# Synthesis and Properties of Copper, Mercury, and Silver (2-Naphthyl)acetylenides

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**Abstract**—(*Z*)-2-Naphthylacetylene was synthesized by the reaction of (*Z*)-3-(2-naphthyl)-3-chloropropenal (prepared from 2-acetylnaphthalene) with aqueous NaOH in dioxane. The reactions of 2-naphthylacetylene with CuCl,  $[Ag(NH_3)_2]NO_3$ , and  $K_2[HgI_4]$  gave copper, silver, and mercury 2-naphthylacetylenides, respectively. Silver naphthylacetylenide reacts with iodine to give the iodoethynyl derivative, which readily takes up bromine across the triple bond.

Naphthalene derivatives are widely used in synthesis of dyes, pesticides, and drugs [1, 2]. One of convenient routes to naphthalene functional derivatives is introduction of the ethynyl group into the side chain of the naphthalene system [3], followed by synthesis of highly reactive metal acetylenides [4, 5].

The goal of this work was synthesis of copper, mercury, and silver 2-naphthylacetylenides from accessible 2-acetylnaphthalene **I**. First, we prepared (*Z*)-3-(2-naphthyl)-3-chloropropenal **II** by Vilsmeier– Haack formylation of ketone **I**. We were able to isolate and identify the intermediate reaction product, 3-(2-naphthyl)-3-chloro-2-propen-1-yl-*N*,*N*-dimethylimmonium chloride **III** (yield 90%), whose treatment with sodium acetate in aqueous solution gave naphthylchloropropenal **II** in 72% yield (see scheme below).



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The compositions and structures of **II** and **III** were determined by elemental analysis, IR and <sup>1</sup>H spectroscopy, and mass spectrometry. In the IR spectra of **II** and **III**, the C=C stretching vibrations are manifested at 1505–1624 cm<sup>-1</sup>. A strong band at 1645 cm<sup>-1</sup> in the spectrum of **III** corresponds to the C=N bond. The C=O vibrations in **II** give rise to a strong band at 1668 cm<sup>-1</sup>.

In the <sup>1</sup>H NMR spectra of **II** and **III**, the signals of aromatic protons (multiplet) and exocyclic CCl=CH group appear at 6.80–8.20 ppm. The singlet at  $\delta$  8.31 and 8.75 ppm for **II** and **III**, respectively, corresponds to the C<sup>1</sup>H fragment of the naphthalene system. The doublets at  $\delta$  10.27 ppm in the spectrum of **III** and 9.10 ppm in the spectrum of **II** are due to CH=N and CH=O protons, respectively.

The  ${}^{3}J$  coupling constants for the protons of the side chain, equal to 7.7 and 9 Hz for II and III, respectively, are indicative of the *s*-*cis* arrangement of these hydrogen atoms [7]. Chakraborty and Ray [8] studied the isomeric composition of aldehydes obtained by the Vilsmeier–Haack reaction from a series of ketones, including 2-acetonaphthone I, and obtained naphthylchloropropenal II exclusively in the form of the Z isomer. Our data show that naphthyl-substituted immonium chloride III and aldehyde II have the *s*-*cis*-Z configuration of the side chain.

The mass spectrum of **III** contains isotopic peaks of the  $[M - Cl]^+$  ion, and the mass spectrum of **II**, strong peaks of the molecular ion. The <sup>35</sup>Cl/<sup>37</sup>Cl isotope ratio in the peaks of the molecular ion of **II**, equal to 100 : 33, indicates that the molecule of **II** contains one chlorine atom [9, 10].

Treatment of **II** in dioxane with aqueous NaOH gave 2-naphthylacetylene **IV** in 35% yield; its structure was confirmed spectroscopically. In the <sup>1</sup>H NMR spectrum of **IV**, protons of the naphthalene residue give a multiplet at 7.4–8.1 ppm. The broadened singlet at 8.0 ppm belongs to the C<sup>1</sup>H proton of the naphthalene core. The acetylenic proton at C<sup>12</sup> (side chain) gives a singlet at 3.16 ppm. The presence of the C=C bond is confirmed by a characteristic IR band at 2100 cm<sup>-1</sup> and by the =C-H band at 3280 cm<sup>-1</sup>. The C=C bond in the CBr=CBr fragment gives bands at 1500–1595 cm<sup>-1</sup>. The mass spectrum of **IV** contains molecular (m/z 152) and fragmentation peaks.

By the reactions of 2-naphthylacetylene **IV** with CuCl,  $[Ag(NH_3)_2]NO_3$ , and  $K_2[HgI_4]$ , we prepared copper, silver, and mercury acetylenides **V**–**VII**, respectively. The reactions occurred at room temperature; the desired acetylenides were obtained in 91–94% yields and did not require additional purification.

Acetylenides V–VII are stable in storage at  $0-5^{\circ}$ C in the dark.

Acetylenides **V**–**VII** were identified by IR spectroscopy and elemental analysis. These compounds are virtually insoluble in acetone, chloroform, benzene, methanol, dimethyl sulfoxide, other organic solvents, and also in water, and therefore we failed to record their <sup>1</sup>H NMR spectra. In the IR spectra of **V**–**VII**, the =C–H absorption band of the starting naphthylacetylene **IV** is absent. The C=C absorption band is not manifested in the spectrum of copper naphthylacetylenide **V**; in the spectra of the silver and mercury derivatives, it is observed at 2037 and 2142 cm<sup>-1</sup>, respectively.

Silver naphthylacetylenide **VI** was subsequently used to prepare exocyclic halo derivatives. The reaction of **VI** with iodine in chloroform gave 2-naphthylethynyl iodide **VIII** in 91% yield. Compound **VIII** readily took up bromine in dichloromethane to form dibromo iodide **IX**. A GC–MS study showed that compound **IX** was formed as a  $\sim$ 3.5 : 1 mixture of the *E* and *Z* isomers. The spectroscopic and analytical data for **VIII** and **IX** are given in the Experimental.

#### EXPERIMENTAL

The IR spectra were recorded on a Nikolet Protege-460 Fourier spectrometer (KBr pellets). The <sup>1</sup>H NMR spectra were taken on a Tesla BS-567A spectrometer in CDCl<sub>3</sub>, internal reference TMS. The mass spectra were obtained on an MKh-1320 high-resolution mass spectrometer at the ionizing electron energy of 50 eV. The GC–MS analysis of **IX** was performed on a Hewlett–Packard GC/MS-5890/5972 device by the EPA 8270 method. The mercury content was determined according to [11].

3-(2-Naphthyl)-3-chloro-2-propen-1-yl-N,N-dimethylimmonium chloride III. To 134 ml of dimethylformamide, we added 50.2 g of  $PCl_5$  in portions at 25-30°C over a period of 30 min. The mixture was stirred for 2.5-3 h at 20-25°C and allowed to stand for 8 h. To the resulting suspension of the Vilsmeier-Haack complex, a solution of 33 g of 2-acetonaphthone in 82.5 ml of dimethylformamide was added at 25-30°C over a period of 30 min. On stirring and heating to 35–40°C, a bright yellow precipitate formed, which was filtered off, washed with water and diethyl ether, and vacuum-dried. Immonium chloride **III** was obtained; yield 48.9 g (90%), mp 168–170°C. Found, %: C 64.50; H 4.93; Cl 25.68; N 4.89.  $C_{15}H_{15}Cl_2N$ .  $[M]^+$  279. Calculated, %: C 64.30; H 5.40; Cl 25.30; N 5.00. M 280.19.

#### s-cis-3-(2-Naphthyl)-3-chloropropenal II. A 30-g

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portion of 3-(2-naphthyl)-3-chloro-2-propen-1-yl-*N*,*N*-dimethylimmonium chloride **III** was treated with heating and stirring with 10 g of aqueous sodium acetate. The precipitate that formed after cooling was filtered off, washed with water and diethyl ether, vacuumdried, and recrystallized from chloroform. Yield of **II** 16.7 g (72%), mp 62–63°C. Found, %: C 72.37; H 4.05; Cl 16.18. C<sub>13</sub>H<sub>9</sub>ClO. [*M*] 216. Calculated, %: C 72.06; H 4.19; Cl 16.36. *M* 216.66.

**2-Naphthylacetylene IV.** A solution of 2 g of **II** in 18 ml of dioxane was added dropwise to a hot solution of 1 g of NaOH in 10 ml of water. The mixture was refluxed for 6 h; after cooling, the solvent was distilled off, the residue was diluted with water, and the flaky precipitate was filtered off, washed with cold methanol, and recrystallized from methanol. Compound **IV** was obtained; yield 0.49 g (35%), mp 35°C. Found, %: C 94.65; H 5.35. C<sub>12</sub>H<sub>8</sub>. [*M*]<sup>+</sup> 152. Calculated, %: C 94.69; H 5.31. *M* 152.18.

**Copper 2-naphthylacetylenide V.** To a solution of 0.4 g of CuCl and 0.5 g of hydroxylamine hydrochloride in a mixture of 1 g of water, 3 ml of monoethanolamine, and 20 ml of methanol, we added in one portion 0.4 g of 2-naphthylacetylene **IV**. The mixture was stirred for 3 h at  $20-23^{\circ}$ C and diluted with 100 ml of water. The product was filtered off on a glass frit, washed with a large amount of water, and vacuum-dried in the dark. Yield of **V** 0.6 g (91%), mp 260°C. Found, %: C 67.30; H 3.48; Cu 29.83. C<sub>12</sub>H<sub>7</sub>Cu. Calculated, %: C 67.12; H 3.28; Cu 29.60. *M* 214.72.

Silver 2-naphthylacetylenide VI. To a solution of 0.6 g of AgNO<sub>3</sub> in 20 g of water and 5 g of 25% aqueous NH<sub>4</sub>OH, we added in one portion 0.4 g of IV in 10 g of dioxane. The subsequent synthesis was performed similarly to V. Yield 94%, mp 170°C. Found, %: C 55.42; H 2.99; Ag 41.72.  $C_{12}H_7Ag$ . Calculated, %: C 55.63; H 2.73; Ag 41.64. *M* 259.05.

**Mercury 2-naphthylacetylenide VII.** To a mixture of 2.5 ml of Thoulet solution (saturated aqueous  $K_2[HgI_4]$ ), 4 g of KOH, and 35 g of water, we added in one portion 0.4 g of **IV** in 10 ml of dioxane. The subsequent synthesis was performed similarly to **V**. Yield 92%, mp 170–171°C. Found Hg, %: 39.92.  $C_{24}H_{14}Hg$ . Calculated, %: C 57.31; H 2.81; Hg 39.88. *M* 502.94.

**2-Naphthylethynyl iodide VIII.** To a suspension of 0.78 g of **VI** in 20 ml of chloroform, we added in one portion 0.78 g of iodine at  $20-23^{\circ}$ C with stirring. The mixture was stirred at  $20-23^{\circ}$ C for 5 h and allowed to stand for 15–18 h, after which the solution was filtered to remove AgI, diluted with 50 ml of

hexane, washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and dried over MgSO<sub>4</sub>. The solvent was removed. Product **VIII** was recrystallized from hexane and purified by column chromatography on Al<sub>2</sub>O<sub>3</sub> (Brockmann grade II), eluent hexane. Yield of **VIII** 0.6 g (91%), mp 198– 199°C. IR spectrum, v, cm<sup>-1</sup>: 2170 (C=C), 1496, 1567, 1592, 1623 (C=C), 481 (CI). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.39–7.84 m (6H<sub>arom</sub>), 7.95 br.s (1H<sub>arom</sub>). Found, %: C 51.64; H 2.75; I 45.28. C<sub>12</sub>H<sub>7</sub>I. Calculated, %: C 51.83; H 2.54; I 45.63. *M* 278.08.

**2-Naphthyl-1,2-dibromoethynyl iodide IX.** To a solution of 2.78 g of **VIII** in 30 ml of methylene chloride, we added in one portion 0.52 ml of bromine at 20–23°C with stirring. After keeping for 24 h under these conditions, the solution decolorized. The solvent was removed, and the residue was recrystallized from hexane. Yield of **IX** 3.63 g (83%), mp 38–39°C. IR spectrum, v, cm<sup>-1</sup>: 1502, 1574, 1596, 1624 (C=C), 670 (CBr), 475 (CI). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.44–7.89 m (7H<sub>arom</sub>). Found, %: C 33.12; H 1.86; Hlg 65.38. C<sub>12</sub>H<sub>7</sub>Br<sub>2</sub>I. Calculated, %: C 32.91; H 1.61; Hlg 65.47. *M* 437.90.

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