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OLEFIN EPOXIDATION FOLLOWED BY EPOXIDE TRANSFORMATION INTO 1,2-DIBROMOALKANE BY A PEROXONICKEL–DIBROMOMOLYBDENUM BIMETALLIC-SYSTEM

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Summary

The interaction of bis(t-butylisocyano)peroxonickel(II) and bis(triphenylphosphine oxide)dibromodioxomolybdenum(VI) in the presence of cyclohexene yields 1,2-dibromocyclohexane as the main product. This result is explained by the prior epoxidation of cyclohexene, followed by its conversion into the 1,2-dibromoalkane.

The epoxidation step implies peroxidation of the dioxomolybdenum by the peroxonickel species. It is shown that this occurs by a dioxygen-ligand transfer accompanied by the back transfer of two bromine atom and two triphenylphosphine oxide molecules.

Introduction

Preliminary catalytic autoxidation reactions of olefins using bimetallic systems [1] had shown promising selectivities when certain metallic couples were used, indicating a possible way to activate O_2. Our early attempts [2,3] to demonstrate this oxygen activation process by a dioxygen-ligand transfer from one metal to another in a Co/Mo system, although satisfactory for a stoichiometric reaction, was not sufficient to account for the results obtained under catalytic conditions [1].

Another bimetallic system which had given, under catalytic conditions, results implying possible oxygen activation was the couple Ni/Mo. In order better to understand the role of the two metals in this process we undertook a study of this metallic couple under stoichiometric conditions.

Results and discussion

The chosen system consisted of tetrakis(t-butylisocyano)nickel(0), which is easily oxidized to bis(t-butylisocyano)peroxonickel(II) [4] (**1**), and bis(triphenylphosphine

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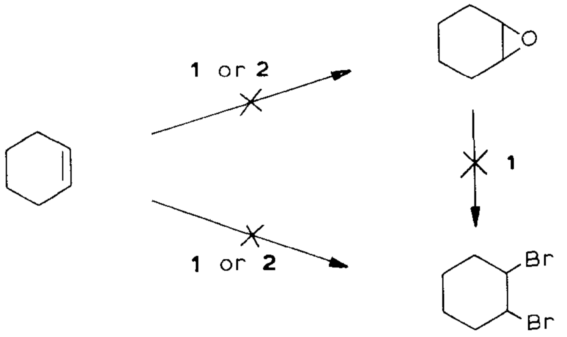
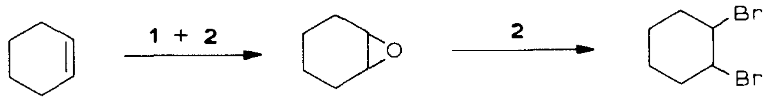
oxide)dibromodioxomolydenum(VI) [5] (**2**) which could not undergo a priori a metal oxidation and thus eliminates all possibility of any redox process at the metal.

When equimolar quantities of **1** and **2** were reacted under N_2 in the presence of cyclohexene the main product was 1,2-dibromocyclohexane (35%). This unexpected product was shown, in control experiments, not to arise from the interaction of **1** or **2** with cyclohexene (eq. 1) but from cyclohexene oxide and **2** [6]. Supporting evidence for this was given when the yield of 1,2-dibromocyclohexane rose to 48% when an excess **2** was used [6]. This strongly implied that an epoxidation had occured first, from the interaction of **1** and **2** and cyclohexene, followed by the conversion of the epoxide into the 1,2-dibromoalkane (eq. 2). This most interesting result led us to investigate in more detail the interaction of **1** and **2** in the absence of olefin.

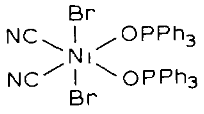


(1)



(2)

When the green dichloromethane solution of **1** was added slowly at −40°C to an equimolar yellow solution of **2**, a deep red mixture was immediately obtained. Addition of diethyl ether precipitated a yellowish paste, which was very hygroscopic, peroxide in character, contained more than 50% of molybdenum and was extremely difficult to purify. The mother liquor gave red crystalline needles which were analyzed and characterized as the hexacoordinate nickel(II) complex **3**. This indicated that a dioxygen ligand transfer from nickel to molybdenum had occured, accompanied by the back transfer of two bromine atoms and two triphenylphosphine oxide ligands from molybdenum to nickel. In order better to characterize the yellow paste, made up apparently of a polymeric molybdenum compound, various ligands were added to the medium.

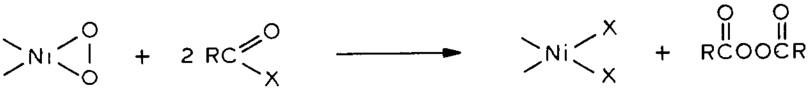


(3)

In the presence of an excess of triphenylphosphine oxide a yellow solid (**4**) was obtained under the same reaction conditions. Its element analysis could be rationalized in terms of an oligomeric species containing approximately one mol of phosphine oxide per two molybdenum atoms. IR spectroscopic analysis showed absorption bands, assignable to various oxo groups, in the regions 900–950 (Mo=O), 890 (Mo–O–O), and 800–840 (Mo–O–Mo). With an excess of hexamethylphosphotriamide, similar results were obtained; the light yellow solid (**5**) analyzed for HMPT/Mo = 1 and, again, showed three types of oxygenated function. Interestingly **5** could also be obtained directly from **4** simply by adding an excess of hexamethylphosphotriamide to a dichloromethane solution of **4**.

Once precipitated, all of these molybdenum species (**3**,**4**,**5**) could not be resolubilized, thus preventing any further recrystallization for more precise characterization. These results clearly reveal, however, the transfer of the peroxo moiety from nickel to molybdenum, indicating the peroxidation of the dioxomolybdenum(VI) species.

This reaction, in which a peroxo moiety is apparently transferred from nickel to molybdenum, accompanied by the back transfer of two bromine atoms, has some analogies with reactions of dioxygen complexes with strong electrophiles such as acyl halides [7] (eq. 3); in our case the electrophile being the dioxomolybdenum species.



(3)

It would seem, a priori, that it is through such a process that the epoxidation of cyclohexene occurs. Peroxo molybdenum species are indeed well known to epoxidize olefins [8]. However, when the isolated peroxomolybdenum species **3**, **4** or **5** were reacted with cyclohexene no formation of epoxide was observed. This could be rationalized by the polymeric character of species **3**, **4** and **5**, formed during their isolation, making them unreactive.

However, if this was not the case, reaction 2 must be explained by an interaction of **1** and **2**. This seems to be necessary for the oxidation of cyclohexene whether the oxidizing agent is a bimetallic species, in which the dioxygen transfer from Ni to Mo is not total, or it is a peroxidic molybdenum complex in solution.

Experimental

Materials

Tetrakis(t-butylisocyano)nickel(0) [4] and bis(t-butylisocyano)peroxonickel(II) [4] were prepared as reported. Cyclohexene was passed through a column packed with alumina prior to use and other chemicals were used as received. All solvents were reagent grade and were thoroughly dried and degassed prior to use.

Physical measurements

Elemental analyses were performed by Alfred Bernhardt Analytische Laboratorium, Engelskirchen, West Germany. IR spectra were recorded on a Perkin–Elmer 397 spectrophotometer using samples in KBr disks or Nujol mulls.

Preparation of bis(triphenylphosphine oxide)dibromodioxomolybdenum(VI) [5]

To 40 ml of degassed acetonitrile was added MoO_2Br_2 (3.6 mmol) and then a 20 ml acetonitrile solution containing triphenylphosphine oxide (7.2 mmol). The orange solution obtained was stirred while a yellow solid precipitated. This was filtered off, washed with n-pentane and dried under vacuum. Yellow crystals were obtained by slow evaporation of a dichloromethane solution of the solid. IR (KBr) 940, 900 cm^{-1} (Mo=O).

Preparation of bis(hexamethylphosphotriamide)dibromodioxomolybdenum(VI)

To a 30 ml dichloromethane solution containing MoO_2Br_2 (8.6 mmol) was added 17.2 mmol of freshly distilled hexamethylphosphotriamide. The mixture was stirred for 30 min at room temperature and then cooled to −30°C. Green crystals were obtained after several days; they were filtered off and dried under vacuum. IR (KBr) 940, 900 cm^{-1} (Mo=O). Anal. Found: C, 22.39; H, 5.42; N, 12.95; P, 9.77; Br, 24.98; Mo, 15.03; O, 9.46 (by difference). $C_{12}H_{36}N_6P_2O_4Br_2Mo$ calcd.: C, 22.28; H, 5.57; N, 13.01; P, 9.59; O, 9.91; Br, 24.75; Mo, 14.85%.

Reaction of bis(triphenylphosphineoxide)dibromodioxomolybdenum(VI) with bis(t-butylisocyano)peroxonickel(II) in the presence of cyclohexene

To a thoroughly degassed dichloromethane solution (20 ml) of bis(triphenylphosphine oxide)dibromodioxomolybdenum(VI) (23 mmol) and triphenylphosphine oxide (46 mmol), cooled to −70°C, was added 0.1 ml (10 mmol) of cyclohexene. To this solution was then added a cooled (−50°C) dichloromethane solution (20 ml) of bis(t-butylisocyano)peroxonickel(II), prepared directly from 1 g (26 mmol) of tetrakis(t-butylisocyano)nickel(0). The mixture was slowly warmed to −40°C, at which temperature a red coloration began to appear. Stirring was continued for 1 h at −40°C and then at room temperature for 24 h. Gas chromatographic analysis, using an internal standard, indicated the presence of cyclohexene oxide (1%), t-butylisocyanate (traces) and 1,2-dibromocyclohexane (35%).

Reaction of bis(triphenylphosphine oxide)dibromodioxomolybdenum(VI) with bis(t-butylisocyano)peroxonickel(II)

To a dichloromethane solution (20 ml) of $MoO_2Br_2(OPPh_3)_2$ (7.3 mmol), cooled to −60°C, was slowly added, while stirring, a cooled (−60°C) dichloromethane solution (20 ml) of $(t\text{-}Bu_2)NiO_2$ obtained directly from $(t\text{-}Bu)_4Ni$ (8.1 mmol). The mixture was slowly warmed to −40°C, at which temperature the greenish solution slowly turned red. Stirring was continued at −30°C overnight. Addition of diethyl ether precipitated a yellowish solid which was filtered off, washed with diethyl ether and dichloromethane, and dried under vacuum. This very hygroscopic solid could not be purified since it had become totaly insoluble in most organic solvents. Addition of n-pentane to the remaining red solution precipitated a red solid which was recrystallized from CH_2Cl_2/Et_2O to give 0.32 g (61%) of dark red needles. IR (KBr) 3045, 1580, 1190, 995 ($OPPh_3$); 2200 cm^{-1} (N≡C). Anal. Found: C, 58.86; H, 5.07; N. 3.16; P, 6.80; Br, 17.52; Ni, 6.46. $C_{46}H_{48}N_2P_2O_2Br_2Ni$ calcd.: C, 58.70; H, 5.10; N, 2.98; P, 6.58; Br, 17.0; Ni, 6.24%.

Reaction of bis(triphenylphosphine oxide)dibromodioxomolybdenum(VI) with bis(t-butylisocyano)peroxonickel(II)

(a) In the presence of triphenylphosphine oxide

The reaction was run as described above but in the presence of an equimolar amount of triphenylphosphine oxide. Addition of diethyl ether precipitated a yellow crystalline solid which was filtered off, washed with CH_2Cl_2 and analyzed. Recrystallization was not possible since it could not be redissolved even in CH_2Cl_2. IR (KBr) 3045, 1580, 1190, 995 ($OPPh_3$); 950, 940, 915, 900 (Mo=O); 890 (O–O), 840, 800 cm^{-1} (Mo–O–Mo). Anal. Found: C, 42.01; H, 3.13; P, 6.53; Mo, 24.33; Ni, 4.42; O, 19.58 (by difference).

(b) In the presence of hexamethylphosphotriamide

The reaction was run as described above but in the presence of hexamethylphosphotriamide instead of triphenylphosphine oxide. The light yellow solid obtained could not, as in the previous case, be recrystallized because of its low solubility. IR (KBr) 3000–2800, 1300, 990 (HMPT); 940, 930, 900 (Mo=O); 890 (O–O); 840, 800 cm^{-1} (Mo–O–Mo). Anal. Found: C, 21.24; H, 5.06; N, 10.61; P, 8.78; Mo, 28.21; Ni, 4.70; O, 21.40 (by difference).

This compound could also be obtained from the triphenylphosphine oxide reaction (see (a) above) by adding hexamethylphosphotriamide prior to the precipitation with diethyl ether.

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