



Cyclotrimerization of alkynes vs. ketone formation in aqueous microemulsion

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ABSTRACT

In the course of our attempts to develop sustainable conditions for the catalytic organic reactions by replacement of the traditional but environmentally disfavored organic solvents by water, we studied the cyclotrimerizations of alkynes, in aqueous microemulsions. The catalyst for these reactions was the rhodium-trichloride encaged within silica sol–gel. In acidic aqueous media, alkynes can undergo addition of water to form their corresponding ketones. In order to eliminate completely the formation of ketones, relatively low reaction temperatures are required. At higher reaction temperatures, however, buffered microemulsion media is preferable.

Cyclotrimerization of alkynes proved to be dependent on the reaction temperatures, the electronic nature of the substrates, the electronic nature of the surfactant and on the hydrophobicity of the sol–gel support. During the cyclotrimerization reaction, the rhodium complex was turned to Rh(0) nanoparticles characterized by TEM measurements.

These investigations may be regarded as model studies for the conversion of alkynes into substituted benzenes in water.

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1. Introduction

The transition-metal catalyzed [2+2+2] cycloaddition of alkynes is a very powerful method for the construction of arenes in a single operational step. It continues to attract great attention by virtue of its intrinsic atom economy and convergent nature, as well as the importance of substituted benzenes as synthetic intermediates [1–4]. Since the first discovery by Reppe and co-workers [5], the cyclotrimerization takes place in the presence of either transition metal-derived catalysts [6,7], in aqueous media and biphasic conditions [8–10], by heterogeneous catalysts [11–14], in supercritical carbon dioxide [15], or under photochemical conditions [16–18].

In the course of our attempts to replace the conventional but harmful solvents in organic processes by benign aqueous media, we have already developed a general system in which the substrates are solubilized in aqueous emulsions or microemulsions and the catalysts can be recycled [19,20]. In these systems suitable surfactants promote the solubilization in the aqueous media

and sol–gel materials support the catalysts. So far, we found that our system can be applied to a variety of hydrogenations processes [20], transfer hydrogenation [21], regioselective hydroformylation [22], double bond migration in allylic compounds [23], disproportionation of dihydroarenes [24], and carbon–carbon bond coupling processes [25,26] (Heck, Suzuki, Stille and multi-component addition reactions). We now find that the combination of aqueous emulsions of the substrates and sol–gel entrapped catalysts – the so-called Emulsion/Solid-heterogenization method for Transport and catalysis (EST) – is applicable to facile alkynes cyclotrimerization processes.

In aqueous microemulsion, however, the cyclotrimerization of alkynes is competed with the ketones formation process in the presence of RhCl₃ entrapped within silica sol–gel. In order to add water to alkynes to form ketones, it is essential to stay at low pH. In aqueous media, RhCl₃ can be easily hydrolyzed and provides low pH solutions. Furthermore, we already demonstrated that efficient metal-free hydration of alkynes can be performed easily in aqueous microemulsion at low pH [27].

In this report we describe an efficient transformation of alkynes to substituted benzenes by RhCl₃ entrapped within sol–gel support in a regioselective manner under relatively mild conditions within environmentally favored media.

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2. Experimental

2.1. Instruments

NMR spectra were recorded with either Bruker DRX-400 or Bruker Avance II-500 instrument. Infrared spectra were recorded with a Perkin-Elmer 65 FTIR spectrometer. Mass spectral measurements were performed with a Q-TOF-II spectrometer. Gas chromatographic analyses were carried out with a Hewlett-Packard model Agilent 4890D equipped with either a 30 m long column packed with Carbowax 20M-poly(ethylene glycol) in fused silica (Supelco 25301-U) or with a 15 m long column packed with bonded crosslinked (5% phenyl) methyl polysiloxane [HP-5]. ICP-MS analyses were performed with a Perkin-Elmer model ELAN DRC II instrument. XPS measurements were performed with a Kratos Axis Ultra X-ray photoelectron spectrometer. Spectra were acquired with monochromated Al K α (1486.7 eV) X-ray source with 0° take off angle. The pressure in the test chamber was maintained at 1.5×10^{-9} Torr during the acquisition process. High resolution XPS scans were collected for Rh 3d and C 1s peaks with pass energy 20 eV. The XPS binding energy was calibrated with respect to the peak position of C 1s at 285.0 eV. Data analysis was performed with Vision processing data reduction software (Kratos Analytical Ltd.) and Casa XPS (Casa Software, Ltd.). Transmission electron microscopy was done with Scanning Transmission Electron Microscope (STEM) Tecnai G2 F20 (FEI Company, USA) operated at 200 kV and equipped with EDAX-EDS for identification of the elemental composition. Transmission electron microscopy was done with a scanning transmission electron microscope (STEM) Tecnai G2F20 (FET company) operated at 200 kV and equipped with EDAX-EDS for identification of elemental compositions.

2.2. Chemicals

Ethynylbenzene, 1-(1,1-dimethylethyl)-4-ethynylbenzene, 3-ethynylthiophene, dodecyltrimethylammonium bromide (DTAB), cetyltrimethylammonium bromide (CTAB), sodium benzene 4-dodecylsulfonate (SDBS), tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), ethyltriethoxysilane, *n*-propyltrimethoxysilane and phenyltrimethoxysilane were purchased from the Sigma-Aldrich Chemical Company. 1-Ethynyl-4-methoxybenzene, 1-ethynyl-4-methylbenzene, 1-ethynyl-4-chlorobenzene, 1-ethynyl-4-fluorobenzene and *n*-octyltriethoxysilane were purchased from the Alfa Aesar Chemical Company. Buffer solution pH 4 [Phthalate], buffer solution pH 7 [Phosphate] and buffer solution pH 9 [Borate] were purchased from the J. T. Baker.

2.3. Preparation of hydrophilic immobilized catalyst

Entrapment of RhCl₃ within hydrophilic silica sol-gel was carried out as follows: to a solution of tetraethoxysilane (3 ml, 13.4 mmol), triply distilled water (TDW, 1.33 ml) and EtOH (3.5 ml) was added RhCl₃·3H₂O (30 mg, 0.114 mmol) and N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride [50% in methanol] (60 mg, 0.114 mmol). Stirring was continued as long as possible (24 h) and the resulting gel was aged for 2 days at room temperature, dried at 80 °C and 0.1 Torr for 12 h. The ceramic material was washed with boiling CH₂Cl₂ (2 × 15 ml) to ensure the removal of any metallic compound that was not entrapped within the sol-gel matrix, and redried at 80 °C and 0.1 Torr to give a constant weight.

2.4. Preparation of hydrophobic immobilized catalyst

Entrapment of RhCl₃ within octylated silica sol-gel was carried out as follows: a solution of *n*-octyltriethoxysilane

(2.1 ml, 6.68 mmol) (or the corresponding ethyltriethoxysilane, *n*-propyltrimethoxysilane or phenyltrimethoxysilane), TDW (0.38 ml) and EtOH (5.6 ml) was stirred for 24 h. Then, to a solution of tetramethoxysilane (3.6 ml, 24.2 mmol), TDW (2.4 ml) and MeOH (2 ml) was added RhCl₃·3H₂O (30 mg, 0.114 mmol) and N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride [50% in methanol] (60 mg, 0.114 mmol). The two mixtures were combined and the stirring was continued as long as possible (2–7 days). The resulting gel was aged for 2 days at room temperature, dried at 80 °C and 0.1 Torr for 12 h. The ceramic material was washed with boiling CH₂Cl₂ (2 × 15 ml) to ensure the removal of any metallic compounds that was not entrapped within the sol-gel matrix, and redried at 80 °C and 0.1 Torr to give a constant weight.

2.5. General procedure for the emulsification of the substrates

Typically, a mixture of TDW (11.4–17.6 ml, 89.3 wt.%), and a suitable surfactant (0.42–0.65 g, 3.3 wt.%) was stirred at room temperature. Then, the substrate (0.102–0.158 g, 1 mmol, 0.8 wt.%) was added dropwise under vigorous stirring. The emulsion, so formed, was titrated with *n*-propanol until a clear transparent mixture was obtained (usually 1.05–1.63 ml, 6.6 wt.%).

2.6. Emulsification of the substrate when SDBS was used as surfactant

A mixture of TDW (11.4–17.6 ml, 89.3 wt.%), SDBS (0.42–0.65 g, 3.3 wt.%) was heated to 50–55 °C on a water bath in order to dissolve the surfactant. Then, the substrate (0.102–0.158 g, 1 mmol, 0.8 wt.% of the desired microemulsion) was added dropwise under vigorous stirring. The emulsion, so formed, was titrated with *n*-propanol until a clear transparent mixture was obtained (usually 1.05–1.63 ml, 6.6 wt.%) that disperses a beam of laser light.

2.7. General procedure for the cyclotrimerization of alkynes

The above microemulsion of the substrate, together with immobilized rhodium catalyst (15 mg RhCl₃), were placed in either an autoclave or in a pressure vessel and heated with stirring to the desired temperature for the required length of time. The reaction vessel was cooled to room temperature and the mixture was filtered. The filtrate was treated with NaCl (2 g), which caused the mixture to separate into two phases. The sol-gel material, as well as the aqueous layer, were extracted with CH₂Cl₂ (2 × 10 ml) to ensure complete removal of the products. The combined organic solutions were dried (MgSO₄), concentrated and analyzed both by GC and ¹H NMR and compared with authentic samples. The heterogenized catalyst was dried at 80 °C and 0.1 Torr for 5 h in order to be ready for use in the next run.

2.8. Spectral data of selected products

- (1) 1,2,4-Triphenylbenzene ¹H NMR (400 MHz, CDCl₃): δ 7.17–7.25 (m, 10H), 7.35–7.72 (m, 8H) [10].
- (2) 1,3,5-Triphenylbenzene ¹H NMR (400 MHz, CDCl₃): δ 7.39–7.54 (m, 9H), 7.70–7.75 (m, 6H), 7.82 (s, 3H) [10].
- (3) 1,2,4-Tris(4-fluorophenyl)benzene ¹H NMR (400 MHz, CDCl₃): δ 6.89–6.97 (m, 4H), 7.07–7.20 (m, 6H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.54–7.67 (m, 4H) [10].
- (4) 1,3,5-Tris(4-fluorophenyl)benzene ¹H NMR (400 MHz, CDCl₃): δ 7.15–7.25 (m, 6H), 7.63–7.68 (m, 6H), 7.69 (s, 3H) [10].
- (5) 1,2,4-Tris(4-chlorophenyl)benzene ¹H NMR (400 MHz, CDCl₃): δ 7.05–7.12 (m, 4H), 7.21–7.24 (m, 4H), 7.42–7.49 (m, 3H), 7.55–7.62 (m, 4H) [10].

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