

W(II)-catalyzed hydroarylation of bicyclo[2.2.1]-hept-2-ene by simple arenes

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Abstract—The tungsten(II) carbonyl compound $(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{SnCl}_3)(\text{CO})_3$ has been found to be a very effective catalyst for the hydroarylation of bicyclo[2.2.1]hept-2-ene (norbornene) conducted in arene solution at room temperature. Norbornene adducts with benzene, toluene, *para*-xylene, and mesitylene have been isolated and their structures have been unambiguously established by means of ^1H and ^{13}C NMR spectroscopy. On the basis of ^1H NMR monitoring of several catalytic reactions, a possible mechanism involving coordination of norbornene to the W(II) atom and its activation has been proposed.

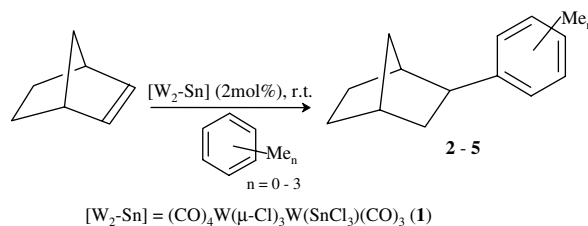
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Catalytic hydroarylation of olefins involving activation of C–H bonds is one of the most efficient methodologies for the formation of a new carbon–carbon bond and from that point of view attracts considerable interest from the chemical and pharmaceutical industries. However, examples of transition metal-catalyzed hydroarylation of C=C double bonds are very rare and involve mainly Pd, Rh, Ir, and Ru complexes.¹ One of the first examples of hydroarylation of olefins was detected during olefin metathesis promoted by transition metal complexes, which possess a strong Lewis acidity.² Similarly, the metathesis of acyclic olefins initiated by tungsten(II) chlorocarbonyls carried out in an aromatic hydrocarbon as solvent is accompanied by arene alkylation.^{3a} The yield of ring-opening metathesis polymerization (ROMP) of bicyclo[2.2.1]hept-2-ene (NBE) obtained in the presence of W–Sn and Mo–Sn heterobimetallic compounds of the type $[(\text{CO})_4\text{M}(\mu\text{-Cl})_3\text{M}(\text{SnCl}_3)(\text{CO})_3]$ has always been lowered by concurrent reactions,^{3b} that is, hydroarylation in toluene solution and dimerization in dichloromethane solution.^{3c}

In this letter we report an efficient addition of simple arenes, such as benzene, toluene, *para*-xylene, and mesitylene to norbornene (NBE) at room temperature in the presence of $[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{SnCl}_3)(\text{CO})_3]$ (**1**) cata-

lyst,⁴ affording predominantly arene/NBE 1/1 adducts. The reaction represents a useful synthetic protocol to form norbornylarenes from simple electron-rich arenes and norbornene in one step. The overall one-pot synthesis of norbornylarenes is shown in Scheme 1.

In the reaction presented in Scheme 1,⁵ compound **1** and norbornene (1:50 molar ratio) in arene solution (10 mL) were stirred at room temperature, and the conversion of NBE was confirmed by the GC–FID method. GC–MS analysis of the crude product obtained after extraction of the residue with heptane showed the formation of an arene/NBE 1/1 adduct in high yield (Table 1). Other products, such as arene/NBE 1/2 and 1/3 adducts and NBE dimers, being different stereoisomers of 2,2'-binorbornylene,^{2d,3c,6} pentacyclotetradecane,⁷ hydroxyl-2,2'-binorbornyl,^{2d,3c} and 2,2'-binorbornyl,^{2d,8} were also detected (Table 1). A small amount of the ROMP polymer was always observed by ^1H NMR spectroscopy during the course of the reaction in benzene-*d*₆ or toluene-*d*₈



Scheme 1. Synthesis of NBE/arene adducts.

Keywords: Hydroarylation; Tungsten(II) catalyst; Norbornene; C–C bond formation; C–H bond activation.

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Table 1. Relative distributions (%) of NBE reaction products detected by GC–MS after 100% conversion of NBE in the presence of **1** in different arene (A) solutions at room temperature^a

NBE+A	A					
	C ₆ H ₆ (a)	C ₆ H ₅ Me (b)	C ₆ H ₅ Me (c)	1,4-C ₆ H ₄ Me ₂ (d)	1,3,5-C ₆ H ₄ Me ₂ (e)	C ₆ H ₅ Cl (f)
NBE+A	73.4	89.4	61.3	83.9	86.5	9.2
2NBE+A	19.8	8.0	33.4	16.1	13.5	
3NBE+A	2.8		5.3			
2NBE	2.7	2.6				62.2
2NBE+2H	1.3					
2NBE+H ₂ O						2.0
3NBE						26.6

Hundred percent conversion reached within: (a) 6 h, (b) 15 min, (c) 3.5 h (four portions of NBE in a **1**/NBE ratio = 1:50 progressively added to the solution of **1**, each next portion was added after 100% conversion of the previous one), (d) 3 h, (e) 8 h, (f) 24 h.

^a **1**/NBE = 1:50.

solution as was evident from the olefinic proton signals at δ 5.32 (*trans*) and 5.20 (*cis*).^{3b,c} The integral ratio of the latter signals and the signal of the hydroarylation product at ca. 2.7 ppm made it possible to calculate the yield of the ROMP polymer, which was below 1% in each case.

In the presence of catalytic amounts of compound **1** (2 mol %), hydroarylation of norbornene by benzene proceeds smoothly. The major product, *exo*-2-phenyl-norbornane (**2**), was detected in 73.4% by GC–MS (Table 1), and its structure was confirmed by ¹H and ¹³C NMR studies.⁹ However, compound **2** undergoes subsequent reaction with NBE to give 1/2 (**2'**) and 1/3 (**2''**) type adducts.¹⁰ Adduct **2'** (19.8%) was detected by GC–MS as a mixture of three isomers in a 0.2:0.6:1 ratio, and adduct **2''** (2.8%) as only one isomer.

The reaction of NBE in toluene gave *exo*-2-(methylphenyl)norbornane (**3**) (89.4%) consisting of three isomers: *meta*, *para*, and *ortho* in a 0.3:1:0.6 ratio, respectively, whose distributions were proved by GC–MS and ¹H and ¹³C NMR studies.^{9c,9d,11} The 1/2 adduct (**3'**)¹² was formed in 8.0% yield. However, the addition of NBE (200 equiv) in four successive portions to the solution of catalyst **1** in toluene made it possible to obtain **3'** and a 1/3 adduct (**3''**)¹² in higher yields: 33.4% and 5.3%, respectively (Table 1).

The addition of *para*-xylene to norbornene gave *exo*-2-(2,5-dimethylphenyl)norbornane (**4**)¹³ in 83.9% yield. The formation of a 1/2 adduct (**4'**) (16.1%) was also observed.¹⁴

The reaction of NBE in mesitylene gave 1/1 (**5**) and 1/2 (**5'**) adducts in 86.5% and 13.5% yields, respectively. However, the major product, 2-(2,4,6-trimethylphenyl)norbornane (**5**),¹⁵ was identified by GC–MS as a mixture of two isomers, which appeared with retention times *r.t.* = 13.16 and 13.28 min, respectively, in a 0.1:1 ratio. Two isomers of **5'** appeared in the GC–MS chromatogram at *r.t.* = 16.4 and 16.7 min, respectively, in a 1:0.6 ratio.¹⁶ Very careful investigation of **5** by NMR spectroscopy (¹H, ¹³C{¹H}, and ¹H–¹³C HMQC) revealed that the major product was *endo*-2-(2,4,6-trimethylphenyl)norbornane (*endo*-**5**),¹⁵ while *exo*-**5** was formed in lower yield. In the ¹H NMR spectrum of **5**, the H²

proton of *exo*-**5** has a characteristic signal (doublet ($J_{endo-exo}$ = 8.7 Hz) of doublets ($J_{endo-endo}$ = 5.8 Hz)),^{9,11,13} centered at δ 2.75, whereas *endo*-**5** exhibits the H² signal at δ 2.99 as a triplet with J = 8.5 Hz (Scheme 2).¹⁵ In the ¹³C NMR spectrum of **5**, the *endo* isomer has a higher upfield shift of the C⁶ signal (δ 28.36) than the *exo* isomer (δ 29.14), while *exo*-**5** has a higher upfield shift of the C⁷ signal (δ 36.31) than the *endo* isomer (δ 38.83). These data are in a good agreement with the description of ‘the γ effect’ on the chemical shifts of *exo*- and *endo*-2-substituted norbornanes by Grutzner et al.¹⁷

The conversion of NBE in the presence of **1** in chlorobenzene solution leads mainly (62.2%) to the formation of NBE dimers; that is, four stereoisomers of 2,2'-binorbornylene^{2d,3c,6} and pentacyclotetradecane (1.7%). A small amount (9.2%) of a chlorobenzene/NBE 1/1 adduct, that is, 2-(chlorophenyl)norbornane (**6**),^{9c} was detected as a mixture of two isomers (**6a** and **6b**) in a 0.6:1 ratio by GC–MS and ¹H NMR (two doublets of doublets at 3.03 and 2.69 ppm due to the H² protons, respectively).¹⁸ Additionally, in the latter reaction, hydroxyl-2,2'-binorbornyl (2.0%) and different isomers of NBE trimers (26.6%)^{2d,3c} were detected by GC–MS.¹⁹

The formation of arene/NBE 1/2 and 1/3 adducts as additional products of hydroarylation of NBE indicates that the reactivity of arenes increases as the number of electron-donating substituents in the arene ring increases. Under the same reaction conditions (**1**/NBE = 1/50, room temperature), 100% conversion of NBE in toluene solution was reached in 15 min, while in benzene it was reached in 6 h. The reactivity of toluene is much higher than that of benzene, which indicates that electronic effects of the substituents in the arene dominate and show characteristics of electrophilic substitution. It is also interesting to note that steric hindrance in the arenes is not a problem for this reaction. The presence of an electron-withdrawing substituent, for example, in chlorobenzene, considerably reduced the formation of the arene/NBE adduct, but norbornene was transformed to 2,2'-binorbornylidene in higher yield.

It is worth mentioning that **1** is able to catalyze the hydroarylation reaction only in neat aromatic hydrocar-

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