Metathesis of Alkynes by a Molybdenum Hexacarbonyl–Resorcinol Catalyst

By André Mortreux and Michel Blanchard

(*Laboratoire de Chimie XI, Groupe de recherches sur la catalyse en Chimie organique, Faculté des Sciences, Avenue du Recteur Pineau, 86022 Poitiers, France*)

Summary A mixture of molybdenum hexacarbonyl and a phenol reagent is an active and selective homogeneous catalyst for the metathesis of aromatic disubstituted alkynes.

DISPROPORTIONATION of olefinic hydrocarbons has been studied in the heterogeneous[1] and the homogeneous phase[2]. An extension of this reaction to acetylenic hydrocarbons has also been studied over solid catalysts consisting of silica-supported tungsten oxide[3] and molybdenum oxide.[4] The general reaction can be represented by equation (1)

$$2R^1\text{–}C{\equiv}C\text{–}R^2 \rightleftharpoons R^1\text{–}C{\equiv}C\text{–}R^1 + R^2\text{–}C{\equiv}C\text{–}R^2 \qquad (1)$$

However, good selectivity can only be obtained with disubstituted alkynes, for cyclotrimerisation occurs almost exclusively with monosubstituted acetylenes.[5]

Successful attempts for the metathesis of internal alkenes and alk-1-enes have been reported using various transition-metal salts or co-ordination compounds in combination with selected organometallic derivatives of Lewis acids;[6] up to now, none have been described for the metathesis of alkynes. We have now found that associations of molybdenum hexacarbonyl and phenol catalyse the metathesis of disubstituted alkynes (R^1 = Ph, R^2 = *p*-PhMe) [equation (2)].

$$\underset{\textbf{(1)}}{2\text{Ph–C}{\equiv}\text{C–PhMe}} \rightleftharpoons \underset{\textbf{(2)}}{\text{Ph–C}{\equiv}\text{C–Ph}} + \underset{\textbf{(3)}}{\text{MePh–C}{\equiv}\text{CPhMe}} \quad (2)$$

In a typical reaction, *p*-tolylphenylacetylene (0·192 g) was added to a mixture of decalin (5 ml), molybdenum hexacarbonyl (0·026 g, C≡C:Mo = 10) and resorcinol (0·066 g, Mo:resorcinol = 1:6) and heated in a sealed vacuum tube at 160°. After 3 h, no further conversion was observed; the results show an approximative equilibrium ratio of starting material and products with a good selectivity [reaction product in mole % for compound **(1)** 55, **(2)** 23·5, **(3)** 21·5; selectivity = 88%]. Reaction products were separated by gas chromatography and identified by n.m.r. and i.r. spectroscopy.

With a Mo:resorcinol ratio of 1:1, we have found that metathesis occurs only after an induction period of about 15 min. The rate of metathesis is also increased significantly by increasing the amount of resorcinol; *e.g.* after 1 h at 160° with a C≡C:Mo ratio of 10 and the same dilution, % metathesis was only 7% for a Mo:resorcinol of 1:1 and 18·2% for Mo:resorcinol = 1:3.

Under the same conditions, we also found that phenol itself and α-naphthol were effective catalysts in combination with molybdenum hexacarbonyl.

The results obtained could explain the rôle of the hydroxyl groups of silica in the preparation of heterogeneous catalysts with molybdenum hexacarbonyl and molybdenum oxide, widely used in the disproportionation of olefinic and acetylenic hydrocarbons.

(*Received*, 1*st July* 1974; *Com.* 787.)

---

[1] R. L. Banks and G. C. Bailey, *Ind. and Eng. Chem.* (*Product Res. and Development*), 1964, **3**, 170.
[2] N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Letters*, 1967, 3327.
[3] F. Pennella, R. L. Banks, and G. C. Bailey, *Chem. Comm.*, 1968, 1548.
[4] A. Mortreux and M. Blanchard, *Bull. Soc. chim. France*, 1972, **4**, 1641.
[5] J. A. Moulijn, H. J. Reitsma, and C. Boelhouwer, *J. Catalysis*, 1972, **25**, 434.
[6] W. B. Hughes, *Organometallics in Chem. Synth.*, 1972, **1**, 341.