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# Fritsch–Buttenberg–Wiechell rearrangement to alkynes from *gem*-dihaloalkenes with lanthanum metal

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## A R T I C L E I N F O

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# ABSTRACT

The first example of the FBW rearrangement using of lanthanum metal and a catalytic amount of iodine was disclosed. When *gem*-diiodo- and *gem*-dibromoalkenes were treated with lanthanum metal in the presence of a catalytic amount of iodine, the reductive dehalogenation of these compounds smoothly proceeded to produce the corresponding alkynes in moderate to good yields.

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# 1. Introduction

Recently, the utilizations of lanthanoid metal salts and organolanthanoid compounds as a reagent or catalyst in organic synthesis have steadily increased [1]. In contrast, there are only a few reports on the direct use of lanthanoid metals except for cerium, samarium, and ytterbium metals for organic reactions [2,3]. Among the lanthanoid metals, we have been interested in the use of lanthanum metal which shows i) higher oxidation-reduction potential, ii) higher bond energy with oxygen, and iii) larger atomic radius than those of other lanthanoid metals [3,4]. During our investigation of the direct use of lanthanum metal in organic synthesis, it was found that the reductive dehalogenation of organohalogen compounds smoothly proceeded by lanthanum metal to generate unstable species such as the alkyl radical [5], benzyne [6] or o-quinodimethane [6b]. To extend the scope of the synthetic protocol employing lanthanum metal. the application of the Fritsch-Buttenberg-Wiechell (FBW) rearrangement [7], which is the 1.2-migration from the alkylidene carbene/carbenoid species as reactive intermediates giving the corresponding alkynes, has been planned. In this paper, we disclose the first example of the FBW rearrangement of gem-dihaloalkenes with lanthanum metal giving the corresponding alkynes [8].

### 2. Results and discussion

The reductive deiodination of the 1,1-diiodo-1-tridecene (1: X = I) smoothly proceeded to give 1-tridecyne (2) in 81% yield together with a small amount of 1-tridecene (3) (7%) and 1-iodo-1-tridecene (trace) (entry 1 in Table 1). In the absence of iodine, the reaction did not occur and 1 (X = I) was recovered (entry 2) [9,10]. When 1,1-dibromo-1-tridecene (1: X = Br) instead of diiodo derivative was treated with lanthanum metal under the same reaction conditions as that of entry 1, the yield of the terminal alkyne 2 significantly decreased; however, the yield of 2 was improved by increasing the amount of iodine (entries 3 and 4). In the case of dichloro derivative 1 (X = Cl), no reaction took place and 1 (X = Cl) was recovered (95%) [11].

Next, we examined the synthesis of the internal alkynes **5** by the treatment of 2-aryl-1,1-dihalo-1-propenes **4** with lanthanum metal (Table 2). When 2-aryl-1,1-diiodo-1-propene (**4**: X = I, Ar = Ph) was allowed to react with lanthanum metal under the same reaction conditions as that of entry 1 in Table 1, 1-phenyl-1-propyne (**5**: Ar = Ph) was obtained in 70% yield (entry 1). The 1-(4'-methylphenyl)- and 1-(4'-methoxyphenyl)-1-propynes were formed by the reaction of the diiodo derivatives **4** (X = I,  $Ar = 4-CH_3C_6H_4$  and 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) with lanthanum metal in 79 and 91% yields, respectively (entries 2 and 3). For the reaction of the 4'-chlorophenyl diiodo derivative **4** (X = I,  $Ar = 4-ClC_6H_4$ ) decreased due to the formation of uncharacterized polymeric materials (entry 4). The reaction of 2-methyl substituted phenyl derivative (X = I,  $Ar = 2-CH_3C_6H_4$ ) gave the corresponding



Note



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#### Table 1

Effect of halogen atom on  $\mathbf{1}$  and  $I_2$ .



•					
Entry	Х	I <sub>2</sub> (mmol)	Recovery (%) <sup>a</sup> <b>1</b>	Yield (%) <sup>a</sup>	
				2	3
1	Ι	0.08	-	81	7
2	Ι	_	93	trace	_
3	Br	0.08	85	3	_
4	Br	0.16	12	68	3
5 <sup>b</sup>	Cl	0.16	95	_	_

 $^{\rm a}\,$  Yield was determined by GC by using an internal standard based on 1.  $^{\rm b}\,$  For 11 h.

#### Table 2

FBW rearrangement of 2-aryl-1,1-dihalo-1-propenes 4.



Entry	Х	I <sub>2</sub> (mmol)	Ar	Yield (%) <sup>a</sup>
1	Ι	0.08	Ph	70
2	Ι	0.08	$4-CH_3C_6H_4$	79
3	Ι	0.08	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	91
4	Ι	0.08	4-ClC <sub>6</sub> H <sub>4</sub>	34
5	Ι	0.08	$2-CH_3C_6H_4$	38
6	Br	0.16	Ph	60
7	Br	0.16	$4-CH_3C_6H_4$	54
8	Br	0.16	$4-CH_3OC_6H_4$	53
9	Br	0.16	4-ClC <sub>6</sub> H <sub>4</sub>	52

<sup>a</sup> Yield was determined by GC by using an internal standard based on **4**.

#### Table 3

FBW rearrangement of 6 having different alkyl chains.



<sup>a</sup> Yield was determined by GC by using an internal standard based on **6**.

#### Table 4

FBW rearrangement of 2,2-diaryl-1,1-diiodoethenes 8.



Entry	R	Yield (%) <sup>a</sup>
1	Н	75
2	CH <sub>3</sub>	52
3	CH <sub>3</sub> O	87
4	Cl	40

<sup>a</sup> Yield was determined by GC by using an internal standard based on **8**.



Scheme 1. Reaction of gem-diiodoalkene 10.

propyne **5** (Ar = 2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) in low yield. Similarly, FBW rearrangement of the dibromo derivatives **4** (X = Br) smoothly proceeded to afford the propynes **5** in moderate yields (entries 6–9). In the case of 1-(4'-chlorophenyl)-1,1-dibromo-1-propene (**4**: X = Br, Ar = 4-ClC<sub>6</sub>H<sub>4</sub>), the yield of the alkyne is higher than that of the diiodo derivative (**4**: X = I, Ar = 4-ClC<sub>6</sub>H<sub>4</sub>) (entry 9).

The rearrangements of the 1,1-dihalo-2-phenyl-1-alkenes **6** having the longer alkyl chains, such as *n*-propyl and *n*-hexyl groups, were also examined (Table 3). In both cases of the diiodo and dibromo derivatives **6**, the elongation of the alkyl chains did not influence the yields of **7** (81–93%) (entries 1, 2, 5 and 6). The reaction of **6** having isopropyl and benzyl groups also occurred to give the corresponding **7** in 87% and 75% yields, respectively (entries 3 and 4). The diarylacetylenes **9** were obtained from the reaction of the corresponding diiodoethenes **8** with lanthanum metal in moderate to good yields (Table 4).

On the other hand, the reaction of the *gem*-diiodoalkene **10** substituted with two benzyl groups with lanthanum metal



Scheme 2. Intramolecular cyclization of 13.



Scheme 3. Plausible Reaction Pathway.

predominantly afforded the alkene **11**, the reductive deiodinated product, in 51% yield together with a trace amount of the alkyne **12** (Scheme 1).

On the reaction of 1,1-dibromo-2-methylundec-1-ene (**13**) having a long alkyl chain and methyl group at the alkene moiety with lanthanum metal, intramolecular cyclization took place to give cyclopentene derivative **14** (59%) as the main product together with alkyne **15** (15%), and debrominated product **16** (8%) (Scheme 2) [12].

Although we cannot clearly determine the reaction pathway, one of the plausible reaction pathways is shown in Scheme 3. Upon the reaction of 1,1-diiodo- and 1,1-dibromoalkenes, 1-iodo- and 1bromoalkenes were detected by GC and GC-mass spectra. These results indicate that mono halo vinyl radicals may be generated in situ. Then we suggested that the first step of the reaction is the reductive dehalogenation of gem-dihaloalkenes by a low-valent lanthanum species, which was generated in situ by the reaction of lanthanum metal with a catalytic amount of iodine [13,14], to form the mono halo vinyl radical. The vinyl radical species are reductively dehalogenated by lanthanum species to afford the alkylidenecarbenes (or alkylidenecarbenoids). Alkynes were formed by the 1,2-shift of alkylidenecarbenes (or alkylidenecarbenoids). It is well known that the alkyl group is less effective than aryl group and hydrogen atom as migrating groups in the FBW rearrangement [15]. In fact, in the case of 1,1-dibromo-2-methylundec-1-ene (13), having long alkyl chain and methyl group, 1,5-C-H insertion of alkylidenecarbene predominantly took place to form cyclopentene derivative 14 [16]. On the reaction of gem-diiodoalkene 10 substituted with two benzyl groups, vinyl iodide was formed by the abstraction of hydrogen from THF used as a solvent by mono halo vinyl radical. The vinyl iodide was reductively deiodinated with lanthanum species to give alkene 11. Another pathway including the directly abstraction of alkylidenecarbene from THF cannot be ruled out.

#### 3. Conclusion

In conclusion, we succeeded in the reaction of the appropriate diiodo- or dibromo-olefinic precursors with lanthanum metal to give the corresponding alkynes in moderate to good yields. This is, to the best of our knowledge, the first example of the FBW rearrangement using of lanthanum metal. Further investigations involving elucidation of the detailed reaction mechanism are currently in progress.

# 4. Experimental

#### 4.1. General procedure for FBW rearrangement by lanthanum metal

A two-necked flask charged with lanthanum powder (0.40 mmol) was equipped with a magnetic stirring bar and then a solution of iodine (for diiodo derivative, 0.08 mmol; for dibromo derivative, 0.16 mmol) and the *gem*-dihaloalkenes (0.20 mmol) in THF (1.2 mL) was added to the flask. The mixture was stirred at 67 °C for 3 h under an argon atmosphere. After the reaction, aq. HCl (5%) was added to the reaction mixture and extracted with EtOAc (10 mL  $\times$  3). The organic layer was washed with saturated aq. sodium thiosulfate (30 mL), dried over MgSO<sub>4</sub> and filtered. The organic layer was concentrated in vacuo. Purification of the product by Kugelrohr afforded the analytically pure alkynes. The products were characterized by a comparison of their spectra data with those of authentic samples.

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#### Appendix. Supplementary material

Experimental details, spectroscopic data associated with this article can be found in the online version, at doi:10.1016/j. jorganchem.2011.02.014.

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