

## 2-Hexadecynoic Acid

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Received November 11, 1955

The hitherto undescribed 2-hexadecynoic acid (III) was prepared by the following route. Dodecylmagnesium bromide was reacted with 2,3-dibromopropene to give 2-bromopentadecene (I) in 35% yield. Refluxing the bromo-compound I with freshly prepared sodium amide in xylene gave pentadecyne (II) in 49.1% yield. This compound was prepared by Ahmad<sup>1</sup> from tridecyl bromide and sodium acetylide in liquid ammonia. The present synthesis of II closely follows the procedure for the synthesis of heptadecyne described by Jenny and Grob<sup>2</sup>. Carbonation of the Grignard complex of II at atmospheric pressure with gaseous carbon dioxide afforded 2-hexadecynoic acid in 13.2% yield.

### EXPERIMENTAL

#### 2-Bromopentadecene (I)

A solution of dodecylmagnesium bromide (from 78.4 g., 0.315 moles of dodecyl bromide<sup>3</sup> and 7.06 g. of magnesium) in ether (235 ml.) was added to a stirred solution of 2,3-dibromopropene<sup>4</sup> (30 g., 0.30 moles) in dry ether (75 ml.) at such a rate that the mixture refluxed gently. The stirring and refluxing was continued for additional four hours. The mixture was cooled and decomposed by careful addition of diluted hydrochloric acid (1:10, 100 ml.). The ether layer was washed with water, dried and evaporated. Distillation of the residue at 23 mm. pressure removed 11 g. of low-boiling products (boiling range 50–130°). The residual oil was fractionated in an atmosphere of nitrogen at 0.15 mm. pressure and the fraction b. p. 92–93/0.15 mm. was collected as practically pure colorless 2-bromopentadecene (30.1 g., i. e. 35% based on 2,3-dibromopropene). For analysis a sample was redistilled, b. p. 92°/0.15 mm. Colorless liquid,  $n_D^{20}$  1.4690.

Anal. 6.765 mg. subst.: 15.29 mg. CO<sub>2</sub>, 6.55 mg. H<sub>2</sub>O  
C<sub>15</sub>H<sub>20</sub>Br (289.3) calc'd C 62.29; H 10.11%  
found: C 61.68; H 10.83%

#### Pentadecyne (II)

A suspension of sodium amide in liquid ammonia (from 8.8 g. of sodium) was prepared according to Vaughn, Vogt and Nieuwland.<sup>5</sup> The ammonia was slowly evaporated while 270 ml. of dry xylene were simultaneously added. The resulting suspension of sodium amide in xylene was heated with stirring at 140° (bath temperature), and 39 g. of I were added in the course of one hour. The evolved ammonia was led, by means of a slow stream of dry nitrogen, through the condenser, and collected in water. The liberated amount of ammonia was measured by titration with 2 N hydrochloric acid. The heating and stirring was continued for additional ten hours when the evolution of ammonia practically ceased. The reaction mixture was cooled and poured on 100 g. of cracked ice and acidified with 45 ml. of concentrated hydrochloric acid. The resulting mixture was exhaustively extracted with ether, the combined extracts washed successively with water, 2 N sodium carbonate, and water. After drying, the solvent was evaporated in vacuo at 60°. Distillation

of the residue at 0.25 mm. pressure gave 11.3 g. of low-boiling products and 13.8 g. (49.1%) of pentadecyne, b. p. 88°/0.25 mm. A sample was refractionated; colorless liquid, b. p. 88°/0.25 mm.,  $n_D^{22}$  1.4545. Ahmad<sup>1</sup> recorded b. p. 99°/0.7 mm.,  $n_D^{20}$  1.4440.

### 2-Hexadecynoic Acid (III)

Pentadecyne (13.8 g.) in dry ether (70 ml.) was added during 45 minutes to a stirred solution of methylmagnesium iodide (from magnesium, 1.66 g.) in dry ether (100 ml.). The mixture was heated under reflux for 17 hours, and then cooled in an ice-salt mixture. A stream of dry carbon dioxide was led over the stirred solution for two hours. The resulting complex was decomposed with ice and hydrochloric acid, and the ethereal layer washed with water and dried. After evaporating the solvent, the oily residue (13.6 g.) was dissolved in acetone (20 ml.). After addition of 5 N methanolic potassium hydroxide (12 ml.) the white potassium salt precipitated. It was filtered, washed with acetone and dried (yield 2.8 g.). The salt was decomposed with diluted hydrochloric acid, and the product dissolved by extraction with ether. The ether solution was dried, and evaporated to dryness. Thus, 2.2 g. (13.2%) of pure 2-hexadecynoic acid, m. p. 54–55° were obtained. The melting point remained unchanged after recrystallization from petroleum ether. Colorless prismatic leaflets.

- Anal. 8.965 mg. subst.: 24.96 mg. CO<sub>2</sub>, 9.11 mg. H<sub>2</sub>O  
 C<sub>16</sub>H<sub>28</sub>O<sub>2</sub> (252.4) calc'd.: C 76.14; H 11.18%  
 found: C 75.98; H 11.37%

Upon catalytic hydrogenation 2-hexadecynoic acid consumed exactly two moles of hydrogen, and pure palmitic acid was obtained (m. p. and mixed m. p. 61–63°).

*Acknowledgment.* We are indebted to Mrs. M. Munk-Weinert for the micro-analyses.

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#### IZVOD

##### Heksadecin-2-kiselina-1

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Opisana je sinteza heksadecin-2-kiseline-1, koja polazi iz dodecil bromida, koji je preveden u Grignardov kompleks, na koji je djelovano s 2,3-dibrompropenom. Tako dobiveni 2-brom-pentadecin (I) s natrijskim amidom u ksilenu — prelazi u pentadecin (II). Djelovanjem ugljičnog dioksida na pentadecinil-magnezijum-jodid dobivena je heksadecin-2-kiselina-1 u obliku bezbojnih prizmatičkih listića, t. t. 54–55°.

MEDICINSKI FAKULTET  
 ZAVOD ZA FIZIOLOGIJU  
 ZAGREB

Primljeno 11. novembra 1955.