cyclooctadiene (54)<br>1,4-Cyclooctadiene (46) | 120 °C, 24 hr |
| | 1,5-Cyclooctadiene (85) | 1,3-Cyclooctadiene (65)<br>1,4-Cyclooctadiene (35) | 120 °C, 120 hr |
| | 1,4-Cyclohexadiene (74) | 1,3-Cyclohexadiene (100) | 110 °C, 24 hr |
| | Allylbenzene (73) | *trans*-β-Methylstyrene (54)<br>*cis*-β-Methylstyrene (46) | 105 °C, 24 hr |
| | Methylenecyclohexane (98) | 1-Methylcyclohexene (100) | 110 °C, 24 hr |
| $(Mes)Mo(CO)_3$ | Allylbenzene (63) | *trans*-β-Methylstyrene (70)<br>*cis*-β-Methylstyrene (30) | 105 °C, 24 hr |
| $(Tol)W(CO)_3$ | Methylenecyclohexane (99) | 1-Methylcyclohexene (100) | 110 °C, 4 hr |
| $(Mes)W(CO)_3$ | Allylbenzene (21) | *trans*-β-Methylstyrene (73)<br>*cis*-β-Methylstyrene (27) | 105 °C, 12 hr |
| $(Tol)Cr(CO)_3$ | 1,4-Cyclohexadiene (1) | 1,3-Cyclohexadiene (100) | 120 °C, 12 hr |
| | Allylbenzene (14) | β-Methylstyrene (100) | 105 °C, 24 hr |
| | Methylenecyclohexane (15) | 1-Methylcyclohexene (100) | 110 °C, 3 hr |
| | Methylenecyclohexane (19) | 1-Methylcyclohexene (100) | 110 °C, 9 hr |

[a] Stereochemistry about the double bond not determined. Abbreviations: Tol = toluene; Mes = mesitylene.

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librium conditions among the three isomers are approached after extended reaction time.

Frankel [2], in studies of the isomerization of 1,4-hexadiene and 1,4-cyclohexadiene by Cr catalysts, proposed a mechanism involving a 1,3-allylic hydrogen shift. We prepared 3-phenyl-3,3-$d_2$-1-propene ($C_6H_5CD_2CH=CH_2$) and studied its isomerization to the deuterated $\beta$-methylstyrene. The nmr spectrum of the product was consistent with that predicted for $C_6H_5CD=CH-CH_2D$. Therefore, our preliminary investigation into the mechanism of isomerization of olefins catalyzed by $ArMo(CO)_3$ is in accord with the allylic process proposed by Frankel.

## Experimental

### *Physical Methods*

Nuclear magnetic resonance spectra were obtained on a Varian EM-360 (60 MHz) spectrometer, and in the case of 3,3-$d_2$-allylbenzene and deuterated $\beta$-methylstyrene, a Varian HR300 MHz spectrometer, using tetramethylsilane as an internal standard. Samples were separated and analyzed on a Hewlett-Packard Analytical Gas Chromatograph model 5750 equipped with a flame ionization detector, using helium as the carrier gas. The packing in the column was composed of 10% Tergitol NP-35 on 50-100 mesh Chromosorb-P. In all cases, retention times were compared to those of authentic samples, and corrected for response ratios.

### *Starting Materials*

Olefins were purchased from Chemical Samples Co. and used as received. The catalysts were prepared according to the method fo Nicholls and Whiting [4]. The deuterated olefin 3-phenyl-3,3-$d_2$-1-propene was prepared according to the procedure of Hendrix and Von Rosenberg [5].

### *Isomerization of Olefins*

Since all olefins were isomerized in essentially the same manner, only the reaction of 1-pentene will be given in detail. Table I gives the reaction times and temperatures for all olefins.

Into a 200 ml pressure reaction bottle was put 10 ml of 1-pentene (6.4 g, 0.09 mol). The olefin was deaerated for 5 min with nitrogen gas, then 0.3 g of $(Tol)Mo(CO)_3$ (0.001 mol) was added. A magnetic stir bar was placed in the bottle, the bottle sealed, and then heated to 100 °C in an oil bath for 24 hr. The reaction mixture was filtered through powdered neutral alumina and subjected to gas chromatographic analysis which showed a yield of 71.5% 2-pentene and 28.5% unreacted 1-pentene.

## References

1 E. N. Frankel and R. O. Butterfield, *J. Org. Chem., 34,* 3930 (1969).
2 E. N. Frankel, *J. Catal., 24,* 358 (1972).
3 E. N. Frankel, *J. Am. Oil Chem. Soc., 47,* 33 (1970).
4 B. Nicholls and M. C. Whiting, *J. Chem. Soc.,* 551 (1959).
5 W. T. Hendrix and J. L. Von Rosenberg, *J. Am. Chem. Soc., 98,* 4850 (1976).