

SYNTHESES OF ALKENES FROM VINYLIC GRIGNARD REAGENTS  
ACTIVATED BY COPPER SALTS.

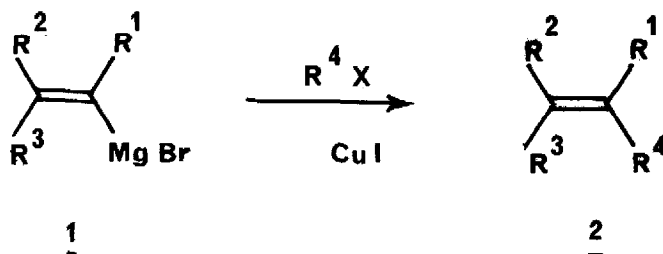
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The synthesis of double bonds has received a great deal of attention. The carbon carbon bond between a vinylic moiety and a hydrocarbon chain can be realized by several procedures. Organocopper<sup>1</sup> and organomagnesium<sup>2-5</sup> compounds are found to be efficient reagents. Vinylic lithium reagents<sup>6</sup> and vinylic cuprates<sup>7</sup> under suitable conditions are easily alkylated.

We have now found that vinylic Grignard reagents<sup>8</sup> can be alkylated<sup>9</sup> in high yields by iodides and tosylates in the presence of copper salts. Thus, when 2-propenyl 2-magnesium bromide (1.3 equiv.) was treated with octyl iodide (1 equiv.) and copper iodide (10%) in tetrahydrofuran at 0° for 1.5 hr, pure 2-methyl decene<sup>6b</sup> was obtained in 95% yield. Under the same conditions, octyl tosylate (1 equiv.) gave an 80% yield. Bromides are less reactive.



As for the lithium vinylic cuprates<sup>7,10</sup>, the purity of the copper iodide is critical for the success of the reaction. The purified salt must be carefully stored under nitrogen<sup>7</sup>. Unpurified samples gave low yields of products.

The Tamura-Kochi complex<sup>2</sup>, dilithium tetrachlorocuprate, with octyl iodide under our conditions, gave the same result with higher amounts of magnesium reagent (50% yield with 1,1 equiv., 95% yield with 2,5 equiv. of isopropenylmagnesium bromide).

Although a slight isomerisation has been observed during the preparation of alkenyl magnesium compounds<sup>11,12</sup>, substituted olefins, such as 2c and 2d, can be prepared with

good stereoisomeric purity.

Preparation<sup>a</sup> of alkenes promoted by copper iodide.

Product	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup> X	equiv. of reagent <u>1</u>	Time (hr)	Yield (%)
<u>2a</u>	H	H	H	n-C <sub>8</sub> H <sub>17</sub> I	1.3 <sup>b</sup>	1.5	82
<u>2b</u>	CH <sub>3</sub>	H	H	n-C <sub>8</sub> H <sub>17</sub> I	1.3	1.5	95
<u>2b</u>	CH <sub>3</sub>	H	H	n-C <sub>8</sub> H <sub>17</sub> OTs	1.3	3	80
<u>2b</u>	CH <sub>3</sub>	H	H	n-C <sub>8</sub> H <sub>17</sub> Br	1.1	3	20
<u>2c</u>	CH <sub>3</sub>	H	CH <sub>3</sub> <sup>c</sup>	n-C <sub>3</sub> H <sub>7</sub> I	1.3	1.5	97 <sup>d, e</sup>
<u>2d</u>	CH <sub>3</sub>	H	CH <sub>3</sub> <sup>c</sup>	n-C <sub>8</sub> H <sub>17</sub> I	1.3	1.5	96 <sup>d</sup>

<sup>a</sup>at 0° in tetrahydrofuran. <sup>b</sup>vinylmagnesium chloride was used. <sup>c</sup>90% Z, 10% E. <sup>d</sup>88% Z, 12%E  
<sup>e</sup>yield determined by glpc using a calibrated internal standard (n-octane).

Typical procedure: 2-methyl decene.

To 124 mg (0.65 mmol) of purified copper iodide<sup>7, 13</sup> and 1.2 g (5 mmol) of octyl iodide in anhydrous tetrahydrofuran, 3.2 ml (2.05 N, 6.5 mmol) of isopropenylmagnesium bromide were added under nitrogen at -30°. After the end of the addition, the reaction was allowed to warm to 0° and maintained at this temperature for 1.5 hr. Work-up in the usual manner and distillation gave 730 mg (95%) of pure 2-methyl decene<sup>6b</sup>.

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