J. Chem. Research (S),
1998, 518–519
J. Chem. Research (M),
1998, 2348–2362

Cyclotrimerization of Alkynes using an Activated Zirconium–Titanium Catalyst Prepared by the Reduction of Zirconium Tetrachloride and Titanium Trichloride with Lithium Powder

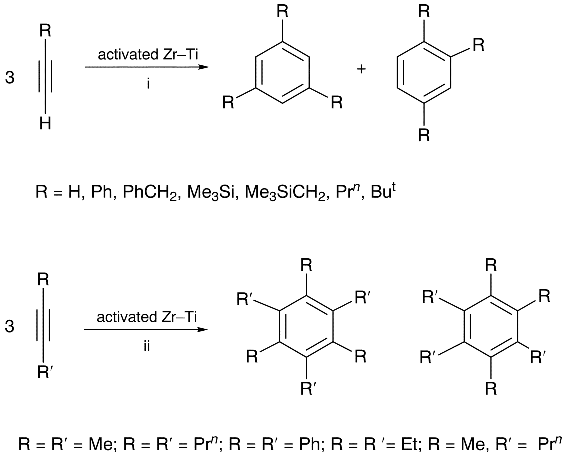
Kyu Sang Chio, Moon Kyeu Park and Byung Hee Han*

Department of Chemistry, College of Natural Sciences, Chungnam National University, Taejon 305-764, Korea

Activated zirconium–titanium prepared by the reduction of zirconium tetrachloride and titanium trichloride with lithium efficiently catalyses the cyclotrimerization of alkynes.

Activated metal powders, prepared by the reduction of the corresponding metal halide with alkali metals in an ethereal solvent, have been employed in a wide variety of synthetic applications.[1] However, no example has been reported for the cyclotrimerization of alkynes using activated metal powders prepared by this method.

We recently reported that activated metals catalyse the hydrosilylation of carbonyls,[2] and olefins,[2,3] the reduction of nitroarenes[4] and the coupling of carbonyls.[5] During the attempted addition of an alkylsilane to alkynes, we observed that an activated zirconium–titanium, prepared by the reduction of zirconium tetrachloride and titanium trichloride with lithium powder, showed exceptional catalytic activity for the formation of 1,2,4- and 1,3,5-triphenylbenzenes from phenylacetylene in high yields. This highly reactive zirconium catalyst was prepared by the treatment of zirconium tetrachloride (1 mmol) and titanium trichloride (1 mmol) with Li powder (7.5 mmol) in dry dimethoxyethane (DME, 4 ml)/tetrahydrofuran (THF, 1 ml). After stirring these reagents under an atmosphere of nitrogen at room temperature for 1 h, the powder changed from grey to black and the finely divided zirconium–titanium appeared as a black powder which settled in the dark solution. The activated zirconium–titanium (Zr–Ti) in a dark solution was used in this investigation without any further treatment. The alkyne (10 mmol) was added to this solution and then stirred under an atmosphere of nitrogen at room temperature of 2 h. Product isolation was straightforward. The resulting solution was evaporated and dichloromethane was added. The solution was filtered to remove the catalyst through a silica gel column pad using hexane/dichloromethane (1:1, v/v) as the eluent. Solvent evaporation gave the corresponding cyclotrimerization products. The isolated yields are based on quantities obtained after this step. The results of the cyclotrimerization of the alkynes with this catalyst are shown in Scheme 1.



R = H, Ph, PhCH$_2$, Me$_3$Si, Me$_3$SiCH$_2$, Pr^n, Bu^t

R = R′ = Me; R = R′ = Pr^n; R = R′ = Ph; R = R′= Et; R = Me, R′ = Pr^n

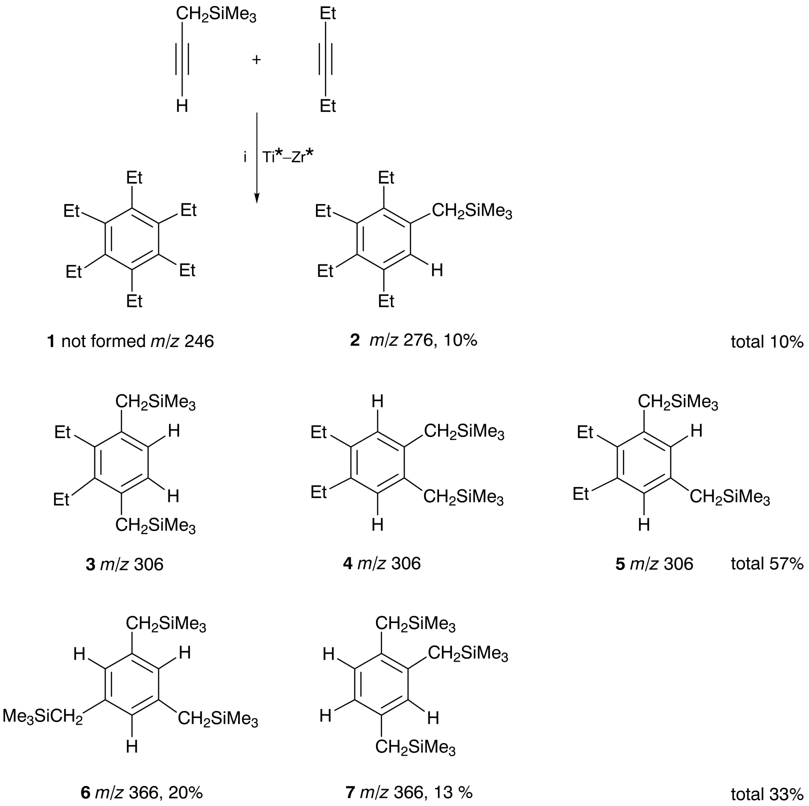
Scheme 1 *Reagents and conditions*: Activated Zr–Ti was prepared as described above. i, After metal activation, alkynes (10 mmol) were added and stirred at 25 °C for 3 h (80–95% isolated yields); ii, after metal activation, alkynes (10 mmol) were added and stirred again at 25 °C for 3 h (70–95% isolated yields)

Using our activated Zr–Ti catalysts, the terminal alkynes as well as internal alkynes were mainly cyclotrimerized to the 1,2,4- and 1,3,5-benzene derivatives in fair yield without the formation of a dimer or polymer. However, the cyclotrimerization of phenylacetylene did not occur using a commercially available zirconium (or titanium) in DME/THF after boiling under reflux under nitrogen for 6 h. Also, when, in the absence of the activated catalyst, zirconium tetrachloride, titanium trichloride and phenylacetylene in DME/THF were boiled under reflux for 8 h, trimerization was not detected at all and most of the phenylacetylene was recovered. Activated zirconium (prepared by the reduction of zirconium tetrachloride with lithium) also catalysed the cyclotrimerization of phenylacetylene and 3-phenylprop-1-yne to afford the corresponding trisubstituted benzene derivatives in 95 and 85% isolated yields (combined yields of 1,3,5- and 1,2,4-isomers), respectively. However, using activated Zr or Ti, the cyclotrimerizations of the 3,3-dimethylbut-1-yne, (trimethylsilyl)acetylene, pent-1-yne and internal alkynes were not successful. The 1,3,5 *versus* 1,2,4-isomer ratio using our activated Zr–Ti showed that the 1,3,5-trisubstituted benzenes were the major products, as expected, in the case of phenylacetylene (1.38:1, 1,3,5/1,2,4-isomer ratio), trimethylsilylacetylene (15.7:1), pent-1-yne (1.7:1) and 3,3-dimethylbut-1-yne (7.33:1). Interestingly, the more hindered 1,2,4-isomers were the major products in the case of 3-phenylprop-1-yne (0.39:1), 3-(trimethylsilyl)prop-1-yne (0.52:1) and hex-2-yne (0.43:1) under the same reaction conditions.

We have also examined the catalytic activities of other activated metals for the cyclotrimerization of phenylacetylene. We found that using activated metals such as Ni, Ti, Cr, Fe, Mn, Mo and W, prepared by the reduction of the metal halides NiI$_2$, TiCl$_3$, CrCl$_3$, FeCl$_3$, MnCl$_2$, MoCl$_5$ and WCl$_6$, respectively, with lithium powder in DME/THF (stirred or boiled under reflux 1–3 h for metal activation, stirred or boiled under reflux 2–6 h for cyclotrimerization), triphenylbenzene (1,2,4- and 1,3,5-isomers) was formed in 80–83% isolated yields (using Ni and Mo), 5–20% (using Fe, Cr, Mn), 10–55% yield, together with the hydrogenated dimer 1,4-diphenylbutane in 5–45% yield (using W, Ti and Nb); unreacted phenylacetylene was also detected (by GLC). These activated metal catalysts were inactive for internal alkynes such as hex-3-yne. We have also studied the reactivity of activated metal catalysts other than activated zirconium–titanium. Surprisingly, it appears that titanium is

---

*To receive any correspondence.



Scheme 2 *Reagents and conditions*: Activated Zr–Ti was prepared as described in the text. i, After metal activation, alkynes (5 mmol) were added and stirred again at 25 °C for 3 h

the best choice of metal for the preparation of catalysts with zirconium. For example, the cyclotrimerization of 3,3-dimethylbut-1-yne using activated Zr–Ti (stirred for 1 h for metal activation, stirred for 3 h for cyclotrimerization) gave 1,3,5- and 1,2,4-tri-*tert*-butylbenzenes in 79% isolated yield (1,3,5:1,2,4 = 7.33:1 isomer ratio). However, the cyclotrimerization of 3,3-dimethylbut-1-yne using activated zirconium (stirred for 1 h for metal activation, boiled under reflux 3 h for cyclotrimerization) gave tri-*tert*-butylbenzene in 35% yields (1,3,5:1,2,4 = 4:1 isomer ratio) along with a dimer, 1,4-di-*tert*-butylbuta-1,3-diene in 20% yield and unidentified compounds (by GLC). The cyclotrimerization of 3,3-dimethylbut-1-yne using activated titanium under the same reaction conditions give much poorer yields along with unidentified products. Also, the yields for the cyclotrimerization of 3,3-dimethylbut-1-yne were not improved when the other activated catalysts, prepared from a mixture of $ZrCl_4$ and metal halides (such as NiI_2, WCl_6, $CrCl_3$, $FeCl_3$, $MnCl_2$, $MoCl_5$) with Li power (stirred 1 h for metal activation, stirred or boiled under reflux 2–6 h for cyclotrimerization), were employed. However, the cyclotrimerization of ethyne to benzene using activated Zr–Ti was very successful. For example, the above mentioned dark solution of activated Zr–Ti (THF was used as solvent) was stirred under an atmosphere of ethyne (through the use of a balloon) at room temperature for 3 h. The mixture was filtered and the remaining liquid upon fractionation yielded benzene (0.1 ml). However, the attempted cyclotrimerization of ethyne to benzene using activated Zr, Ni, W and Ti under the same reaction conditions was unsuccessful.

As an extension of this work, we studied the cyclocotrimerization with hex-3-yne and 3-(trimethylsilyl)prop-1-yne. Using our activated Zr–Ti in DME/THF with stirring for 3 h, the cyclocotrimerization products, such as compounds **2**, **3**, **4** and **5**, were exclusively formed along with the cyclotrimerization products, **6**, **7** (by GC-MS). However, hexaethylbenzene was not detected (Scheme 2). The source of this reactivity of the highly activated metals species in the cyclotrimerization of alkynes may be the high surface area, and the existence of unique metal species.

In conclusion, we have demonstrated that activated Zr–Ti is a suitable catalyst for the cyclotrimerization of alkynes. Efforts are being made to apply these highly reactive metal powders to the Diels–Alder reaction as well as to the transformation of organic functional groups.

Financial support for this work was provided by the Korea Science and Engineering Foundation (961-0302-024-2) and the Basic Science Research Institute program, Ministry of Education of the Republic of Korea (BSRI-97-3433).

Techniques used: ^1H NMR, GLC, TLC, GC-mass spectrometry

References: 24 Schemes: 2

Table 1: Activated-metal-catalysed cyclotrimerization of alkynes

Received, 16th February 1998; Accepted, 28th May 1998
Paper E/8/01320I

References cited in this synopsis

1 R. D. Rieke, S. H. Kim and X. M. Wu, *J. Org. Chem.*, 1997, **62**, 6921 and recent refs for the preparation of activated metals cited therein.

2 P. Boudjouk, B. H. Han, J. R. Jacobsen and B. J. Hauch, *J. Chem. Soc., Chem. Commun.*, 1991, 1424.

3 S. J. Lee, T. Y. Kim, M. K. Park and B. H. Han, *Bull. Korean Chem. Soc.*, 1996, **17**, 1082 (*Chem. Abstr.*, 1997, **126**, 60010).

4 (*a*) T. H. Yun, M. K. Park and B. H. Han, *J. Chem. Res.* (*S*), 1992, 336; (*b*) S. H. Pyo and B. H. Han, *Bull. Korean Chem. Soc.*, 1995, **16**, 181 (*Chem. Abstr.*, 1995, **122**, 239237).

5 S. J. Lee, T. Y. Kim, K. S. Choi, M. K. Park and B. H. Han, *Bull. Korean Chem. Soc.*, 1997, **18**, 224 (*Chem. Abstr.*, 1997, **126**, 263662).