JOURNAL OF THE TENNESSEE ACADEMY OF SCIENCE
Volume 28, Number 3, July, 1953

PREPARATION OF A NEW *ALPHA*-AMINOSULFONIC ACID[1]

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The synthesis of *alpha*-amino-*beta*-benzylmercaptoethanesulfonic acid recently became of interest to the authors in connection with certain projected work. This synthesis proceeded along the standard lines shown by the equations. It is considered worthy of record since few *alpha*-aminoalkanesulfonic acids are known.

$$C_6H_5CH_2SNa + ClCH_2CH(OCH_3)_2 \longrightarrow C_6H_5CH_2SCH_2CH(OCH_3)_2$$

$$\downarrow H_2SO_4$$

$$C_6H_5CH_2SCH_2CHO \xrightarrow{NaHSO_3} C_6H_5CH_2SCH_2CH(OH)SO_3Na$$

$$\downarrow NH_4OH$$

$$C_6H_5CH_2SCH_2CH(NH_2)SO_3Na \xrightarrow{HCl} C_6H_5CH_2SCH_2CH(NH_2)SO_3H$$

The pure dry *alpha*-aminosulfonic acid seems to be reasonably stable for a period of several months but decomposes rather easily in boiling water. It is of interest that attempted acetylations of the amino nitrogen using either acetic anhydride or isopropenyl acetate were unpromising; no pure N-acetyl derivative could be isolated.

EXPERIMENTAL

Benzylmercaptoacetaldehyde dimethyl acetal was prepared by essentially the procedure of Gawron and Glaid (1949) from dimethyl chloroacetal (kindly provided by General Aniline and Film Corporation, New York, New York); yield 78%, b. p. 109°-118° (1-3 mm.), $n^{25}D$ 1.5283-1.5319. An intermediate fraction had $n^{25}D$ 1.5290, d^{25}_4 1.0758; MD 60.87 (calcd., 60.48).

Conversion to benzylmercaptoacetaldehyde was effected (cf. Gawron and Glaid, 1949) by heating 425 g. of the acetal with 425 ml. of methanol and 850 ml of 3N sulfuric acid under reflux for 4.5 hrs. Neutralization and ether extraction followed by distillation gave 305 g. (92%) of the aldehyde, b. p. 119°-129° (7-9 mm.), $m^{25}D$ 1.5591-1.5618; 2, 4-dinitrophenylhydrazone (85% yield) constant m. p. 154.5-155.5° (Gawron and Glaid, 1949, reported 155-156°) after recrystallization.

For conversion of the aldehyde to the bisulfite addition product, 80 g. of sodium bisulfite was dissolved in sufficient water to make 200 ml. of solution, 50 ml. of ethanol was added and a small amount of solid which precipitated was removed by filtration. Benzylmercaptoacetaldehyde (66.4 g.) was then added during ten minutes with stirring and the mixture was allowed to stand

[1]Work supported in part by a Frederick Gardner Cottrell Grant from the Research Corporation. Melting points are corrected and boiling points uncorrected. Analyses by Clark Microanalytical Laboratory (C, H), Urbana, Ill., and Dorothy Hagen (N), Veterans Administration Hospital.

for 15 minutes. Solid which separated on subsequent brief chilling was removed by filtration, washed with cold ether, and dried under reduced pressure over alumina; yield 48.2 g. (44%).

The sulfonic acid was prepared by a procedure based on one of Shriner and Land (1941). Concentrated ammonium hydroxide (26 ml.) and 70.4 g. of the bisulfite addition product were heated in 400 ml. of water at 55-64° for 35 minutes, after which supernatant liquid was decanted from gum and filtered. *Alpha*-Amino-beta-benzylmercaptoethanesulfonic acid was obtained by acidification of the filtrate with 30 ml. of concentrated hydrochloric acid. After separation by filtration and drying under reduced pressure over alumina, the yield of light tan powder was 22.1 g. (34%), m.p. 120-123° (dec.). The acid (2 g.) was purified by washing by centrifugation with one 10-ml. portion of water, one of ethanol, and four of ether; yield of white powdery acid after drying, 1.4 g., m.p. 121-124° dec.

Anal. Calcd. for $C_9H_{13}NO_3S_2$: C, 43.70; H, 5.29; N, 5.66; S, 25.92. Found: C, 43.68; H, 5.13; N, 5.37; S, 25.56.

Literature Cited

Gawron, O., and A. J. Glaid, III. 1949. A synthesis of S-Benzyl-dl-cysteine. *Jour. Amer. Chem. Soc.*, 71:3232-3233.

Shriner, R. L., and A. H. Land. 1941. The structure of the bisulfite compound of acetaldehyde. *Jour. Organic Chem.*, 6:888-894.

THE GRAPEFERNS IN TENNESSEE

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CUTLEAF GRAPEFERN

Botrychium dissectum Spreng. var. **typicum** Clausen

The common name, Grapefern, and the technical name of the genus, *Botrychium* (from the Greek, *Botrys*—a cluster of grapes), call attention to one characteristic of the group as seen in Tennessee, namely, the globular sporangia in a spike on a fertile branch separate from the sterile branch of the leaf with both branches joining to form a very short common stalk. The fertile spike resembles greatly