dearrangement reactions of the substance in aqueous solutions. Guanidine and nitrous acid are formed in acidic aqueous solutions, nitrous acid having been recovered quantitatively and guanidine nitrate and picrate being isolated from the reaction solution. In neutral solution cyanamide and nitrogen are formed as Thiele[2] observed. In alkaline solutions carbon dioxide, ammonia, cyanamide and nitrogen have been detected.[4]

Measurements of velocity constants of the decomposition in acidic, neutral and basic solutions show that the reactions are all monomolecular or rather pseudo-monomolecular. The constants vary with the hydrogen-ion concentration in acid solution and with the hydroxyl-ion concentration in basic solution. The energy of activation in acidic and basic solutions is about 19,000 calories per mole and is probably somewhat higher in neutral solutions.[5]

Analytical Methods

Five methods for the determination of nitrosoguanidine are indicated from the studies of its properties and have been developed: (1) colorimetric; (2) estimation of nitrous acid formed by hydrolysis of nitrosoguanidine in a dilute solution of nitric acid; (3) titration with a standard solution of potassium permanganate; (4) weighing as silver nitrosoguanidine; (5) weighing silver chloride from the conversion of silver nitrosoguanidine. These methods have all been found to be of moderate precision and (3) which has been used in the routine establishment of the purity of nitrosoguanidine will be described in more detail.

A sample of nitrosoguanidine (approx. 0.2 g.) is dissolved in 100 ml. of 3 M sulfuric acid to which has been added about 2 g. of manganous sulfate. A standard solution of potassium permanganate (0.1 N) is added only as rapidly as the solution is decolorized and when about three-fourths of the nitrosoguanidine has been decomposed the reaction proceeds slowly. The end-point is taken when the pink color of permanganate ion persists for two minutes during which period the solution is violently agitated.

Analytical Results.—Method 2: Nitrosoguanidine taken: 0.1246, 0.1578, 0.1703, 0.1728 g. Found: 0.1250, 0.1576, 0.1708, 0.1735 g. Method 3: Nitrosoguanidine taken: 0.2000 g. (5 samples). Found: 0.2016, 0.1996, 0.2006, 0.2003, 0.1993 g. Method 4: Nitrosoguanidine taken: 0.1440, 0.2042, 0.1654 g. Found: 0.1447, 0.2046, 0.1653 g. Method 5: Nitrosoguanidine taken: 0.2332, 0.2449, 0.2830 g. Found: 0.2332, 0.2440, 0.2836 g.

Summary

A method for the preparation of nitrosoguanidine by reduction of nitroguanidine with zinc in a solution of ammonium chloride is proposed. Some of the characteristic physical and chemical properties of nitrosoguanidine are described. Five methods for the determination of nitrosoguanidine are suggested.

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[4] For suggestions regarding possible reactions see (a) Pellizzarri, *Atti accad. Lincei*, **30**, I, 171 (1921); (b) Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, **61**, 437 (1926).

[5] These observations are based upon a large number of quantitative measurements under a variety of environmental conditions; see Ref. 3 and also Schmookler, B.S. Thesis, 1932; Weaver, B.S. Thesis, 1934, Polytechnic Institute of Brooklyn.

[CONTRIBUTION NO. 28 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reduction of Nitroguanidine. IV. Preparation of Nitrosoguanidine by Catalytic Hydrogenation

BY EUGENE LIEBER AND G. B. L. SMITH

Introduction

In this extended investigation of the reduction of nitroguanidine[1] catalytic hydrogenation to nitrosoguanidine has been accomplished over both the Adams platinum[2] and the Raney nickel catalysts.[3] These reactions may be used for the preparation of nitrosoguanidine, which is obtained in excellent yield and relatively high purity.

Method

Nitroguanidine[1a] (10.4 g.) is suspended in 150 ml. of water and 0.5 g. of Adams or 5 g. of Raney nickel catalyst is added. The reduction is carried out either at four atmospheres pressure using the Burgess–Parr apparatus[2] (p. 452) or at one atmosphere, in which case the hydrogen is introduced from a 100-ml. buret and the Burgess–Parr shaking equipment is employed. The reaction is discontinued when slightly more than one mole of hydrogen (2300 ml.) has been adsorbed. The contents of the reduction bottle are transferred to an Erlenmeyer flask and decolorizing charcoal is added. The solution is diluted to 700–800 ml., heated to 65° and then rapidly filtered. The filtrate is again treated

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[1] See (a) *Ind. Eng. Chem.*, **23**, 1124 (1931); (b) THIS JOURNAL, **54**, 1034 (1932); (c) **57**, 2478 (1935).

[2] Gilman, "Organic Synthesis," Coll. Vol. I, John Wiley and Sons, Inc., New York City, 1st ed., 1932, p. 53.

[3] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

with decolorizing charcoal at 65° and refiltered. The filtrate is cooled to 5°, the nitrosoguanidine is separated on a Büchner funnel and dried *in vacuo*. The yield varies from 36 to 62% (3.2–5.5 g.). Typical preparations are summarized in Table I.

TABLE I

TYPICAL DATA REGARDING THE CATALYTIC HYDROGENATION OF NITROGUANIDINE[1c]

H_2 press. atm.	Time of redn.	Rate ml. H_2/min.	Nitroso-guanidine yield, %	Purity of nitroso-guanidine, %
Adams Platinum Oxide Catalyst				
1	108	20.6	55.7	93.5
1	109	20.6	59.2	94.3
4	45	45.2	58.5	98.3
Raney Nickel Catalyst				
1	139	16.6	43.4	96.3
1	137	16.8	39.8	99.5
4	110	18.5	44.3	100.3
4	99	20.5	36.6	100.0

Discussion

Water, methanol, ethanol, dioxane and benzene were used as reaction media and water was found to be the most suitable for the Adams catalyst and satisfactory for the Raney catalyst. Methanol gave somewhat higher adsorption rates with Raney nickel (23 ml. of hydrogen per minute) and yields of 45% were obtained consistently. Higher pressures gave increased adsorption rates for the Adams catalyst but were without much effect for the Raney catalyst. The yields of nitrosoguanidine were not affected markedly. The optimum temperature is 25–35° and a decrease or increase of 10° resulted in a lowering of the rate of hydrogen adsorption of 40–70%. The yields of nitrosoguanidine were not affected with the Adams catalyst but with the Raney nickel the yields were materially decreased.

With the Raney nickel catalyst it was found that the optimum ratio of catalyst mass to nitroguanidine was 0.5 g. of catalyst per gram of nitroguanidine. A smaller ratio decreases the rate of adsorption of hydrogen while a ratio of 1 gives a maximum rate but at the same time the yields of nitrosoguanidine are very greatly lowered.

A more comprehensive study of the catalytic hydrogenation of nitroguanidine, now in progress, will include the further reduction to aminoguanidine, the effect of other catalysts and the reduction of nitroaminoguanidine, alkylnitroguanidines and nitrourea.

Summary

Nitroguanidine can be reduced by catalytic hydrogenation using either the Adams platinum oxide catalyst or the Raney nickel catalyst to give a satisfactory yield of nitrosoguanidine.

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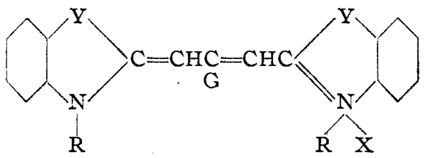
[COMMUNICATION NO. 562 FROM THE KODAK RESEARCH LABORATORIES]

Studies in the Cyanine Dye Series. II. Carbocyanines with Substituents in the Three-Carbon Chain

BY L. G. S. BROOKER AND FRANK L. WHITE

Ethyl orthoformate was employed for the preparation of dyes of the thiacarbocyanine series by König and Meier[1] and by Hamer.[2] The latter, using ethyl orthoacetate, prepared thiacarbocyanines containing an 8-methyl group.[3]

It is now found that ortho esters of higher aliphatic, of substituted aliphatic and of aromatic acids may be employed for the preparation of new thiacarbocyanines (I, Y = S) where G represents a higher alkyl, a substituted alkyl or an aryl group, according to the ortho ester used.[4]



I

Ortho esters of propionic, *n*-butyric, *n*-valeric, *n*- and isocaproic, phenylacetic, phenoxyacetic and benzoic acids have been made and used in the course of this work, and of these the majority are new. The general method used in the preparation of these ortho esters consists in allowing an alcohol to act upon an imino-ester hydrochloride (preferable to "imino-ether hydrochloride"), prepared in turn from a nitrile. This

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[1] König and Meier, *J. prakt. Chem.*, **109**, 324 (1925).

[2] Hamer, *J. Chem. Soc.*, 2796 (1927).

[3] Hamer, *ibid.*, 3160 (1928).

[4] Brooker, U. S. Patents 1,934,657, 1,934,658, 1,934,659, Kodak Ltd., British Patent 394,692.