[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE VISKING CORPORATION]

THE CHEMISTRY OF ALIPHATIC NITROSULFONATES. II. β-AMINO SULFONIC ACIDS

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The paper of Heath and Piggott (1) disclosed the catalytic reduction of aliphatic nitrosulfonates to amino sulfonic acids and in general agrees with the results obtained in these laboratories. However the present work also describes two additional reductive methods for the preparation of β-amino sulfonic acids (2).

Of the three methods that were tried, catalytic reduction with Raney nickel catalyst gives by far the best yields. The next most useful method is an electrolytic reduction with lead electrodes. This method gives only about a 45–55% yield but it is very simple to operate. The third method using a neutral iron reduction gives 80–90% yields on 5- to 50-gram quantities. However when larger amounts are used the yields are very poor.

The ammonium salt is generally the most useful in these reactions. At the end of the reduction the product is then an ammonium salt of the β-amino sulfonic acid. The ammonia is then readily removed merely by evaporation of an aqueous solution of the reduction product. Thus it becomes unnecessary to fractionally crystallize the amino sulfonic acid from other salts formed as a result of neutralization of the cation.

EXPERIMENTAL

A. CATALYTIC REDUCTIONS

The reductions were run in a Parr Instrument Co. hydrogenation apparatus at pressures of 500–1500 p.s.i. The salt of the β-nitrosulfonic acid was dissolved in about four or five times as much water and reduced with Raney nickel. The catalyst prepared by the method of Mozingo (3) caused the reduction to proceed at temperatures of 75–90°. However, using the specially activated catalyst of Pavlic and Adkins (4) the reaction occurred very readily at 30° with less decomposition due to hydrolysis. The yields at the lower temperature were 90% or better, whereas those run at the higher temperature were in the neighborhood of 85–90%.

Table I lists a number of the β-amino sulfonic acids prepared by one or more of the described procedures.

B. ELECTROLYTIC REDUCTION

2-Aminobutane-1-sulfonic acid. In each of six 1-liter beakers was placed 50 g. of ammonium 2-nitrobutane-1-sulfonate in 500 ml. of water. Then within each beaker was placed a porous porcelain cup 12.5-cm. high and 5-cm. in diameter containing a solution of 15% sulfuric acid as the anolyte. Lead sheets were used for both electrodes. A convenient size was found to be about 20 cm. by 13 cm. using sheet 2 mm. thick.

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The six cells were connected in series with a source of direct current. Then the solutions were electrolyzed with an average current of 6.3 amperes at 13 volts for fifteen hours. The reaction temperature was maintained at 50–65° by cooling with a water-bath. At the end of the reaction period the six catholyte solutions were combined and evaporated to a concentrated solution. Upon cooling there was deposited 131.7 g. (57.5%) of white crystals. One recrystallization from water resulted in a product, m.p. 298–301° (d).

C. IRON REDUCTION

2-Aminobutane-1-sulfonic acid. In a 3-necked flask equipped with a reflux condenser, dropping-funnel, and stirrer were placed 35 g. of iron powder and 75 ml. of water. The stirrer was set in motion and 1 ml. of concentrated hydrochloric acid was added. After stirring a few minutes 50 g. of ammonium 2-nitrobutane-1-sulfonate was added, followed by 75 ml. of water. The mixture was gradually heated to reflux. During this period the solution turned green and then orange-brown. At this point ferric hydroxide began precipitating on the walls of the flask, indicating that the solution was becoming alkaline. When the mixture finally began to reflux, a solution of 16 ml. of concentrated hydrochloric acid in 20 ml. of water was added dropwise over a period of 20 minutes. After stirring and refluxing for an hour the reaction was stopped and the mixture filtered while hot. The black iron oxides were washed with warm water and the washings combined with the clear filtrate. To this solution was then added about 1 ml. of 15% hydrogen peroxide to oxidize any ferrous ions remaining in solution. The solution was then heated to boiling and filtered again to remove a small amount of coagulated ferric hydroxide. Then it was evaporated to about 60 ml. The sides of the flask were scratched and the product allowed to crystallize in the refrigerator. The crystalline product was separated and washed with alcohol to give 20.7 g. of white crystals, m.p. 303–306° *dec.* The filtrate was worked up by further concentration and dilution with alcohol. A second crop of equally pure material was recovered weighing 10.4 g.; total yield, 31.1 g. (81.5%).

Taurine (2-aminoethane-1-sulfonic acid) was prepared in the same manner as above. A mixture m.p. of this product with an authentic sample obtained from the Eastman Kodak Co. gave no lowering in m.p.

TABLE I

β-AMINO SULFONIC ACIDS

COMPOUND	M.P., °C. *dec.*[a]	ANALYSIS			
		Sulfur		Nitrogen	
		Found	Calc'd	Found	Calc'd
$NH_2CH_2CH_2SO_3H$	310	25.48	25.62	11.09	11.20
$NH_2CH(CH_3)CH_2SO_3H$	318–320[b]	23.04	23.03	10.14	10.06
$NH_2CH_2CH(CH_3)SO_3H$	283–286[c]	22.95	23.03	9.73	10.06
$NH_2CH(C_2H_5)CH_2SO_3H$	303–306	20.76	20.93	9.05	9.14
$NH_2CH_2CH(C_6H_5)SO_3H$	379[d]	16.05	15.92	7.07	6.97
$NH_2CH(C_2H_5)CH(C_3H_7)SO_3H$[e]	318	16.7	16.4	7.3	7.2

[a] All melting points are uncorrected.
[b] Gabriel and Ohle, *Ber.*, **50**, 805 (1917), report m.p. 323°.
[c] Young and Crooks, *J. Chem. Soc.*, **21**, 307 (1905), report m.p. 284–285°.
[d] Barnett, *et al.*, *J. Chem. Soc.*, 94 (1944), report m.p. 258°.
[e] Prepared from the potassium salt.

SUMMARY

Aliphatic β-amino sulfonic acids are readily prepared by the reduction of the corresponding β-nitrosulfonates. Of the three methods described catalytic reduction with Raney nickel catalyst is most practical. Electrolytic reduction gives fair yields while a neutral iron reduction appears to be useful only on small quantities.

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REFERENCES

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(4) PAVLIC AND ADKINS, *J. Am. Chem. Soc.*, **68**, 1471 (1946).