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# Zinc-Promoted Barbier-Type Reaction of Propargyl Bromide with Aldehydes in Aqueous Media<sup>1</sup>

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#### Abstract

In the presence of metallic zinc, propargyl bromide is found to react with aldehydes at room temperature in tetrahydrofurane-saturated aqueous ammonium chloride (5:2) to afford the corresponding homopropargylic alcohols in moderate to high yields together with small amounts of  $\alpha$ -allenic alcohols.

Recently, there has been considerable interest in performing organometallic reactions in aqueous madia. <sup>2-7</sup> We were intrigued by a unique C-C bond forming reaction, the allylation of aldehydes in aqueous madia reported by Luche.<sup>8-10</sup> This reaction is one of the few C-C bond forming reactions that occurs in water.<sup>11</sup> We report here that propargylation of aldehydes can be easily effected in tetrahydrofuran (THF) and saturated aqueous ammonium chloride in a Barbier-type reaction using zinc as the metal, to afford the corresponding homopropargylic and  $\alpha$ -allenic alcohols in fairly good yields.

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1a-h		2	2a-h	3a-h
	Zn, stirring, r. t.			
$Ar-CHO + HC \equiv CCH_2Br$	>	Ar -CH-CH <sub>2</sub> C≡	CH + Ar-CHCH=	C=CH <sub>2</sub>
	THF-saturated aq. NH4Cl	ОН	он	

1, 2, 3 Ar

a	$C_6H_5$
b	$4-CH_3C_6H_4$
c	$4-CH_3OC_6H_4$
d	$2-HOC_6H_4$
e	2-BrC <sub>6</sub> H <sub>4</sub>
f	3-CIC <sub>6</sub> H <sub>4</sub>
g	4-ClC <sub>6</sub> H <sub>4</sub>

 $4 - Me_3 N^+ C_6 H_4 I^-$ 

The synthesis of homopropargylic and  $\alpha$ -allenic alcohols via classical organometallic reactions have been extensively studied,<sup>12</sup> but only scant attention have been paid to the synthesis of these compounds in aqueous media. Boaretto *et al.*<sup>13</sup> have described a Grignard-type reaction using allenyl-di-butyltin chloride for preparation of propargylic and allenyl carbinols. Recently, Wu *et al.*<sup>14</sup> reported a Barbier-type procedure using metallic tin and hydrobromic acid. Although this procedure can be applied to substrates having nitro group, it has the disadvantage of producing side reactions, *viz.*, conversion of  $\alpha$ -allenic alcohols to  $\alpha$ ,  $\beta$ -enones under the acidic condition of the reaction.

#### **Results and Discussion**

Stirring a mixture of an aldehyde, propargyl bromide, and zinc powder in THF-saturated aqueous ammonium chloride, proceeds smoothly at room temperature to give the corresponding homopropargylic and  $\alpha$ -allenic alcohols. The reaction is exothermic and accompanied by gas

h

The procedure has been applied to benzaldehyde and a variety of its derivatives and the results are shown in the Table. The reactions are often completed within 10-20 minutes as evidenced by the total disappearance of the metal. A failure is observed when this reaction is applied to nitobenzenaldehydes. This may be attributed to the reduction of the nitro group under the reaction conditions.

As shown in the Table, the reaction of benzaldehydes with propargyl bromide gives predominantly homopropargylic alcohols (87-97% regio-selectivity). When an equimolar mixture of benzaldehyde and acetophenone was subjected to the reaction with propargyl bromide (1 equivalent), no addition product from acetophenone was detected. The proportion of the allenic isomer slightly increases with decrease of the electron-donating character of the substituents. As shown for benzaldehyde (entries 1-3), the proportion of the allenic alcohol is also influenced by the nature of the solvent system. In the absence of THF (entry 2), the total yield of the products obtained from benzaldehyde drops from 68% to 48%. The reaction can be carried out without protection of hydroxy functional group. Thus, salicylaldehyde (entry 6) gives the products in 69% yield. Entry 10, a quaternary ammonium salt, is an example of the substrates which are insoluble in common solvents for organometallic synthesis, namely, diethyl ether or THF, but readily soluble in water.

In conclusion, the zinc-mediated addition of propargyl bromide to a carbonyl function in fact occur in aqueous media. The proportion of the allenic minor product is influenced by the electrophilic character or the carbonyl carbon atom and the type of solvent system used. This method combines advantages such as simplicity, high degree of chemo- and regio-selectivity, and compatibility with the presence of functional groups which usually cannot coexist with organometallic derivatives.

#### Experimental

All produts except the quaternary ammonium salts (1h, 2h, and 3h) are known compounds, they are identified by comparision of their physical and spectral data with those reported in the literature.<sup>13-17</sup> IR spectra were recorded (KBr) on a Shimadzu 470 spectrophotometer. Microanalyses were performed on a Heraeus CHN-O-RAPID analyzer.<sup>1</sup>H-NMR spectra were

Entry <sup>b</sup>	Reactant	Products	Yield <sup>a</sup> (%)	2/3 Ratio		IR $v_{max}/cm^{-1}$ (KBr)	
				<sup>1</sup> H NMR	GC-MS	<b>2</b> (C ≡C)	3 (C=C=C)
1	1a	2a,3a	68	89/11	87/13	2120	1951
2 <sup>c</sup>	1a	2a, 3a	44	95/5	93/7	2120	1951
3 <sup>d</sup>	1a	2a, 3a	55	95/5	93/7	2120	1951
4	1b	2b, 3b	57	95/5	94/6	2110	1951
5	1 <b>c</b>	2c, 3c	53	96/4	97/3	2110	1950
6	1d	2d, 3d	69	-	98/2	2115	1951
7	1e	2e, 3e	82	-	91/9	2115	1953
8	1f	2f, 2f	84	92/8	88/12	2120	1953
9	1g	2g, 2g	85	92/8	88/12	2120	1953
10 <sup>e</sup>	1h	2h, 3h	41	91/9	-	2115	1946

Table Yields and selected physical data for 2 and 3

<sup>a</sup> Total isolated yield, based on the aldehyde, by preparative TLC. <sup>b</sup> All reactions were carried out using the aldehyde (2 mmol), propargyl bromide (4 mmol) and zinc powder (4 mmol) in THF-saturated aqueous NH<sub>4</sub>Cl (5:2) unless otherwise stated. <sup>c</sup> As in (b), but without THF.

<sup>d</sup> Benzaldehyde (2 mmol), propargyl bromide (2 mmol), zinc powder (2 mmol).

<sup>e</sup> (1h) 1H-NMR  $\delta$  3.73 (9H, s, NMe<sub>3</sub>); 8.16 (2H,  $\delta$ , J 9.2 Hz, arom.); 8.29 (2H, d, J 9.2 Hz, arom.); 10.16 (1H, s, CHO). (Found: C, 4.16; H, 4.9; N, 5.0. C<sub>10</sub>H<sub>14</sub>INO requires C, 41.26; H, 4.85; N, 4.81%). (2h) 1H-NMR  $\delta$  2.31 (1H, t, J 2.5 Hz, C=CH); 2.67 (2H, dd, 6.2, 2.5 Hz, CH<sub>2</sub>); 3.60 (9H, s, NMe<sub>3</sub>); 4.97 (1H, t, J 6.2 Hz, CH); 7.61 (2H, J 9.8 Hz, arom.); 7.81 (2H, d, J 9.8 Hz, arom.). (3h) 1H-NMR  $\delta$  3.65 (9H, s, NMe<sub>3</sub>); 5.05-5.10 (2H, m, CH<sub>2</sub>); 5.25-5.60 (2H, m, C=CH and CH); 7.61 (2H, d, J 9.8 Hz, arom.).; 7.81 (2H, d, J 9.8 Hz, arom.). (Found: C, 47.6; H, 5.6; N, 4.3. C<sub>13</sub>H<sub>18</sub>INO requires C, 47.15; H, 5.48; N, 4.23%).

measured on JEOL EX-90 (90 MHz) or Bruker AC-100 (100 MHz) spectrometers in CDCl<sub>3</sub> and chemical shifts are expresses in  $\delta$  ppm. <sup>1</sup>H-NMR spectrum of 1h was recorded in DMSO-*d*<sub>6</sub> and **2h** and **3h** were recorded in D<sub>2</sub>O (see Table ). GC analyses were performed on a Varian 3400 gas chromatograph equiped with polydimethylsiloxane HP-101 column, 25 m, steel. GC-Mass spectra were recorded with the same GC combined with a Hewlett Packard 5976 mass spectrometer. Mass spectral (MS) data of the salts were recorded on a Varian MAT 311A spectrometer.

### Preparation of (4-formylphenyl)trimethylammonium iodide (1h)

A solution of 4-dimethylaminobenzaldehyde (4.5 g, 30 mmol) in large excess (40 cm<sup>3</sup>) of methyl iodide was refluxed for 18 h in 250-cm<sup>3</sup> flask. The solid product (18%) was removed by filteration and recrystalized from absolute methanol, mp (decomp.) 137 °C. The IR and MS spectral data of 1h are as follows: IR (KBr) 1698, 1596 cm<sup>-1</sup>; MS m/e (5) 164 (7), 149 (100, - CH<sub>3</sub>), 148 (54), 91 (10), 79 (39), and 77 (75).

#### General procedure for preparation of homopropropargylic and $\alpha$ -allenic alcohols

To the suspension of an aldehyde (2 mmol), zinc powder (4 mmol), and saturated aqueous ammonium chloride (1 cm<sup>3</sup>), a solution of propargyl bromide (4 mmol) in THF (2.5 cm<sup>3</sup>) was added dropwise with stirring at room temperature. After stirring for 1 h, the reaction mixture was extracted with ether (30 cm<sup>3</sup> X 3), the combined organic extracts was washed with water and dried over sodium sulfate. The solvent was evaporated and the residue was purified by preparative TLC on silica gel, using CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (10:1) as eluent.

#### Characterization and analysis of products.

All products were characterized by IR and <sup>1</sup>H-NMR spectroscopy and GC-Mass or Mass spectrometry. The product mixture obtained from preparative TLC were separated and analyzed by GC-Mass. The GC-Mass analysis of the mixture showed two well resolved peaks of similar masses. In all cases, the first peak with shorter GC retention time corresponds to the major isomer, namely, homopropargylic alcohol. The GC-Mass analysis of the evolved gas also showed two well resolved peaks of m/e 40, the former is attributed to propadiene (78%) and the later to propyne (22%).

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