Tetrahedron Letters, Vol. 33, No. 18, pp. 2581-2582, 1992 Printed in Great Britain

0040-4039/92 \$5.00 + .00 Pergamon Press Ltd

Carboindation of Alkynols. A Facile Synthesis of Yomogi Alcohol

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Key Words: Indium, Carbometallation, Alkynol, Allylic Alcohol, Yomogi Alcohol

Abstract: Carboindation of alkynols by allylic indium sesquihalides proceeded in DWF at 100 - 140 °C via a syn-addition; yomogi alcohol was prepared in one-pot by this method.

We have recently demonstrated that organoindium reagents are new and useful tools in synthetic chemistry.<sup>1</sup> In particular, allylic indium sesquihalides are easily preparable and show unique reaction behaviour with satisfactory regio- and chemo-selectivity.<sup>2</sup> In this paper are described the first example of carbometallation<sup>8</sup> of alkynols by allylic indium reagents (carboindation) and its application to the one-step synthesis of the naturally occurring monoterpene alcohol, yomogi alcohol.

A mixture of propargyl alcohol (1 mmol) and prenylindium sesquibromide, prepared from indium metal (1 mmol) and prenyl bromide (1.5 mmol), was heated in N.N-dimethylformamide (DMF) (2 ml) at 115 °C for 6 h. Aqueous workup and purification by column chromatography on silica gel gave two carboindation products, 4,4-dimethyl-2,5-hexadien-1-ol and 2-methylene-3,3-dimethyl-4penten-1-ol, in 91% combined yield. The ratio of these anti-Markownikov to Markownikov adducts was 65 : 35. Results for other allylic indium reagents and alkynols are summarized in Table. which shows the following characteristics: (i) allylic indium reagents react selectively at the  $\gamma$ -carbon, (ii) regioselectivity concerning alkynol (anti-Markownikov vs. Markownikov) depends upon the structures of both alkynol and allylindium, (iii) double bond geometry of the anti-Markownikov adducts is E, indicating that the carboindation process is a syn-addition. (iv) only terminal alkynes undergo carboindation: 2-butyn-l-ol, for example, did not react at all with prenylindium, and (v)hydroxyl functionality near triple bond is essential; i.e. propargyl methyl ether and 4-pentyn-1-ol were unsusceptible to carboindation.

Entry 2 demonstrates a facile synthesis of yomogi alcohol.<sup>4</sup> Although several synthetic methods have hitherto been developed for this terpene.<sup>8</sup> multi-step sequences are required. Our procedure based on carboindation is highly regio- and stereo-selective, providing 83% yield of the isomerically pure product in one-pot.

Detail mechanistic considerations and further synthetic applications of this carboindation will be reported elsewhere.

Entry	Alkynol	Allylindium	Produ	Yield/% <sup>C</sup>	
1	<b>≫∕</b> он	( J <sup>JIn</sup> 2 <sup>Br</sup> 3	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Пон	91 (65:35)
2	<b>М</b> он	•	Т		83 (100:0)
3	<i>≫∕∕</i> °#		ОН	мон	85 (73:27)
4	<b>В</b> олен	( <sup>ph</sup> /3 <sup>In</sup> 2 <sup>Br</sup> 3	Ph	Ph	56 (14:86)
5	Мон		Ph OH	Ph	68 (90:10)
6	<i>р</i> ов	( <b>7773</b> <sup>1</sup> <b>n</b> 2 <sup><b>B</b>1</sup> <b>3</b>	The second	Т	59 (75:25)
7	<b>№</b> Х <sub>ов</sub>	×	Y OH		75 (100:0)

## Table. Carboindation of Alkynols by Allylic Indium Reagents\*

\*All reactions were carried out in DNF at 100 - 140 °C for 3 - 6 h. \*All products gave spectral and analytical data in agreement with the proposed structures. 'Figures in parentheses refer to the ratio anti-Warkownikov : Warkownikov adducts.

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(Received in Japan 7 February 1992)