In the above sulfonation, a maximum yield of 800 mg. of (IV) and a very small amount of (III) were obtained by heating 2 g. of (I) with 10 moles of chlorosulfonic acid at 100°.

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Sulfonation of Ethyl γ-Phenylbutyrate with Sulfuric Acid

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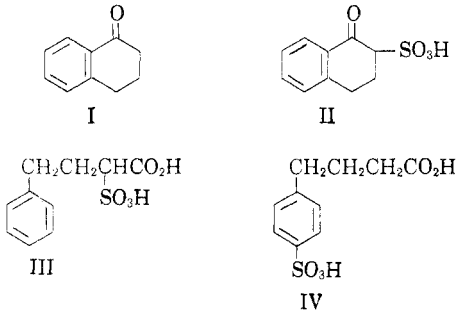
Received October 8, 1956

The direct sulfonation of phenylacetic acid with concentrated sulfuric acid,[1] chlorosulfonic acid,[2] and sulfur trioxide,[3] and of β-phenylpropionic acid with fuming sulfuric acid[4] all gave the corresponding ring substituted sulfophenylalkanoic acids.

Sulfonation of γ-phenylbutyric acid however failed to yield γ-(*p*-sulfophenyl)butyric acid (IV).[5,6] Instead, 50% yield of α-tetralone (I) was obtained when the sulfonation reagent was concentrated sulfuric acid,[5] and α-tetralonesulfonic acid (II) (78%) and γ-phenyl-α-sulfobutyric acid (III) (13%) were obtained when dioxane sulfur trioxide was the sulfonation agent.[6]



The present work shows that the action of excess 99% sulfuric acid on ethyl γ-phenylbutyrate at 60–65° gave predominately the ring substituted product, γ-(*p*-sulfophenyl)butyric acid (IV) isolated as its sodium salt. Small amounts of α-tetralone and acetaldehyde-sodium bisulfite adduct were the only by-products isolated.

Since addition of a solution of a simple ester (methyl benzoate) in 100% sulfuric acid to ice water did not result in hydrolysis,[7] it seems likely that the hydrolysis of the present ester took place during sulfonation, although the acid strength in the present case was only 99%. Formation of acetaldehyde can best be explained by oxidation of ethanol which became detached from the ester during sulfonation. Apparently, sulfonation of the benzene ring preceded the hydrolysis, otherwise excessive tetralone formation would ensue as in the case of γ-phenylbutyric acid. The implication is that under the experimental conditions used, ring sulfonation prevented the cyclization of γ-phenylbutyric acid.

(1) Hausman, German Patent **289,028**.
(2) Stewart, *J. Chem. Soc.*, **121**, 2555 (1922).
(3) Brust, *Rec. trav. chim.*, **47**, 153 (1928).
(4) Senderens and Aboulenc, *Compt. rend.* **186**, 1497 (1928).
(5) Krollpfeiffer and Schaefer, *Ber.*, **56**, 624 (1923).
(6) Truce and Olson, *J. Am. Chem. Soc.*, **75**, 1651 (1953).
(7) Treffers and Hammett, *J. Am. Chem. Soc.*, **59**, 1711 (1937).

EXPERIMENTAL[8]

Ethyl γ-phenylbutyrate. Ethyl γ-phenylbutyrate was prepared from 100 g. (0.58 mole) of γ-phenylbutyric acid[9] and absolute ethanol using the method of Hershberg and Fieser.[10] A standard work-up and distillation produced 94.5 g. (84.5%) of ethyl γ-phenylbutyrate, b.p. 80° (0.5 mm.), n_D^{20} 1.4919.

Sulfonation of ethyl γ-phenylbutyrate. To 45 g. (0.234 mole) of ethyl γ-phenylbutyrate, 236 g. of 99% sulfuric acid was slowly added with stirring. With constant agitation the mixture was heated to and maintained at 60–65° for 4 hr. The mixture was cooled to 33° and 100 ml. of water was added slowly, maintaining the temperature at below 50°. The mixture was then poured into 300 g. of ice and stirred for 1 hr. The resulting turbid mixture was extracted 4 times with 50 ml. portions of benzene, and the extracts were combined.

Identification of α-tetralone (I). The benzene extract was washed 3 times with 25 ml. portions of water and then concentrated to 14 g. by evaporation on a steam bath. The benzene concentrate was refluxed with 100 ml. of 10% sodium hydroxide for 16 hr. Acidification of the aqueous phase gave no precipitation indicating the absence of γ-phenylbutyric acid. The oil phase was dried over anhydrous sodium sulfate and distilled under diminished pressure to yield 5.3 g. (15%) of a colorless oil, b.p. 125–129° (11 mm). I was identified as its semicarbazone, m.p. 216.5–217.5°. A mixed melting point with an authentic sample of the semicarbazone of I, m.p. 217°, showed no depression.

Identification of the acetaldehyde-sodium bisulfite adduct. The mother aqueous acid solution was carefully neutralized with a 50% sodium hydroxide solution, and then evaporated to dryness yielding 353 g. of salt. The salt mixture was stirred with 2.4 l. of boiling 70% alcohol and filtered while hot. On cooling the filtrate gave 5.3 g. of a white crystalline salt which was identified as its *p*-chlorobenzylthiuronium derivative,[11] m.p. 218–219° (dec.). A mixture with the *p*-chlorobenzylthiuronium derivative of an authentic sample of acetaldehyde-sodium bisulfite adduct, m.p. 220–221° (dec.) melted at 218–219° (dec.).

Anal. Calcd. for $C_{18}H_{24}Cl_2N_4O_4S_3$:[12] C, 40.98; H, 4.59; N, 10.62; S, 18.23. Found: C, 40.20; H, 4.65; N, 10.45; S, 17.74.

(8) All melting points and boiling points are uncorrected. Elementary analyses were made by Mr. C. W. Nash and his staff, Rohm and Haas Co.
(9) Christian, *J. Am. Chem. Soc.*, **74**, 1591 (1952).
(10) Hershberg and Fieser, *Org. Syntheses*, **Coll. Vol. II**, 196 (1950).
(11) Campaigne and Suter, *J. Am. Chem. Soc.*, **64**, 3040 (1942).
(12) The requirement of two moles of p-chlorobenzylthiuronium chloride for each mole of the acetaldehyde-sodium bisulfite adduct is interesting, but not unanticipated. This means that the hydroxyl group alpha to the sulfonic acid group in the adduct is weakly acidic. The dissociation constant for a similar group in benzaldehyde-sodium bisulfite adduct is 7×10^{-10} (Bayer, Ger. Pat. **464,010** (July 26, 1928).

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 $C_{15}H_{21}ClN_2O_5S_2$: 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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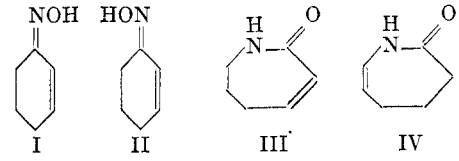
Received November 26, 1956

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 II 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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(3) R. S. Montgomery and Gregg Dougherty, *J. Org. Chem.*, **17**, 823 (1952).

(4) E. C. Horning, V. L. Stromberg, and H. A. Lloyd, *J. Am. Chem. Soc.*, **74**, 5153 (1952).

(5) F. C. Whitmore and G. W. Pedlow, Jr., *J. Am. Chem. Soc.* **63**, 758 (1941).

(6) P. D. Bartlett and G. F. Woods, *J. Am. Chem. Soc.* **62**, 2933 (1940).

(7) O. E. Edwards and Tara Singh, *Can. J. Chem.*, **32**, 683 (1954).

Catalytic Reduction of 2-Acylthiophenes

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Received December 26, 1956

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