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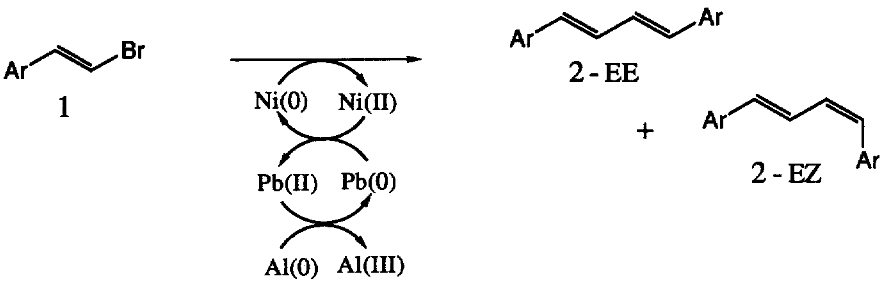
REDUCTIVE DIMERIZATION OF VINYL HALIDES IN AN Ni/Pb/Al THREE METAL REDOX SYSTEM. A FACILE ACCESS TO TERPHENYL DERIVATIVES

Hideo Tanaka, Atsuko Kosaka, Shiro Yamashita, Kazuo Morisaki,
and Sigeru Torii*
Department of Applied Chemistry, School of Engineering,
Okayama University, Okayama 700, Japan

A novel three metal redox system, $NiCl_2(bpy)/PbBr_2/Al$, is found to be potent in the reductive coupling of vinyl halides, affording 1,4-biaryl-1,3-butadienes, precursors of terphenyl derivatives.

Recently, metal salts (MX_n) and aluminum metal combinations have attracted much attention due to their potentiality as a reductant for various synthetic purposes,[1] in which aluminum metal shares as an electron source and MX_n acts as an electron transfer catalyst. Notably, aluminum metal is an ideal reducing agent since it is cheap, easy to handle, and able to release enough electrons (3 e^-/atom). The chemical behavior of the MX_n/Al combination is highly dependent on the nature of MX_n. The metal salts usable as an electron transfer catalyst are, however, limited to some of IVA, IVB and VB group elements, e.g., Ti, Ge, Sn, Pb, Bi, etc.,[1] owing to lack of the efficient electron transfer process between aluminum metal and metal salts, e.g., Ni, Co, Pd, etc., of other group elements. Herein, we describe a new three metal redox system, involving $NiCl_2(bpy)$ (bpy = 2,2'-bipyridine), $PbBr_2$, and aluminum metal (0.1/0.1/0.7 equiv.), which can promote reductive coupling of vinyl halides[2] via a successful electron transfer through three redox couples as illustrated in Scheme 1.



Scheme 1

A typical reaction procedure is as follows; A mixture of β-bromostyrene **1a** (Ar = phenyl, 1 mmol), $NiCl_2(bpy)$ (0.1 mmol), $PbBr_2$ (0.1 mmol), KI (1.5 mmol), and aluminum metal (0.7 mmol) in MeOH (5 ml) was stirred at ambient temperature under argon atmosphere until most of aluminum metal was consumed (6 h). Usual workup of the mixture affoded EE and EZ isomers of 1,4-diphenyl-1,3-butadiene (**2a**, 83%) in a ratio of 97/3.[3] The presence of KI in the media is not essential to the reaction,[4] but affects the reaction rate and EE/EZ ratio of **2a** in some extent. For example, in the absence of KI (entry 2 in Table 1), prolonged reaction time (21 h) was required to complete the reaction and the EE/EZ ratio of **2a** decreased to 85/15. Notably, both $NiCl_2(bpy)$ and $PbBr_2$ are essential for the reduction system, since the absence of $NiCl_2(bpy)$ or $PbBr_2$ resulted in almost complete recovery of the starting material **1a** (entries 3 and 4). As for the role of $PbBr_2$, it is likely that the Pb(0)/Pb(II) redox couple works as an electron transfer catalyst between Al(0)/Al(III) and Ni(0)/Ni(II) redox couples (Scheme 1).[5] The Ni(0) generated in this way would promote the reductive coupling of **1a**.[6] In place of $PbBr_2$, $BiCl_3$ can be used with a slight decrease in the yield of **2a** (entry 5), while $SnBr_2$ and $GeCl_4$ are less effective (entries 6 and 7). The proper choice of the solvent is also important. Methanol and DMF can be used for the present purpose (entries 1 and 8), whereas THF, MeCN, CH_2Cl_2, and benzene can effect no coupling reaction (entries 9-12).

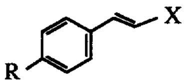
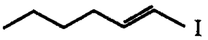
Table 1. Reductive Coupling of β-Bromostyrene (**1a**)[a)]

Entry	$NiCl_2(bpy)$ mmol	MX_n (mmol)	KI mmol	Solvent	Time h	Product **2a** Yield,%[b)]	(EE/EZ)
1	0.1	$PbBr_2$ (0.1)	1.5	MeOH	6	83	(97/3)
2	0.1	$PbBr_2$ (0.1)	---	MeOH	21	88	(85/15)
3	---	$PbBr_2$ (0.1)	---	MeOH	20	--[c)]	
4	0.1	---	---	MeOH	20	--[c)]	
5	0.1	$BiCl_3$ (0.1)	1.5	MeOH	6	73	(98/2)
6	0.1	$SnBr_2$ (0.1)	1.5	MeOH	9	56	(97/3)
7	0.1	$GeCl_4$ (0.1)	1.5	MeOH	24	21	(97/3)
8	0.1	$PbBr_2$ (0.1)	1.5	DMF	7	70	(97/3)
9	0.1	$PbBr_2$ (0.1)	1.5	THF	6	--[c)]	
10	0.1	$PbBr_2$ (0.1)	1.5	MeCN	6	--[c)]	
11	0.1	$PbBr_2$ (0.1)	1.5	CH_2Cl_2	6	--[c)]	
12	0.1	$PbBr_2$ (0.1)	1.5	Benzene	6	--[c)]	

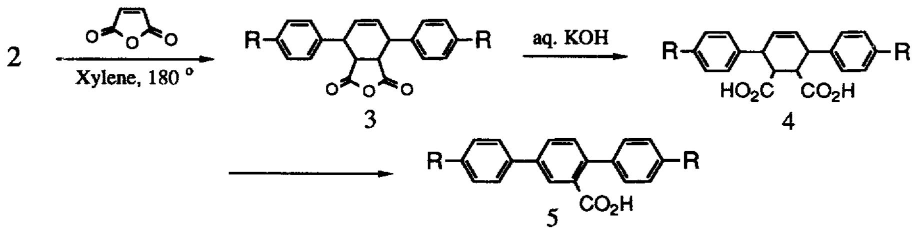
a) Carried out in the manner as described in the text unless otherwise noted.
b) Isolated yields after column chromatography (SiO_2 ; hexane).
c) β-Bromostyrene **1a** was recovered (86-96%, E/Z > 97/3).

The present three metal redox system can be successfully applied to the reductive coupling of various vinyl halides **1** (Table 2). β-Bromo- and β-iodostyrenes **1a-1f** gave the corresponding coupling products **2a-2e**, respectively, whereas β-chlorostyrene **1g** was recovered intact under these conditions. 1-Hexenyl iodide **1h** was dimerized smoothly to give the corresponding dimer **2h** (entry 8).

Table 2. Coupling of Vinyl Halides **1** in an $NiCl_2(bpy)/PbBr_2/Al$ System$^{a)}$

Entry	Vinyl Halide **1**	Time, h	**2** Yield, %$^{b)}$	(EE/EZ)
1				
	1a :R = H, X = Br	6	83	(97/3)
2	**1b** :R = CH_3, X = Br	6	82	
3	**1c** :R = OMe, X = Br	7	91	
4	**1d** :R = Cl, X = Br	20	70 (21)$^{c)}$	
5	**1e** :R = COOMe, X = Br	20	76 (7)$^{c)}$	
6	**1f** :R = H, X = I	6	70	(>99/1)
7	**1g** :R = H, X = Cl	24	-- (71)$^{c)}$	
8	 **1h**	4	72	(98/2)

a) Carried out in the manner as described in the text unless otherwise noted.
b) Isolated yields after column chromatography (SiO_2; hexane/AcOEt: 4/1).
c) Recovered 1.



Scheme 2

Table 3. Synthesis of Terphenyls **5** from 1,4-Biaryl-1,3-butadienes **2**

R	**3** Yield, %	**4** Yield, %	Conditions (**4** - **5**)	**5** Yield, %
H	83	98	Chloranil/Xylene, 138 °C	81
Cl	97	100	$K_3Fe(CN)_6$/aq. $NaHCO_3$, 100 °C	77

Thus far obtained dienes **2** are a promising precursor for terphenyl derivatives **3**; for example, addition of maleic anhydride to dienes **2**, subsequent decarboxylative aromatization of the adducts by alkaline hydrolysis, and heating of dicarboxylic acids **4** with chloranil in xylene (180 °C) or with $K_3Fe(CN)_6$ in aqueous $NaHCO_3$ afforded terphenyls **5** (Scheme 2, Table 3). The details will be discussed in due course.

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2) Recently, Ni(0)-promoted reductive coupling of vinyl halides by use of catalytic $NiCl_2(PPh_3)_2$ and zinc combination ; (a) M. Iyoda, S. Tanaka, and M. Oda, J. Chem. Soc., Chem. Commun., 1983, 1058; (b) K. Takagi, N. Hayama, and S. Inokawa, Chem. Lett.; 1983, 637; (c) K. Takagi, N. Hayama, and K. Sasaki, Bull. Chem. Soc. Jpn., 57, 1887 (1984); (d) K. Takagi, H. Mimura, and S. Inokawa, ibid., 57, 3517 (1984).

3) 500 MHz ^{1}H NMR ($CDCl_3$), **2a-EE** : δ = 6.66 (ddd, J = 2.8, 8.9, 20.9 Hz, 2H, CH=C), 6.94 (ddd, J = 2.8, 9.1, 21.0 Hz, 2H, CH=C), 7.22 (t, J = 7.4 Hz, 2H, Ar), 7.31 (t, J = 7.6 Hz, 4H, Ar), 7.42 (d, J = 8.3 Hz, 4H, Ar) ; **2a-EZ** : δ= 6.42 (t, J = 11.4 Hz, 1H, CH=C), 6.51 (d, J = 11.2 Hz, 1H, CH=C), 6.71 (d, J = 15.6 Hz, 1H, CH=C), 7.15-7.53 (m, 11H, Ar, CH=C).

4) The role of KI in a similar Ni(0)-promoted coupling of vinyl halides has been discussed ; see references 2b-2d

5) Actually, in the initial stage of the reaction, black precipitates of Pb metal appeared on the surface of Al. Commercially available Pb metal (99.99% pure) is not effective for the coupling reaction, suggestig that the Pb metal generated on the Al surface is much more reactive than commercial one.

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