Pergamon

Tetrahedron Letters, Vol. 37, No. 8, pp. 1157-1160, 1996

0040-4039/96 $15.00 + 0.00

0040-4039(95)02389-5

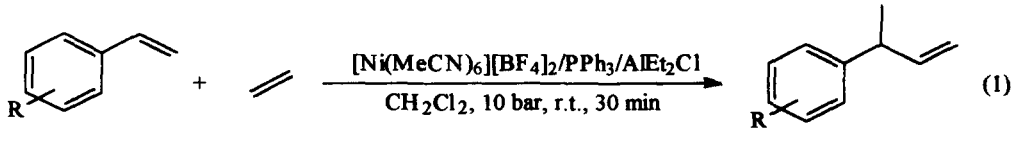
Synthesis of 3-Aryl-1-butenes by the Nickel Catalyzed Hydrovinylation of Styrene Derivatives

Adriano Lisboa Monteiro*, Marcus Seferin, Jairton Dupont, Roberto Fernando de Souza

Grupo de Catálise, Instituto de Química, Universidade Federal do Rio Grande do Sul,
Av. Bento Gonçalves,9500, CEP 91591-970, Porto Alegre, Brazil.

Abstract: The synthesis of 3-aryl-1-butenes is performed by hydrovinylation of styrene and alkyl-substituted styrenes catalyzed by $[Ni(MeCN)_6][BF_4]_2/Et_2AlCl/PPh_3$ under mild conditions with very good activities and selectivities.

The 3-aryl-1-butenes are important intermediaries for the synthesis of 2-arylpropionic acids that are widely used as anti-inflammatory drugs, such as Ibuprofen and Naproxen.[1] Moreover, these olefins have been also used as monomers for homopolymerization or copolymerization of olefins.[2] Among various routes, the catalytic hydrovinylation of styrene by transition metal complexes has been shown to be particularly adequate for the syntheis of such compounds.[3-5] Indeed, it has been already shown that the combination of nickel allyl complexes/alkylaluminum compounds in the presence of a chiral azaphospholene at low temperatures (- 70 °C) enables the enatioselective hydrovinylation of styrene.[3b] We have recently described the selective ethylene dimerization to 1-butene with high activity catalyzed by a dicationic nickel complex and alkylaluminum compound.[6] We now report the application of this catalytic system to the hydrovinylation of various styrene derivatives under mild conditions (eq.1).



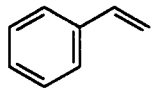
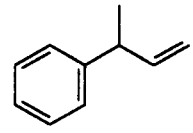
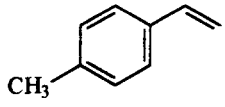
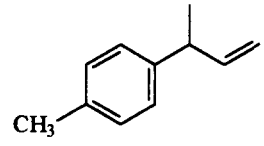
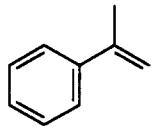
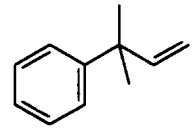
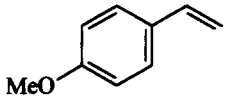
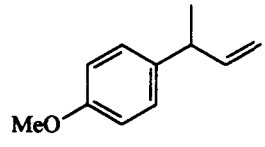
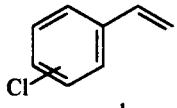
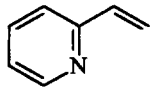
(1)

After intensive investigation on the reaction conditions (nature of cocatalyst: $Al_2Et_3Cl_3$, $AlEtCl_2$, $AlEt_2Cl$, $AlEt_3$; PPh_3/Ni ratio, reaction time and temperature) we have found mild reaction conditions and procedure that afford 3-phenyl-1-butene with high regioselectivity and yield. Thus 4.6 mL of styrene (40 mmol), 48 mg of $[Ni(MeCN)_6][BF_4]_2$ (0.1 mmol), 105 mg of triphenylphosphine (0.4 mmol), 0.28 mL of diethylaluminum chloride 1.8M solution in toluene (0.5 mmol) and 20 mL of dichloromethane were placed in a 100 mL-stainless steel autoclave under argon and the mixture was stirred at room temperature for 30 minutes under 10 atm of ethylene. After releasing the excess of ethylene, the reaction mixture was distilled (58-60° C, 7 torr) to afford 4.8 g of 3-phenyl-1-butene (90% yield).[7] The *cis* and *trans* 2-phenyl-2-butene have been the only by-products detected in the reaction mixture. The most probable catalytic species for the dimerization and codimerization olefin reaction is a nickel-hydride complex. [2] These species are probably formed from alkylnickel complex formed by the reaction between dicationic nickel complex and the alkylaluminum compound. The observed high chemoselectivity is presumably the result of the Ni-H bond reacting more rapidly with the activated C=C bond of the styrene than with that of the ethylene and/or the higher stability of the η^3-benzylic-nickel compared with an ethyl-nickel intermediate. Steric effects of triphenylphosphine ligand prevent a second styrene molecule from approaching the resulting Ni-C bond, but not the smaller ethylene molecules, and as a result the styrene is only hydrovinyled as 3-phenyl-1-butene and neither oligomerized nor polymerized. It is interesting to note that the formation of butenes was observed in all the reactions, however under the best conditions, the hydrovinylation of styrene is highly favored.

The hydrovinylation of styrene derivatives substituted at the aromatic ring or vinyl group has been performed under the same conditions as for styrene (Table 1). There is no noticeable influence of an alkyl group alkyl in *p*-position at the aromatic ring and so the hydrovinylation of *p*-methylstyrene gave results similar to those observed with styrene (compare entries 1 and 2). Despite of a low activity, the hydrovinylation is completely chemo- and regio-selective if the styrene is substituted by a methyl in the vinyl fragment (entry 3). This low activity is probably due to the steric effects of the methyl group at the α-carbon that aggravates the approach to the nickel-hydride bond present in the catalytically active species. The hydrovinylation of α-methyl-styrene catalyzed by a cationic allyl-nickel gave lower conversion and yield (0.6%)[3c]. The *p*-methoxy-styrene is hydrovinyled with a low conversion and only 70% of the hydrovinyled product is the 3-(*p*-methoxy-phenyl)-1-butene (entry 4). There is no reaction at all in the case of the *o*-, *m*-, and *p*-chloro-styrene or 2-vinyl-pyridine (entries 5 and 6).

This lack of activity can be explained by the Lewis basicity of these substrates that are present in excess and can react with the alkylaluminum Lewis acid so preventing the formation of the catalytic active species. The same effect can account for the very low activity of the *p*-methoxy-styrene.

Table 1. Hydrovinylation of styrene derivatives with $[Ni(MeCN)_6][BF_4]_2/AlEt_2Cl/PPh_3$

Entry	Substrate	Conversion (%)	Product	Selectivity (%)	Regioselectivity (%)
1		100		90	97
2		98		86	97
3		6		>99	>99
4		10		70	70
5	 *o*-, *m*-, and *p*-	-	no reaction	-	-
6		-	no reaction	-	-

In summary, we have described a simple and efficient method for the preparation of a series of 3-aryl-1-butenes that are valuable intermediates for the synthesis of important biologically active drugs. Studies of asymmetric induction and heterogenization of the catalytic system are in progress.

The authors acknowledge CAPES (M.S.) and CNPq (A.L.M.) for a Fellowship.

References and Notes

1. Rieu, J. -P.; Boucherle, A.; Cousse, H.; Mouzin, G. *Tetrahedron* **1986**, 42, 4095-4131.

2. Wilke, G. *Angew. Chem.; Int. Ed. Engl.* **1988**, 27, 185-206.

3. Nickel systems : (a) Kawata, N.; Maruya, K.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.*, **1971**, 44, 3217.

(b) Wilke, G.; Monkkiewicz, J.; Kunh, H. US Patent US 4,912,274, 1990, CA **1991** 109:6735j.

(c) Ceder, R.; Muller, G.; Ordinas, J.I. *J. Mol. Catal.* **1994**, 92, 127-139.

4. Palladium systems: (a) Hattori, S.; Munakata, H.; Tatsuoka, K.; Shimizu, T. US Patent US 3,0803,254, 1974, CA **1975** 82:44004b.

(b) Drent, E. US Patent 5,227,561, 1993, CA **1994** 120:31520v.

(c) Britovsek, G. P.; Keim, W.; Mecking, S.; Sainz, D.; Wagner, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1632-1634.

5. Ruthenium and rhodium system: Umezaki, H., Fujiwara, Y.; Sawara, K.; Teranishi, S. . *Bull. Chem. Soc. Jpn.* **1973**, 46, 2230-2231.

6. Souza, R. F.; Souza, M. O.; Monteiro, A. L.; Almeida, L.; Seferin, M. *New J. Chem.* **1993**, 17, 437-438.

7. 3-phenyl-1-butene selected data: ^{1}H NMR ($CDCl_3$/TMS): δ 1.37 ppm (d, J = 6.9 Hz, 3H, -CH_3), δ 3.44 - 3.49 ppm (m, 1H, -C**H**(CH_3)CH=CH_2), δ 5.01 - 5.09 ppm (m, 2H, C**H$_2$**=CH-), δ 5.98 - 6.07 ppm (m, 1H, -C**H**=CH_2), δ 7.19 - 7.30 ppm (m, 5H, arom.). ^{13}C NMR (CDCl3/TMS): δ 20.5 ppm (-**C**H3), δ 43.1 ppm (-CH_2-Ph), δ 113.0 ppm (**C**H_2=CH-), δ 126.1 ppm (**C$_p$**), δ 127.2 ppm (**C$_o$**), δ 128.4 ppm (**C$_m$**), δ 143.2 ppm (CH_2=**C**H-), δ 145.5 ppm (**C$_{ipso}$**). IR (neat) 1638 cm^{-1} (s; $\nu_{C=C}$), 1602 cm^{-1} (s), 998 cm^{-1} (s), 915 cm^{-1} (s). GC-MS (EI, 70 eV) m/z: 132 (M^+, 21%), 117 (100%), 105 (8%), 91 (27%), 77 (18%), 65 (9%), 51 (17%), 39 (12%).

(*Received in USA* 16 *November* 1995; *accepted* 12 *December* 1995)