

to 95% of the theoretical yield (about 8.25 g.). It follows that the reaction between glycolic nitrile and liquid ammonia, under the conditions noted, is smooth, clean, and, allowing for unavoidable loss through indirect measure of yield, practically quantitative.

The same method, with modified technique in individual cases, was successfully applied to the preparation of other

known aminonitriles, desired for pharmacological investigation. Further study of the method and its application was interrupted by the author's change in affiliation and field of activity and has not been resumed because of lack of opportunity.

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COMMUNICATIONS TO THE EDITOR

OXIDATION OF CYSTINE WITH PERMONOSULFURIC ACID

Sir:

Sulfur oxides of cystine [Toennies and Lavine, *J. Biol. Chem.*, **100**, 463 (1933)] should be obtainable in presence of water if oxygenation is rapid compared with speed of hydrolysis of the —S—S— bond. As cystine disulfoxide [Lavine, Toennies and Wagner, *THIS JOURNAL*, **56**, 242 (1934)] proved to be relatively stable toward aqueous acids the action on cystine of a potent oxygen donor such as permonosulfuric acid (prepared from $K_2S_2O_8$ and H_2SO_4 [Gleu, *Z. anorg. allgem. Chem.*, **195**, 70 (1931)]) seemed interesting. The following is a preliminary report on this investigation. In presence of 10.7 mole equivalents of H_2SO_5 oxygen consumption stopped after two hours at 5.0 atoms, the theoretical amount for oxidation to cysteic acid, suggesting that absence of free electron pairs in the acid form ($-NH_3^+$) protects the amino group against oxygen addition. The speed of oxygen consumption with different H_2SO_5 :cystine ratios (cystine 0.025 *M*, H_2SO_4 3.5 *M*, 0°) was as follows:

	H_2SO_5 :cystine	Atoms O consumed per mol. of cystine, after min.					
		2	9	13	20	30	70
I	1.01:1	0.75	1.00	1.01			
II	2.10:1	1.2	1.7	1.9	2.0	2.10	
III	5.37:1	2.6	3.8	4.0	4.2	4.3	4.5

After oxidation I the direct cyanide-nitroprusside test indicated 15% of unchanged cystine while by a preceding reduction with iodide [Toennies and Lavine, *J. Biol. Chem.*, **105**, 119 (1934)] the test was increased to 93% of the cystine used. After oxidation II the corresponding figures were 5 and 95%. Thus the chief reaction products seem to be the monosulfoxide in oxidation I and the disulfoxide in oxidation II.

By diluting the H_2SO_5 solution (Ref. 3) with

methanol the potassium sulfate present was nearly completely precipitated and the filtrate (0.1 *M* H_2SO_5 , 0.9 *M* H_2SO_4 , 75% CH_3OH), in which H_2SO_5 is as stable as in aqueous solution, was used to oxidize cystine, dissolved as perchlorate in CH_3CN (Ref. 1), with 1 mole equivalent of H_2SO_5 . Precipitates obtained—after oxidation—by neutralization with pyridine, contained at least twice as much cystine as was indicated by direct test on the oxidized solution. Further evidence of a dismutative change of the primary oxidation product was obtained by fractionated neutralization of the precipitate, inasmuch as it resulted in further formation of cystine together with a decrease of total precipitate, and by polarimetric observation. On oxidation of cystine with 1 mole of H_2SO_5 the initial high negative rotation decreases in less than one hour to a slightly positive value, only to slowly turn negative again during two to three days, passing through a maximum of about one-third of the initial value and slowly decreasing again during the next two weeks. This last decrease presumably represents esterification (Ref. 1) by methanol of the cystine formed by dismutation during the second stage of change. Addition of ethanol and ether immediately after the first brief reaction stage yielded a white precipitate which, according to analysis and properties, consists of sulfates of cystine (10%) and its monosulfoxide (90%) and which in *N* sulfuric acid gives an initial specific rotation of about $+5^\circ$ for the total content of unoxidized and oxidized cystine. This value however, changes during the next five days to a constant negative level which would correspond to an amount of free cystine equivalent to 70% of the organic sulfur present.

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