Synthesis of 6-Heptenoic Acid

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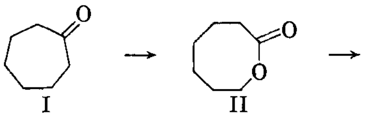
A convenient method for the synthesis of 6-heptenoic acid by means of the pyrolysis of ω-heptano lactone (II) is reported. The lactone was prepared by Baeyer-Villiger oxidation of cycloheptanone (I).

IN A SEARCH for a convenient synthesis of 6-heptenoic acid (III) and higher homologs of this ω-unsaturated acid, a study of the pyrolysis of ω-heptano lactone (II) was undertaken. The lactone (II) was prepared by the oxidation of cycloheptanone (I) under Baeyer-Villiger conditions (1, 2). The pyrolysis of II was effected by dropping the substance under a nitrogen atmosphere into a heated column packed with glass beads.

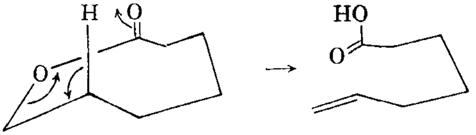


I II

$CH_2{=}CH(CH_2)_4COOH$

III

A mechanism for this pyrolytic elimination consistent with that reported for acyclic systems (3) is



EXPERIMENTAL[1]

ω-Heptano Lactone (II).—One-hundred and two milliliters (0.72 mole) of trifluoroacetic anhydride was added over the course of 30 minutes from a cooled dropping funnel to a stirred suspension, cooled in ice, of 16.4 ml. (0.60 mole) 90% hydrogen peroxide in 100 ml. of dry methylene chloride. Stirring was continued for an additional 30 minutes. The resulting peroxytrifluoracetic acid solution was added over a 1-hour period from a cooled dropping funnel to a vigorously stirred suspension of 160 Gm. of anhydrous disodium hydrogen phosphate in 400 ml. of dry methylene chloride containing 44.8 Gm. (0.40 mole) of cycloheptanone (I). The reaction mixture was cooled to 0° during the addition, stirred for an additional 3 hours at 0°, then at room temperature for 3 hours.

The reaction mixture was filtered, and the insoluble salts were dissolved in 100 ml. of water and extracted with 50-ml. portions of methylene chloride six times. The methylene chloride solutions were combined and washed twice with 100-ml. portions of saturated sodium carbonate solution. After removing the methylene chloride *in vacuo,* the resulting oil, when distilled, gave 36.95 Gm. (72.3%) of a clear colorless liquid, b.p. 52–58°/.5 mm. [lit. (2) 68°/2 mm.]; the hydrazide, m.p. 123–124° [lit. (2) 123–124°].

Vapor phase chromatography indicated only one compound to be present n_D^{25} 1.4660 [lit. (2) n_D^{25} 1.4670]; I.R. ($CHCl_3$) 5.85 μ (C=O).

6-Heptenoic Acid (III).[2]—In a dropping funnel attached to the top of the pyrolysis column was placed 5.76 Gm. (0.044 mole) of the lactone II which was then dropped at a rate of 20 to 30 drops per minute on the column of glass beads heated at 500°. The nitrogen flow rate through the column was maintained at 4.5 ml. per minute. The pyrolysis product was collected at the bottom of the column in a trap cooled by a mixture of solid carbon dioxide and acetone. After cooling, the column was washed with ether. The ether washings were combined with the trapped pyrolysis material, and this solution was extracted four times with 10% sodium hydroxide and the washings combined and acidified with hydrochloric acid. Ether extraction of the aqueous solution gave a slightly yellow solution which was dried over anhydrous magnesium sulfate and concentrated to give an oily residue. On distillation, this residue gave 2.89 Gm. (50%) of a clear faintly yellow oil, b.p. 100–103°/5 mm.; n_D^{15} 1.4404; *p*-toluidide, m.p. 59.5° [lit. (4) b.p. 225–227°/760 mm.; $n_D^{14.9}$ 1.4404; *p*-toluidide, m.p. 59.6°]. I.R.($CHCl_3$) 5.85 (–COOH), 6.10 (C=C), 10.05 and 10.9 μ (–CH=CH$_2$).

Oxidative ozonolysis of the acid gave adipic acid, m.p. 152–153° [lit. (5) m.p. 149–150° (153°)]. The phenylhydrazine salt of 6-heptenoic acid (III) was prepared.

Anal.—Calcd. for $C_{13}H_{20}N_2O_2$: C, 66.16; H, 8.54; N, 11.87. Found: C, 65.91; H, 8.50; N, 11.57.

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[1] Melting points were obtained on a calibrated Thomas-Hoover Unimelt and are corrected. Infrared data were recorded on a Beckman IR-5 spectrophotometer, and microanalyses were conducted by Huffmann Microanalytical Laboratories, Wheatridge, Colo.

[2] Pyrolyses were performed in a 12-in. (24-mm. o.d., 21-mm. i.d.) column packed with carbon-coated 4-mm. glass beads. The column was heated with a Hoskins electric furnace, and temperatures were controlled by a Barber-Colman model 407 P Capacitrol, model 601 A amplifier, and a power saturable core reactor.