

Synthesis of 2-Substituted 1,3-Butadienes by Cross-coupling Reaction of 2-(1,3-Butadienyl)magnesium Chloride with Alkyl or Aryl Iodides

Sadaaki NUNOMOTO,* Yuhsuke KAWAKAMI,** and Yuya YAMASHITA**

Faculty of Chemical Engineering, Toyama Technical College, Hongo, Toyama 930

**Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University,
Chikusa-ku, Nagoya 464

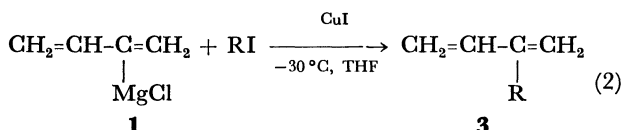
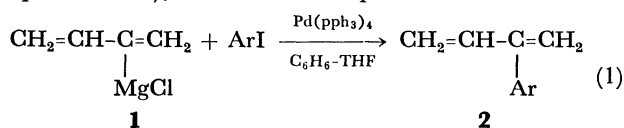
(Received January 12, 1981)

Synopsis. The cross-coupling reactions of 2-(1,3-butadienyl)magnesium chloride (**1**) with aryl and alkyl iodides were investigated in the presence of transition metal catalysts. Tetrakis(triphenylphosphine)palladium(0) catalyzes the cross-coupling reactions of **1** with aryl iodides, and copper(I) iodide catalyzes the reaction with alkyl iodides. These cross-coupling reactions offer convenient routes for the synthesis of 2-substituted 1,3-butadienes.

It has been reported that the cross-coupling reactions of Grignard reagents with allyl or alkenyl halides occurred in the presence of nickel or palladium complexes under mild conditions.¹⁻⁵⁾

Allyl Grignard reagent was reported to be alkylated by alkyl iodides or tosylates in the presence of copper(I) iodide.^{6,7)}

The authors carried out the synthesis of 2-substituted 1,3-butadienes by the cross-coupling reactions of **1** with aryl iodides in benzene-tetrahydrofuran (THF) catalyzed by tetrakis(triphenylphosphine)palladium(0) (**4**) or alkyl iodides in THF by copper(I) iodide (**5**) (Eqs. 1 and 2), and wish to report the results.



The results of cross-coupling reactions of **1** with iodobenzene are shown in Table 1. Only **4** is highly active among the transition metal complex catalysts examined, and 2-phenyl-1,3-butadiene (**2**) was obtained in increasing yield with an increase in the

TABLE 1. THE EFFECTS OF CATALYSTS ON THE CROSS-COUPPLING REACTION OF **1** WITH IODOBENZENE IN C₆H₆/THF (50:100 ml)^{a)}

No.	Catalyst	Catalyst amount mol%	Cross-coupling product 2 Yield/%
1	Ni(acac) ₂	2	0
2	Ni(pPh ₃) ₄	2	Polymerized
3	Pd(OCOCH ₃) ₂	6	5
4	Pd(pPh ₃) ₄	1	40
5	Pd(pPh ₃) ₄	2	55
6	Pd(pPh ₃) ₄	3	75
7	Pd(pPh ₃) ₄	4	90

a) [RMgX]₀: 1.0 mol/l, [RMgX]:[C₆H₅I]=1:1 molar ratio.

amount of the catalyst. Nickel(II) acetylacetonate was inactive for the reaction. As **4** showed a high activity, the cross-coupling reactions of **1** with aryl and alkyl halides were investigated in the presence of **4**. However, **4** was not an effective catalyst for the cross-coupling reaction of **1** with bromobenzene, alkyl iodide, or iodocyclohexane, as shown in Table 2.

Only aryl iodides gave the cross-coupling products

TABLE 2. PREPARATION OF 2-SUBSTITUTED 1,3-BUTADIENES BY THE CROSS-COUPPLING REACTIONS OF **1** WITH ARYL AND ALKYL HALIDES IN C₆H₆/THF USING **4**^{a)}

No.	ArX	Catalyst amount mol%	Cross-coupling product 2 Yield/%	Bp/°C (mmHg)
8	C ₆ H ₅ Cl	4	0	
9	C ₆ H ₅ Br	4	0	
10	<i>c</i> -C ₆ H ₁₁ I	3	0	
11	<i>p</i> -BrC ₆ H ₄ I	3	Polymerized ^{b)}	
12	<i>p</i> -CH ₃ OC ₆ H ₄ I	3	50	66—69 (3)
13	1-C ₁₀ H ₇ I	3	40	122—126 (3)
6	C ₆ H ₅ I	3	75	62—65 (20)
14	<i>p</i> -CH ₃ C ₆ H ₄ I	3	56	60—64 (5)
15	C ₆ H ₅ CH ₂ I	3	71	71—75 (5)

a) [RMgX]₀: 1.0 mol/l, [RMgX]:[ArX]=1:1 molar ratio. b) 2-(*p*-Bromophenyl)-1,3-butadiene was separated by preparative GLC, and was identified by MS and NMR spectra.

TABLE 3. PREPARATION OF BUTADIENE DERIVATIVES FROM **1** AND ALKYL HALIDES CATALYZED BY **5**^{a)}

No.	RX	CuI mol%	Cross-coupling product 3 Yield/%	Bp/°C (mmHg)
16	C ₆ H ₅ Br	20	0	
17	C ₆ H ₅ I	20	0	
18	<i>c</i> -C ₆ H ₁₁ I	20	5	
19	<i>n</i> -C ₆ H ₁₃ CHICH ₃	20	0	
20	<i>n</i> -C ₈ H ₁₇ Cl	20	0	
21	<i>n</i> -C ₈ H ₁₇ Br	20	5	
22	<i>n</i> -C ₆ H ₁₃ I	20	60	75—79 (20)
23	<i>n</i> -C ₈ H ₁₇ I	10	45	74—77 (3)
24	<i>n</i> -C ₈ H ₁₇ I	20	67	
25	<i>n</i> -C ₁₀ H ₂₁ I	20	68	95—99 (5)
26	<i>n</i> -C ₁₆ H ₃₃ I	20	40	155—160 (2)
27	ClCH ₂ CH ₂ CH ₂ I	20	30 ^{b)}	62—66 (30)

a) [RMgX]₀: 1.0 mol/l, [RMgX]:[RX]=1:1 molar ratio, solvent: THF. b) The product, 2-(3-chloropropyl)-1,3-butadiene was identified by MS and NMR spectra.

in reasonably good yield. In order to overcome the low activity of **4** in the reaction, **5**, which is known to form an ate complex with a Grignard reagent, was used as a catalyst and the results with aryl and alkyl halides are shown in Table 3.

Although **5** was not active for iodobenzene, iodo-cyclohexane, or alkyl bromides, reasonable yields could be obtained with linear alkyl iodides, giving 2-alkyl-1,3-butadienes. These selectivities can be applied to the chemoselective cross-coupling reaction (Table 2 No. 11 and Table 3 No. 27) for the synthesis of functionalized 1,3-butadienes.

Experimental

Reagents. **1** was prepared as described in the previous report.⁸⁾ **4** and **5** were prepared by the procedures described elsewhere.^{9,10)}

Cross-coupling Reaction of 1 with Aryl Iodides. To a mixture of an aryl iodide (0.1 mol), **4** (1–3 mol% to an aryl iodide) and dry benzene (50 ml) in a 300 ml four-necked flask, **1** (0.1 mol) in THF (100 ml) was added dropwise with stirring under nitrogen atmosphere.

An exothermic reaction occurred during the addition, and the color of the contents gradually changed from yellowish green to black. After the completion of the addition, stirring was continued for 30 min at the refluxing temperature of the reaction system.

The organic layer was separated after hydrolyzing with 6 mol dm⁻³-HCl, and the aqueous layer was extracted with two portions of diethyl ether (80 ml). The combined organic layer was washed first with 5% aqueous sodium hydrogencarbonate, then with water, then dried (Na₂SO₄) and distilled.

Cross-coupling Reaction of 1 with Alkyl Iodides. To a mixture of an alkyl iodide (0.1 mol), **5** (10–20 mol% to an alkyl iodide) and THF (50 ml) in a 300 ml four-necked flask cooled to –30 °C, **1** was added dropwise with stirring under nitrogen atmosphere.

The color of the contents gradually changed from light yellow to black. After the completion of the addition, stirring was continued for 2 h at 0 °C. The products were isolated by the work-up used for aryl iodides. The reaction products were identified by comparing their IR and NMR spectra with the reported data.

References

- 1) A. S. Kende, L. S. Liebeskind, and D. M. Braitsch, *Tetrahedron Lett.*, **1975**, 3375.
- 2) H. P. Dang and G. Linstrumelle, *Tetrahedron Lett.*, **1978**, 191.
- 3) F. D. Boumechal, R. Lorne, and G. Linstrumelle, *Tetrahedron Lett.*, **1977**, 1181.
- 4) K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, and M. Kumada, *Bull. Chem. Soc. Jpn.*, **49**, 1958 (1976).
- 5) S. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kondo, *J. Org. Chem.*, **44**, 2408 (1979).
- 6) C. R. Johnson and G. A. Dutra, *J. Am. Chem. Soc.*, **95**, 7777 (1973).
- 7) F. D. Boumechal and G. Linstrumelle, *Tetrahedron Lett.*, **1976**, 3223 (1976).
- 8) S. Nunomoto and Y. Yamashita, *J. Org. Chem.*, **44**, 4788 (1979).
- 9) D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972).
- 10) G. B. Kauffman and R. P. Pinnell, *Inorg. Synth.*, **6**, 3 (1960).