

## REDUCTION OF THE DOUBLE BOND WITH MOLYBDENUM CARBONYL

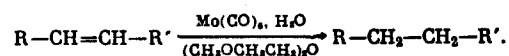
Academician A. N. Nesmeyanov, G. B. Shul'pin,  
V. V. Krivykh, and M. I. Rybinskaya

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It is known that the carbonyls of transition metals are good reductants and can be used in this way in various organic syntheses. The reduction usually proceeds in the presence of a hydrogen donor. Thus iron dodecacarbonyl reduces nitroaryls to primary amines [1] and hydrogenates the C=N bond [2] in the presence of methanol; ironpentacarbonyl in the presence of traces of water [3] or a NaOH solution in methanol [4] yields the products from the reduction of the double bond in  $\alpha,\beta$ -unsaturated carbonyl compounds.

Examples of reduction with molybdenum carbonyl are also known. The reaction of alkyl- and arylsulfonchlorides with  $\text{Mo}(\text{CO})_6$  in anhydrous tetramethylurea leads to the formation of disulfides [5], and aromatic nitrosamines are converted to secondary amines at the boil in 1,2-dimethoxyethane with molybdenum carbonyl [6].

We found that the double bond is easily reduced when an olefin is reacted with molybdenum carbonyl in the presence of a proton donor:



Certain ferrocene derivatives containing a conjugated double bond in the side chain, ( $\text{Fc}: \text{C}_5\text{H}_5\text{FeC}_5\text{H}_4^-$ ):  $\text{FcCOCH}=\text{CHC}_6\text{H}_5$  (I),  $\text{FcCH}=\text{CHCOC}_3\text{H}_7-n$  (II), and  $\text{FcCH}=\text{CH}_2$  (III), were chosen as the olefins.

The reduction of the double bond proceeds in good yield within a few hours in a boiling solution of the olefin and molybdenum carbonyl in diethyleneglycol dimethyl ether (diglyme) containing a small amount of water. It should be noted that only a small amount of the reduction products is formed in anhydrous diglyme preliminarily distilled over sodium. This permits one to assume that the hydrogenation proceeds through the hydrogen in the water.

The reduction of cinnamoyl ferrocene (I) in diglyme to which  $\text{D}_2\text{O}$  was added resulted primarily in a product containing two deuterium atoms. However the mass spectrum shows that mono-, tri-, and tetradeuterated compounds are also formed in this reaction. This could indicate that H-D exchange takes place under the reaction conditions.

During the reduction of  $\alpha,\beta$ -unsaturated compounds, products from the selective hydrogenation of the double bond are the principal ones, although it should be mentioned that small quantities of unidentified substances, which possibly are more extended reduction products, were also detected by TLC.

Under the reaction conditions described the double bond is reduced to purely organic compounds (for example for benzalacetone  $\text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}_3$ : Here the formation of the reduction product  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COCH}_3$  was detected by its PMR spectrum).

The action of  $\text{Cr}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  on olefinic ferrocene derivatives also leads to the formation of products from the reduction of the double bond.

**Reduction of Cinnamoyl Ferrocene.** A solution of 0.79 g of cinnamoyl ferrocene (I) and 1.05 g of  $\text{Mo}(\text{CO})_6$  in 30 ml of diglyme containing 1 ml of water was heated to boiling for 3 h. The solvent was evaporated in vacuo, the residue was dissolved in benzene and transferred to an  $\text{Al}_2\text{O}_3$  column. Benzene eluted 3-phenylpropionyl ferrocene (0.70 g, 87%), orange-red crystals, mp 83-84°C. Melting point in literature 85.5-86°C [7]. PMR spectrum (in  $\text{CS}_2$ ,  $\delta$ , ppm from TMS): 2.95 (4H,  $\text{CH}_2\text{CH}_2$ ); 3.98 (5H,  $\text{C}_5\text{H}_5$ ); 4.37 (2H,  $\beta\text{-HC}_5\text{H}_4$ ); 4.67 (2H,  $\alpha\text{-HC}_5\text{H}_4$ ); 7.30 (5H,  $\text{C}_6\text{H}_5$ ). In the IR spectrum (in KBr): 1666  $\text{cm}^{-1}$  (C=O).

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A reaction in diglyme containing D<sub>2</sub>O was carried out analogously. The intensity of the signal of the methylene groups in the PMR spectrum of deuterated 3-phenylpropionyl ferrocene corresponds to approximately 2H. Mass spectrum (m/e (I, %) the isotope composition of the methylene groups in M<sup>+</sup>): 318 (29) C<sub>2</sub>H<sub>4</sub>, 319 (79) C<sub>2</sub>H<sub>3</sub>D, 320 (100) C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>, 321 (50) C<sub>2</sub>HD<sub>3</sub>, and 322 (17) C<sub>2</sub>D<sub>4</sub>.

Reduction of 2-n-Propionylvinylferrocene. A solution of 0.20 g of 2-n-propionylvinylferrocene (II) and 0.50 g of Mo(CO)<sub>6</sub> in 25 ml of diglyme containing 2 ml of water was heated to boiling for 5 h. The solvent was evaporated in vacuo, the residue was separated on Al<sub>2</sub>O<sub>3</sub> plates. A total of 0.02 g of unreacted II and 0.15 g (75%) of 1-ferrocenyl-3-hexanone was obtained, orange crystals, mp 30°C (from hexane). In the IR spectrum (in KBr): 1711 cm<sup>-1</sup> (C=O). PMR spectrum (in CCl<sub>4</sub>): 0.90 (3H, triplet, CH<sub>3</sub>); 1.20-1.90 (2H, multiplet, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 2.30 (2H, triplet, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 2.55 (4H, singlet, CH<sub>2</sub>CH<sub>2</sub>); 3.98 (4H, singlet, C<sub>5</sub>H<sub>4</sub>); and 4.07 (5H, singlet, C<sub>5</sub>H<sub>5</sub>).

C<sub>18</sub>H<sub>20</sub>FeO. Found, %: C 87.58; H 7.09  
Calculated, %: C 87.82; H 7.09

Reduction of Vinylferrocene. A solution of 0.50 g of vinylferrocene (III) and 1.05 g of Mo(CO)<sub>6</sub> in 20 ml of aqueous diglyme was heated to boiling for 4 h. The solvent was evaporated in vacuo, the residue was separated on Al<sub>2</sub>O<sub>3</sub> plates. A total of 0.30 g (60%) of ethylferrocene (identified by its PMR spectrum) and also a small amount of an unidentified product were obtained.

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