Identification of (IV). The salt remaining from the hot 70% alcohol extraction was allowed to stand with 2 l. of 70% alcohol at room temperature for two and one-half days. The filtrate was combined with the filtrate from the previous step. On evaporation to dryness 58.6 g. of disodium γ-(*p*-sulfophenyl) butyrate, probably contaminated with a little sodium sulfate, was obtained. It was identified as its *p*-chlorobenzylthiuronium derivative, m.p. 150–152°.

Anal. Calcd. for $C_{18}H_{21}ClN_2O_5S_2$: C, 48.59; H, 4.76; N, 6.30; S, 14.41. Found: C, 49.18; H, 4.57; N, 6.44; S, 14.25.

A 4 g. sample of disodium γ-(*p*-sulfophenyl)butyrate was oxidized with potassium permanganate according to the procedure of Campaigne and Suter.[11] The benzylthiuronium derivative of the resulting *p*-sulfobenzoic acid, m.p. 213–214° (lit. 212–214°),[6] established the position of ring substitution.

Anal. Calcd. for $C_{15}H_{16}N_2O_5S_2$: N, 7.61. Found: N, 7.78.

Continued extractions of the residual salts with 40% alcohol yielded only sodium sulfate.

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6-Amino-2-Hexenoic Acid Lactam[1]

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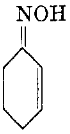
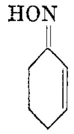
Although work has been reported concerning the Beckmann rearrangement of various substituted cyclohexenone oximes,[3,4] the rearrangement of 2-cyclohexenone oxime itself has not been reported. This rearrangement has been studied as a route to 6-amino-2-hexenoic acid lactam (III) which was of interest in connection with a projected synthesis of azepine.

2-Cyclohexenone[5] was converted to a mixture of stereoisomeric oximes by the method of Bartlett and Woods.[6] This mixture was separated into the corresponding *syn* (I) and *anti* (II) oximes melting at 97–98° and 87–88°, respectively. These melting points are in substantial agreement with those reported by Montgomery and Dougherty.[3]

A modification of the method of Horning, Stromberg, and Lloyd[4] was used in studying the Beckmann rearrangement. It was not possible to convert the *anti* oxime (II) to any isolable amount of 6-amino-5-hexenoic acid lactam (IV). The *syn* oxime (I), however, yielded 6-amino-2-hexenoic acid lactam (III) which was characterized by analysis, infrared and ultraviolet spectra, and catalytic hydrogenation to ε-caprolactam. The ultraviolet spectrum shows a shoulder in the range 235–245 mμ, ε (average) 2400, corresponding in position to the maxima reported by Montgomery and Dougherty for the lactams of 3,5,5-trimethyl- and 3-methyl-5-phenyl-6-amino-2-hexenoic acid and in position and intensity to those reported by Edwards and Singh[7] for 6-methyl and 1,6-dimethyl-5,6-dihydro-2-pyridone. These results, coupled with the known stereochemisty of the Beckmann rearrangement, confirm the assignment of the *syn* conformation to the high melting oxime.


I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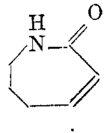
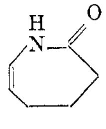

III


IV

EXPERIMENTAL

One hundred twenty grams of polyphosphoric acid (prepared by dissolving 65.0 g. of phosphorus pentoxide in 55 ml. of 85% phosphoric acid) was heated to 135°, the heat removed and 4.0 g. of *syn*-2-cyclohexenone oxime added with stirring. The temperature rose to 148° and after 10 min. stirring the reaction mixture was poured into 1500 ml. of an ice and water mixture. The mixture was made alkaline at 0° and adjusted to *p*H 12 by the slow addition of cold 15% sodium hydroxide. The solution was extracted exhaustively with chloroform. The extract was dried with sodium sulfate and concentrated to yield 2.3 g. of a dark brown oil. The crude product was subjected to steam distillation and the residue in the boiler decanted from a small amount of polymeric material and extracted with chloroform. The extract was dried with sodium sulfate, treated with decolorizing carbon, filtered, and concentrated to yield 1.9 g. of a light yellow oil. Distillation of this oil yielded 1.0 g. (25%) of colorless product, b.p. 60–65° at 0.5 mm; n_D^{25} 1.5238; d^{25} 1.092. The infrared spectrum shows peaks at 2.96, 6.02, and 6.20 μ. The ultraviolet spectrum shows a shoulder at 235–245 mμ and ε (average) 2400.

Anal. Calcd. for C_6H_9ON: C, 64.84; H, 8.16; N, 12.6. Found: C, 64.66; H, 8.38; N, 12.4.

Catalytic hydrogenation of the lactam at room temperature using 5% palladium-charcoal yielded ε-caprolactam as determined by infrared spectrum comparison and mixed melting point.

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Catalytic Reduction of 2-Acylthiophenes

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The removal of sulfur from the thiophene nucleus attached to aromatic compounds has been reported to proceed satisfactorily when the parent substance