

0040-4039(94)02028-0

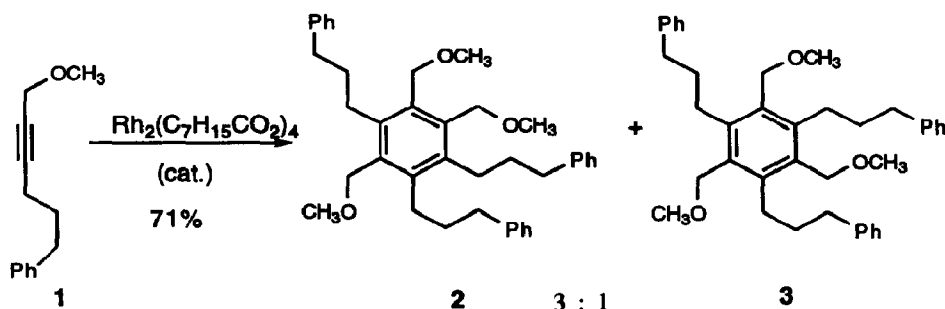
HEXASUBSTITUTED BENZENES BY ALKYNE CYCLOTRIMERIZATION

Douglas F. Taber* and Mohammed Rahimizadeh¹

Department of Chemistry & Biochemistry, University of Delaware, Newark, DE 19716 USA

Abstract: Rhodium octanoate is shown to be an effective catalyst for the cyclotrimerization of a disubstituted alkyne.

One of the most powerful methods for the assembly of highly substituted benzene derivatives is the cyclotrimerization of an alkyne (1 → 2 + 3). Several quite reactive organometallic reagents have been used to effect this transformation.^{2, 3} We now report that rhodium octanoate⁴ efficiently catalyzes the cyclotrimerization of an alkyne.



The substrate for the cyclization was prepared by alkylation⁵ of the THP ether of propargyl alcohol⁶ with 3-phenyl-1-bromopropane. Hydrolysis of the THP ether followed by O-methylation of the derived alcohol then gave 1.

Cyclization Procedure: Alkyne **1** (105 mg, 0.56 mmol) and $\text{Rh}_2(\text{C}_7\text{H}_{15}\text{CO}_2)_4$ (10 mg, 0.013 mmol, 2 mol %) in toluene (4 mL) were heated (sealed vial) at 190° for 30 h. The mixture was chromatographed on silica gel to give recovered **1** (10 mg), followed by **2** (36 mg) and **3** (13 mg) as colorless oils, TLC $R_f = 0.66$ and 0.55 (5% acetone / CH_2Cl_2) respectively. In addition, a mixed fraction of **2** and **3** was recovered (18 mg), for a total combined yield from **1** of 71%. **2**: ^1H NMR (δ): 7.3-7.1, m, 15 H); 4.27 (s, 2 H); 4.26 (s, 2H); 4.09 (s, 2H); 3.25, s, 6 H); 3.09 (s, 3 H); 2.7-2.4 (m, 12 H); 1.7-1.5 (m, 6 H). ^{13}C NMR (δ): 142.2, 141.4, 140.5, 138.7, 136.0, 13.0, 133.7, 128.6, 128.3, 125.8, 68.7, 68.6, 58.4, 58.3, 58.1, 36.5, 36.3, 33.7, 33.2, 28.9, 28.7. MS (m/z , %): 564 (0.7), 532 (27), 487 (41), 413 (58), 381 (13), 91 (100). **3**: ^1H NMR (δ): 7.3-7.1 (m, 15 H); 4.1 (s, 6 H); 3.11 (s, 9 H); 2.7-2.6 (m, 12 H); 1.8-1.7 (m, 6 H). ^{13}C NMR (δ): 143.1, 142.1, 132.4, 128.6, 128.3, 125.7, 68.7, 58.1, 36.5, 33.7, 29.2. MS (m/z , %): 532 (4) ($\text{M}^+ - \text{CH}_3\text{OH}$), 500 (19), 468 (36), 456 (28), 455 (38), 377 (16), 91 (100).

Of the transition metal complexes that we have so far investigated (which also include $(\text{Ph}_3\text{P})_3\text{RhCl}$, $\text{Mo}(\text{CO})_6$, $(\text{Ph}_3\text{P})_4\text{Pd}$, $(\text{Ph}_3\text{P})_4\text{Pt}$, $\text{Rh}_2(\text{trifluoroacetate})_4$, and dppp-PdCl_2), rhodium octanoate is unique in affording synthetically useful conversion of **1** to **2** and **3**. As rhodium octanoate⁴ is commercially available and air stable, this cyclodimerization should be a useful addition to the armamentarium of organic chemistry.

Acknowledgments: We thank CRDEC/Aberdeen and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. M.R. thanks the University of Mashad for a sabbatical leave.

References and Notes:

1. Permanent address: Department of Chemistry, Mashad University, Mashad, Iran.
2. Generally useful reagents for alkyne cyclotrimerization include (a) $\text{R}_3\text{Al} / \text{TiCl}_4$: Franzus, B.; Canterino, P.J.; Wickcliffe, R.A. *J. Am. Chem. Soc.* **1959**, *81*, 1514. (b) $\text{L}_n\text{NiCl}_2 / \text{NaBH}_4$: Luttinger, L.B.; Colthup, E.C. *J. Org. Chem.* **1962**, *27*, 3752. (c) $\text{Co}_2(\text{CO})_8$: Kruerke, U.; Hoogzand, C.; Hubel, W. *Chem. Ber.* **1961**, *94*, 2817. (d) $\text{CpCo}(\text{CO})_2$: Vollhardt, K.P.C. *Pure & Appl. Chem.* **1985**, *57*, 1819. (e) $(\text{Ph}_3\text{P})_3\text{RhCl} / \text{EtOH}$: Grigg, R.; Scott, R.; Stevenson, P. *Tetrahedron Lett.* **1982**, *23*, 2691. (f) Pd / TMSCl : Jhingan, A.K.; Maier, W.F. *J. Org. Chem.* **1987**, *52*, 1161. (g) $\text{NbCl}_5 / \text{Zn}$: Kataoka, Y.; Takai, K.; Oshima, K.; Utimoto, K.; *J. Org. Chem.* **1992**, *57*, 1615.
3. Cyclotrimerization of phenyl acetylene to the statistical mixture of triphenyl benzenes using $(\text{RhCl}_4)^-$ bound to a quaternary ammonium ion exchange resin was reported quite recently: Setty-Fichman, M.; Blum, J.; Sasson, Y. *Tetrahedron Lett.* **1994**, *37*, 781.
4. Rhodium octanoate, purchased from Strem, is an air-stable blue powder.
5. Chong, J.M.; Wong, S. *Tetrahedron Lett.* **1986**, *27*, 5445.
6. Furita, K.; Ishiguro, M.; Haruta, R.; Ikeda, N.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2768.

(Received in USA 5 April 1994; revised 22 April 1994; accepted 11 October 1994)