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## Conversion of Alkyland Arylallenes into 1-Alkynes Through Metallated Intermediates

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### CONVERSION OF ALKYL- AND ARYLALLENES INTO 1-ALKYNES THROUGH METALLATED INTERMEDIATES

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Abstract: A number of acetylenes  $RCH_2C \equiv CH$  have been obtained by metallation of the allenes  $RCH = C = CH_2$  or mixtures of acetylenes and allenes with *n*-BuLi in THF-hexane and hydrolysis after allowing the metallated allenes to rearrange at room temperature or by heating under reflux.

In 1974 Meijer *et al.*<sup>1</sup> published a method for the preparation of acetylenes, involving copper catalyzed reaction of Grignard compounds with methoxyallene.

$$CH_{3}O_{C} = C = CH_{2} \xrightarrow{RMgX} R - CH_{2} - C \equiv CH_{2}$$

We here present an alternative method, which uses the readily available propargyl bromide as starting material. Reaction of Grignard compounds with propargyl bromide in diethyl ether or THF in the presence of catalytic amounts of copper(I)-halide generally affords a mixture of an acetylene and the isomeric allene.

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The ratio of the isomers strongly depends on the nature of the Grignard reagent (see Table). We succeeded in completely converting the products mixtures into acetylides by treatment with a slight (10 mol %) excess of *n*-BuLi in THF-hexane and subsequently allowing to rise the temperature to 20 °C or –in the case R = alkyl or cyclohexyl– by heating the solutions for some period under reflux. The conversion of **1a** into the much more weakly basic **2a**, which takes place under aprotic conditions, probably proceeds by a 1,3-sigmatropic H-shift, as suggested by Klein *et al.*<sup>2</sup>

Table

			Tuble		
En	ıtry R	Yield $(\%)^{a}$ of <b>1</b> + <b>2</b>	Ratio 1/2 (NMR)	h.p. ("C) 12 mm Hg <sup>d</sup>	Yield (%) <sup>b</sup> of RCH <sub>2</sub> C≡CH
1	<i>n</i> -C <sub>7</sub> H <sub>15</sub>	80	96 / 4	62-63	90
2	c-hexyl	80	10070	50	90
3	$C_6H_5$	70	72/28	62-65	77
4	4-(CH <sub>3</sub> ) <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> <sup>c</sup>	; 70	52 / 48	103-106	76
5	2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> <sup>c</sup>	70	19/81	90-93	89
6	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> <sup>c</sup>	78	55/45	105-108	90
7	$4-FC_6H_4$	67	53 / 47	62-65	75

<sup>a</sup> Isolated yields after distillation; purity  $\ge 97\%$  (300 <sup>1</sup>H-NMR and GLC).

- b Yield based on mixtures of 1 and 2; see Experimental Section for physical and spectroscopic properties.
- <sup>c</sup> The corresponding Grignard reagents were prepared in THF.
- <sup>d</sup> B.p. of 1 or the mixtures of 1 and 2.

#### Experimental Section Materials and Instrumentation

All reactions were performed under a dry nitrogen atmosphere in flame-dried glassware. THF was freshly distilled from sodium sand/benzophenone under a dry nitrogen atmosphere. Diethyl ether was dried by shaking with freshly machine-powdered KOH (100 g/l) and subsequent filtration. Commercially available *n*-BuLi (1.6 M solution in hexane) was used for all isomerization reactions. Grignard reagents were prepared in the usual way from magnesium turnings and alkyl or aryl bromides in diethyl ether or THF. In the case R = cycloalkyl the chloride was used. NMR spectra were recorded on a Bruker AC 300 (<sup>1</sup>H: 300 MHz, <sup>13</sup>C: 75 MHz) using deuterochloroform as a solvent and internal standard. Mass spectra were recorded on a Jeol JMS-AX 505 W, GC-MS combination.

# General procedure for the preparation of allenes (1) or mixtures of allenes (1) and acetylenes (2)

All reactions were carried out using the following typical procedure (modified procedure, cf. Ref. 3).

To a solution of the Grignard reagent in 130 ml of diethyl ether or THF, prepared from 0.10 mol of the halides RX, was added at ~ -60 °C a solution of 1 g of copper(I)bromide and 2 g of anhydrous lithium bromide in 8 ml of THF. Subsequently, a solution of 0.12 mol of propargyl bromide and 10 ml of THF was added dropwise over 30 min, while keeping the temperature of the reaction mixture between -50 and -60 °C. After stirring for an additional period of 15 min, the cooling bath was removed and the temperature of the suspension allowed to rise to between 10 and 20 °C. The reaction mixture was then cautiously poured into a solution of 10 g of ammonium chloride in 100 ml of water. After vigorous shaking and extraction of the aqueous layer with pentane, the combined organic solutions were dried over MgSO<sub>4</sub> and concentrated in vacuo. The product mixtures were isolated by distillation through a 30-cm Vigreux column.

# General procedure for the conversion of alkylallenes into the corresponding acetylenic compounds

A solution of 0.11 mol of *n*-BuLi in 71.5 ml of hexane was added dropwise for 20 min to a solution of 0.10 mol of the alkylallene ( $R = n-C_7H_{15}$  or *c*-hexyl) in 60 ml

of THF with cooling between -80 and -70 °C. After stirring for an additional period of 15 min at -60 °C, the cooling bath was removed and the temperature was allowed to rise to room temperature. Subsequently, the reaction mixture was heated under reflux for 5 hours. After cooling the reaction mixture to room temperature, water (100 ml) was added, the layers were separated and the aqueous layer was extracted with ether. The combined organic fractions were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Distillation of the remaining liquid through a 30-cm Vigreux column gave the acetylenic compounds.

#### 1-Decyne (Entry 1, Table)

The product was obtained in 90% yield, from 0.11 mol of *n*-BuLi in 71.5 ml of hexane and 0.10 mol (13.8 g) of heptylallene. B.p. 60-63 "C /14 mm Hg (Lit<sup>4</sup> 80-82 "C/22 mm Hg);  $n^{21}$ <sub>D</sub> 1.4273.

#### 3-Cyclohexyl-1-propyne (Entry 2, Table)

The product was obtained in 90% yield, from 0.11 mol of *n*-BuLi in 71.5 ml of hexane, 60 ml of THF and 0.10 mol (12.2 g) of cyclohexylallene. B.p. 46 °C/12 mm Hg (Lit<sup>4</sup> 61-62 °C/24 mm Hg);  $n^{20}$ D 1.4571.

# General procedure for the conversion of arylallenes into the corresponding acetylenic compounds

A solution of 0.11 mol of *n*-BuLi in 71.5 ml of hexane was added dropwise for 20 min to a solution of 0.10 mol of the mixture 1 and 2 (R = aryl) with cooling between -90 and -80 °C. After allowing the temperature to rise to -40 °C the cooling bath was removed and water (100 ml) was added at room temperature. The isolation of the products was carried out as described above.

#### 3-Phenyl-1-propyne (Entry 3, Table)

The product was obtained in 77% yield, from 0.11 mol of *n*-BuLi in 71.5 ml of hexane, 60 ml of THF and 0.10 mol (11.6 g) of the mixtures 1 and 2 ( $R = C_6H_5$ ). B.p. 62-63 "C/12 mm Hg (Lit<sup>1</sup> 60-61 °C / 12 mm Hg); n<sup>20</sup><sub>D</sub> 1.5273.

#### 1-Isopropyl-4-(2-propynyl) benzene (Entry 4, Table)

The product was obtained in 76% yield from 55.0 mmol of n-BuLi in 36 ml of

hexane, 30 ml of THF and 50 mmol (7.9 g) of the mixtures 1 and 2 (R = 4- $(CH_3)_2CHC_6H_4$ ). B.p. 60-62 "C/2 mm Hg;  $n^{18}_D$  1.5144; MS (EI<sup>+</sup>): 158, exact mass: calcd for  $C_{12}H_{14}$  158.1096, found 158.1075; <sup>1</sup>H-NMR: 1.26 (d, 6H, <sup>2</sup>J = 6.9 Hz), 2.18 (t, 1H, <sup>4</sup>J = 2.7 Hz), 2.92 (sep, 1H, <sup>2</sup>J = 6.9 Hz), 3.59 (d, 2H, <sup>4</sup>J = 2.7 Hz), 7.21 (dd, 2H, <sup>3</sup>J = 6.3 Hz, <sup>4</sup>J = 1.8 Hz), 7.30 (dd, 2H, <sup>3</sup>J = 6.3 Hz, <sup>4</sup>J = 1.8 Hz); <sup>13</sup>C-NMR: 24.1 (2C), 24.4, 33.9, 70.1, 82.3, 126.6, 127.8, 133.4, 147.4.

#### 1,3-Dimethyl-2-(2-propynyl) benzene (Entry 5, Table)

The product was obtained in 89% yield from 38.46 mmol of *n*-BuLi in 25 ml of hexane, 21 ml of THF and 35.0 mmol (5.04 g) of the mixtures 1 and 2 (R = 2,6- $(CH_3)_2C_6H_4$ ). B.p. 88-90 °C/12 mm Hg;  $n^{20}_D$  1.5304; MS (EI<sup>+</sup>): 144, exact mass: calcd for C<sub>11</sub>H<sub>12</sub> 144.0939, found 144.0901; <sup>1</sup>H-NMR: 1.98 (t, 1H, <sup>4</sup>J = 2.8 Hz), 2.43 (s, 6H), 3.52 (d, 2H, <sup>4</sup>J = 2.8 Hz), 7.04-7.13 (m, 3H); <sup>13</sup>C-NMR: 19.0 (2C), 20.8, 68.2, 81.5, 126.8, 128.2 and 128.6 (2C), 133.6, 136.3.

#### 1-Methoxy-4-(2-propynyl) benzene (Entry 6, Table)

The product was obtained in 90% yield from 0.11 mol of *n*-BuLi in 71.5 ml of hexane, 60 ml of THF and 0.10 mol (14.6 g) of the mixtures **1** and **2** (R = 4-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>). B.p.110 °C/15 mm Hg;  $n^{20}$ <sub>D</sub> 1.5350; **MS** (EI<sup>+</sup>): 146, exact mass: calcd for C<sub>10</sub>H<sub>10</sub>O 146.0732, found 146.0766; <sup>1</sup>H-NMR: 2.18 (t, 1H, <sup>4</sup>J = 2.7 Hz), 3.56 (d, 2H, <sup>4</sup>J = 2.7 Hz), 3.80 (s, 3H), 6.80 (dd, 2H, <sup>2</sup>J = 6.6 Hz, <sup>4</sup>J = 2.0 Hz), 7.28 (dd, 2H, <sup>2</sup>J = 6.6 Hz, <sup>4</sup>J = 2.0 Hz); <sup>13</sup>C-NMR: 23.9, 55.3, 70.1, 82.4, 114.0 (2C), 128.1 128.8, (2C), 158.4.

#### 1-Fluoro-4-(2-propynyl) benzene (Entry 7, Table)

The product was obtained in 75% yield from 0.11 mol of *n*-BuLi in 71.5 ml of hexane, 60 ml of THF and 0.10 mol (13.4 g) of the mixtures **1** and **2** (R = 4-FC<sub>6</sub>H<sub>4</sub>). B.p. 60 °C/12 mm Hg;  $n^{20}$ <sub>D</sub> 1.5284; **MS** (EI<sup>+</sup>): 134, exact mass: calcd for C<sub>9</sub>H<sub>7</sub>F 134.0532, found 134.0548; <sup>1</sup>H-NMR: 2.20 (t, 1H, <sup>4</sup>J = 2.7 Hz), 3.58 (d, 2H, <sup>4</sup>J = 2.5 Hz), 6.97-7.05 (m, 2H), 7.26-7.35 (m, 2H); <sup>13</sup>C-NMR: 24.0, 70.4, 81.7, 115.3, (2C, <sup>1</sup>J = 21.6 Hz), 129.3 (2C, <sup>1</sup>J = 8.5 Hz), 131.7 (<sup>1</sup>J = 3.2 Hz), 161.8 (<sup>1</sup>J = 244.5 Hz).

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