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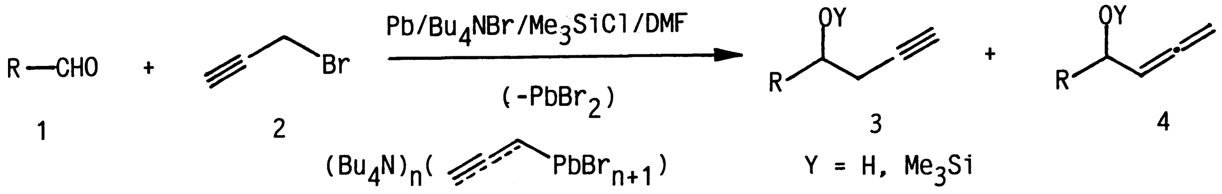
Lead Promoted Barbier-Type Reaction of Propargyl Bromide with Aldehydes

Hideo TANAKA, Takeshi HAMATANI, Shiro YAMASHITA, and Sigeru TORII*
Department of Industrial Chemistry, School of Engineering,
Okayama University, Okayama 700

The first example of lead-promoted "Barbier-type" (in situ Grignard) reaction has been demonstrated by the reaction of propargyl bromide with aldehydes in a Pb/Bu_4NBr/Me_3SiCl/DMF system.

Recently, Barbier-type reaction using a variety of metals, e.g., Li, Mg, Cr, Mn, Zn, Sn, Sn/Al, Bi, Ce/Hg, Yb, and Sm, has been extensively investigated and the characteristic feature of each metal reagent has been well documented.$^{1)}$ Meanwhile, lead has not been utilized for this purpose, presumably due to the lack of suitable reaction medium for both the generation of organolead reagents and the subsequent reaction with carbonyl compounds. This communication describes the first demonstration of the lead-promoted Barbier-type reaction (Scheme 1) in a Pb/Bu_4NBr/Me_3SiCl/DMF system, in which Bu_4NBr plays a significant role in generating an active organolead reagent.



Scheme 1.

A typical reaction procedure is as follows. Into a stirred mixture of benzaldehyde **1a** (R = Ph, 1 mmol), propargyl bromide **2** (2 mmol), Bu_4NBr (1.1 mmol), and Me_3SiCl (0.2 ml) in DMF (6 ml) was immersed a lead plate (>99.9% ; 1.5 x 2.0 cm^2, 0.5 mm thick) and the stirring was continued at ambient temperature until most of **1a** was consumed (1.5 h). After taking out the Pb plate (loosing 1.8 mmol of Pb), extractive workup with aq. 10% HCl/AcOEt (entry 1) afforded a mixture of **3a** and **4a** (Y = H, 95%, **3a**/**4a** = 4/1), while workup with aq. $NaHCO_3$/AcOEt gave the corresponding silyl ether **3a** and **4a** (Y = Me_3Si, 70%, 4/1). In a similar manner, the reaction of a mixture of **1a** and **2b** (1 mmol each) afforded 75% yield of a mixture of **3a** and **4a** (Y = H) with loosing 1.1 mmol of lead (entry 2). The observed stoichiometry (**1**/**2**/Pb = 1/1/1) suggests that the lead-promoted reaction involves the formation of an active divalent organolead reagent in contrast to the tin-version.$^{2)}$

The effect of Bu_4NBr was remarkable. As shown in Fig. 1, the yields of **3a** and **4a** were affected by the amount of Bu_4NBr, indicating that roughly one equiv. of Bu_4NBr was required to complete the reaction. When Bu_4NBr was replaced with other salts, the yields of **3a** and **4a** decreased in the order: NaBr (60%), NH_4Br (49%), KBr (40%), $MgBr_2$ (trace), Bu_4NClO_4 (none), $LiClO_4$ (none). Interestingly, in the last two cases, no appreciable consumption of the lead plate (< 8 mg) was observed. Although the role of Bu_4NBr is still unclear, it is likely that Bu_4NBr effects the generation of an active organolead reagent, e.g., ammonium salts **5** (in Scheme 1),[3] which would in turn react with aldehyde **1** to give **3** and **4** ($Y=Bu_4N^+$) with liberating $PbBr_2$.

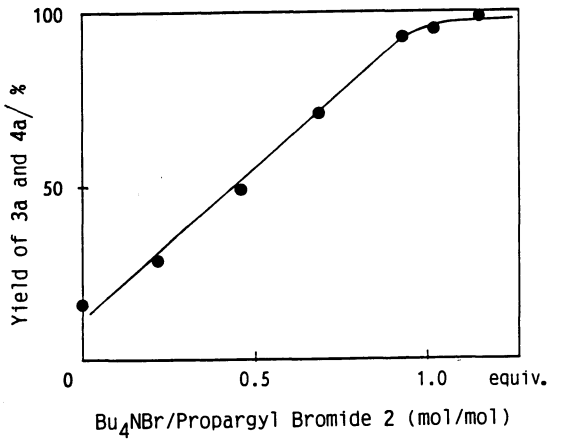
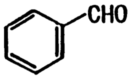
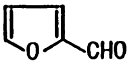
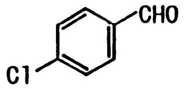
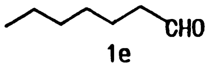
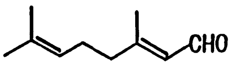
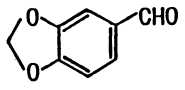
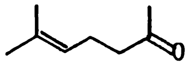


Fig. 1. Effect of Bu_4NBr

The present lead-promoted reaction was successfully applied to aldehydes **1b-f** while ketone **1g** was recovered even after prolonged reaction time (5 h) (Table 1).

Table 1. Barbier-Type Reaction in a $Pb/Bu_4NBr/Me_3SiCl/DMF$

Entry	Aldehyde 1	Bromide 2 equiv.	Yield/% (3/4)	Entry	Aldehyde 1	Bromide 2 equiv.	Yield/% (3/4)
1	 1a	2	95(4/1)	5	 1d	2	83(9/1)
2		1	76(4/1)				
3	 1b	2	97(4/1)	6	 1e	2	90(7/3)
				7	 1f	2	66(1/-)
4	 1c	2	81(1/-)	8	 1g	2	--

References

1) For example: a) K. Uneyama, N. Kamaki, A. Moriya, and S. Torii, J. Org. Chem., 50, 5396 (1985); b) M. Wada and K. Akiba, Tetrahedron Lett., 26, 4211 (1985); c) J. Nokami, T. Tamaoka, T. Koguchi, and R. Okawara, Chem. Lett., 1984, 1939; d) T. Hiyama, M. Sawahata, and M. Obayashi, ibid., 1983, 1237; e) J. Souppe, J. L. Namy, and H. B. Kagan, Tetrahedron Lett., 23, 3497 (1982); f) Y. Yamamoto and K. Maruyama, Heterocycles, 18, 357 (1982), g) T. Mukaiyama and T. Harada, Chem. Lett., 1981, 621, and references cited therein.

2) Tetravalent organotin reagent has been proposed as the in situ generated active species in the tin-promoted reaction: Ref. 1c.

3) P. G. Harrison, "Comprehensive Organometallic Chemistry," Vol. 2, G. Wilkinson Ed., Pergamon Press, (1982), p. 629.

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