

tion by aqueous sodium hydroxide and although very slightly soluble in methyl alcohol it dissolves freely in methyl alcoholic sodium hydroxide. The crude product contained no material that was not extracted from ether by aqueous sodium hydroxide; it therefore contained neither ethers nor dimethyl derivatives.

### Summary

This paper contains an account of the results obtained in a study of the acylation and alkylation of a series of  $\beta$ -diketones and  $\beta$ -sulfonyl ketones.

CAMBRIDGE, MASS.

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[CONTRIBUTION NO. 32 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

## Reduction of Nitroguanidine. VII. Preparation of Aminoguanidine by Catalytic Hydrogenation

BY EUGENE LIEBER AND G. B. L. SMITH

The catalytic hydrogenation of nitroguanidine to nitrosoguanidine with nickel and platinum catalysts in neutral media has been reported.<sup>1</sup> The further reduction to aminoguanidine has not been studied extensively.<sup>2</sup> Recently McGill<sup>3</sup> has suggested the manufacture of aminoguanidine by catalytic hydrogenation with a catalyst of nickel dispersed on kieselguhr (all of the ordinary hydrogenating catalysts are also claimed) at temperatures between 25 and 125° (the preferred temperature is 80°) in the absence of any substantial amounts of acid. However, it has been found that the optimum conversion to aminoguanidine is obtained in media of relatively high acid concentration. McGill,<sup>3</sup> in the examples cited in the patent, gives no yields but claims that for nickel catalyst the use of elevated pressure is essential for increased yields. We have found that the yields for a nickel catalyst are conditioned not solely by pressure but by the type of solvent used.

The molar ratio of hydrogen to hydrogen acceptor obtained in the catalytic hydrogenation of nitroguanidine depends upon the environmental conditions of the solvent. For the first molar proportion of hydrogen the reduction proceeds as follows.

Media	Principal product	Ratio, H <sub>2</sub> : Acceptor
Neutral	Nitrosoguanidine	1:1
Basic	Nitrosoguanidine	1:1
Acid	Aminoguanidine	3:1

In acid media of such a concentration that the molar ratio of nitroguanidine to acid is one or higher the reduction proceeds without the forma-

(1) Lieber and Smith, *THIS JOURNAL*, **57**, 2479 (1935).

(2) Audrieth and Schmidt, University of Illinois, private communication, used Raney nickel in ethyl alcohol and identified the aminoguanidine through the melting point of the benzalazine obtained by hydrolysis of the reduction mixture.

(3) McGill, U. S. Patent 2,033,203, March 10, 1936.

tion of nitrosoguanidine. This is a new observation and is of significant importance for the preparation of aminoguanidine by catalytic hydrogenation. If the molar ratio of acid to nitroguanidine be below one then the distribution of reduction products depends upon the acid concentration. At ratios of acid above one, the hydrazino formation was found to be linear with hydrogen absorption.

Raney nickel catalyst can be used in both neutral and alkaline media. The Adams platinum oxide catalyst can be used in neutral and acid media but is completely poisoned in alkaline media of even low concentrations. The reduction in neutral aqueous media at atmospheric pressure and room temperature gives low yields of aminoguanidine, the principal products appearing to be ammonia and guanidine. At higher hydrogen pressures superior yields of aminoguanidine are obtained with platinum oxide in 15% aqueous acetic acid as compared with Raney nickel in neutral solvents. With increasing temperatures to 125° the yields of aminoguanidine with Raney nickel fall off more rapidly than with platinum oxide as shown by Fig. 1. This also illustrates the effect of type of solvent, especially at 75°.<sup>3</sup>

### Experimental

**Method.**—The Adams platinum oxide and Raney nickel catalysts were prepared in the usual manner. The apparatus employed has been described previously,<sup>1</sup> while the high pressure equipment was of the Adkins type.

The experimental technique and procedures devised for the recovery of the aminoguanidine with minimum loss will be made clear by the description of typical reductions obtained with platinum and nickel catalysts.

**Reduction in Acid Media with Platinum Oxide Catalyst.**—20.8 g. of nitroguanidine and 1 g. of platinum oxide are suspended in 125 ml. of 15% aqueous acetic acid. The reduction is carried out at 125 atm. and room temperature

and is allowed to continue until no further hydrogen is absorbed. Slightly more than 3 molar quantities of hydrogen is usually taken up. A small amount of Norit is added and the solution filtered from catalyst into a 500-ml. volumetric flask. After washing the filter paper the volume is adjusted and a 2-ml. portion is titrated with 0.1 *N* potassium iodate solution.<sup>4</sup> From the titer required the titration yield of aminoguanidine was found to be 81.8%. From these data the amount of sulfuric acid required for the formation of aminoguanidinium sulfate is calculated (the addition of too large an excess of sulfuric acid causes the formation of the less easily crystallizable primary salt) and is added after concentrating the solution of the acetate under 10 mm. pressure on a water-bath maintained at 50–60°. The sulfate should be reconcentrated until crystallization of the salt takes place in the warm solution. An equal volume of ethyl alcohol is added and after cooling the white crystals are filtered on a Büchner funnel, pressed dry and washed with a small amount of cold absolute alcohol, dried in a vacuum desiccator and then at 100° for three hours to remove the water of crystallization; yield 16.8 g. or 68.3%; m. p. (Dennis bar) 206°. *Anal.* Calcd. for  $(\text{CH}_6\text{N}_4)_2\text{H}_2\text{SO}_4$ :  $\text{H}_2\text{SO}_4$ , 39.84;  $\text{N}_2\text{H}_4$ , 26.02. Found:  $\text{H}_2\text{SO}_4$ , 39.77;  $\text{N}_2\text{H}_4$ , 26.11, 26.07. *Benzal-aminoguanidine.*— $\text{C}_6\text{H}_5\text{CH}=\text{NNHC}(\text{NH})\text{NH}_2$ ; m. p., found, 177–78°, reported 178°.<sup>5</sup> *Anal.* Calcd. for  $\text{C}_8\text{H}_{10}\text{N}_4$ : C, 59.26; H, 6.17;  $\text{N}_2\text{H}_4$ , 19.75. Found: C, 59.60; H, 6.79;  $\text{N}_2\text{H}_4$ , 20.16, 20.02.

**Reduction in Absolute Methyl Alcohol with Raney Nickel.**—20.8 g. of nitroguanidine and 10 g. of Raney nickel are suspended in 125 ml. of methyl alcohol and reduced at 125 atm. and room temperature. The reduction mixture is treated with Norit and filtered. The solution is saturated with carbon dioxide for several hours and the voluminous white precipitate which forms is filtered and washed with alcohol and ether; yield 15 g. or 55.2%. *Anal.* Calcd. for  $\text{CH}_6\text{N}_4\text{H}_2\text{CO}_3$ :  $\text{N}_2\text{H}_4$ , 23.53. Found:  $\text{N}_2\text{H}_4$ , 22.78.

**Distribution of Reduction Products with Acid Concentration.**—Ten grams of nitroguanidine and 0.5 g. of platinum oxide are suspended in 100 ml. of water, 0.1 and 1 *N* hydrochloric acid, respectively, and reduced at 1 atm. until 1 molar proportion of hydrogen has been absorbed (2300 ml.). The reduction mixture was examined for nitrosoguanidine, aminoguanidine and unreacted nitroguanidine. The results obtained were:

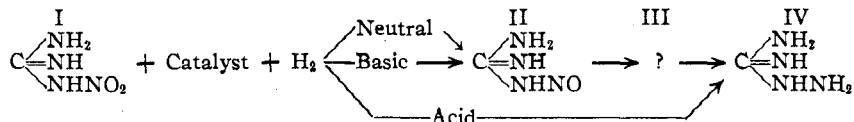
Molar ratio HCl/nitroguanidine	0	0.1	1.0
Acid concentration, <i>N</i>	0	.1	1
Reduction products:			
% Nitrosoguanidine	59	17.5	Absent
% Aminoguanidine	None	Present	46.2
% Nitroguanidine recovered	None	11.5	61.5

### Discussion

The catalytic hydrogenation of nitroguanidine may be summarized as follows

(4) Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., New York, N. Y., 1926, p. 36.

(5) Thiele, *Ann.*, **270**, 35 (1892).



In neutral and basic media, nitrosoguanidine is the first product of reduction and may be readily isolated in good yield,<sup>1</sup> while in acid media the reduction proceeds directly to aminoguanidine. Of the substances I and II, nitrosoguanidine is the least stable and it is therefore reasonable that route I to IV by way of II should yield less of IV, than its direct formation in acid media in which II does not appear as an intermediate reduction

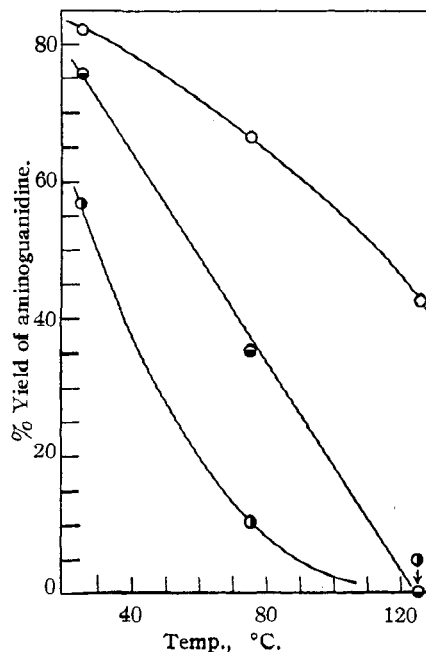


Fig. 1.—Hydrogenation of nitroguanidine at 125 atm.: ○, Pt in 15% acetic acid; ●, Raney Ni in water; ●, Raney Ni in  $\text{CH}_3\text{OH}$ .

product. The increased yields of IV with Raney nickel using alcohol as a solvent may be explained on the basis that II is less subject to dearrangement in alcohol than it is in water. The products obtained in the reduction of II with one molar proportion of hydrogen ( $\text{II} \rightarrow \text{III}$ ) have never been studied and we are at present engaged upon that phase of this investigation. Preliminary experiments have yielded small quantities of unknown reduction products of nitroguanidine including a reddish-orange substance having dye and indicator properties.

### Summary

The catalytic hydrogenation of nitroguanidine in neutral, acid and basic media to aminoguanidi-

dine has been studied and optimum conditions for the preparation of aminoguanidine with satisfactory yields by that method are described. BROOKLYN, NEW YORK RECEIVED AUGUST 1, 1936

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## The Condensation of Certain Aromatic Methyl Ketones

BY DANIEL B. CLAPP AND AVERY A. MORTON

Bernhauer, Müller and Neiser<sup>1</sup> have studied recently the condensation of aromatic methyl ketones by means of potassium pyrosulfate and sulfuric acid. They were successful by this method, in obtaining 1,3,5-tri-*p*-diphenylbenzene from *p*-acetyldiphenyl, but failed in an attempt to prepare 1,3,5-tri- $\alpha$ -naphthylbenzene and 1,3,5-tri- $\beta$ -naphthylbenzene from  $\alpha$ - and  $\beta$ -acetylnaphthalene, respectively. In the course of other work we have prepared the above three compounds by the method of Reddelien,<sup>2</sup> which involves the use of aniline and aniline hydrochloride. This method is more suitable for the preparation of 1,3,5-tri-*p*-diphenylbenzene than that with potassium pyrosulfate, since in the former case purification involves only a few recrystallizations of the crude product.

### Experimental

**1,3,5-Tri-*p*-diphenylbenzene.**—*p*-Acetyldiphenyl (120 g., 0.61 mole), aniline hydrochloride (6.4 g.), and freshly distilled aniline (86 g.) were heated together at 175° under a carbon dioxide atmosphere for three hours. The aniline was removed by distillation, and the residue was poured, while still hot, into a pan, where it quickly set to a brittle, red-brown resin. On grinding the resin in a mortar with ether, and filtering, 43.5 g. of crude product was obtained. Three recrystallizations from toluene gave 25 g. of pure 1,3,5-tri-*p*-diphenylbenzene; yield 23%; white needles; m. p. 230.5–231°; gives no color with cold concentrated sulfuric acid; almost insoluble in ether, alcohol and acetone; slightly soluble in glacial acetic acid; soluble in benzene and toluene.

*Anal.* Calcd. for C<sub>42</sub>H<sub>30</sub>: C, 94.34; H, 5.66; mol. wt., 534. Found: C, 94.50, 94.31; H, 5.71, 5.68; mol. wt. (Rast), 536, 538.

**1,3,5 - Tri -  $\alpha$  - naphthylbenzene.**— $\alpha$ -Acetylnaphthalene<sup>3</sup> (26 g., 0.153 mole), aniline (21.4 g.) and aniline

(1) Bernhauer, Müller and Neiser, *J. prakt. Chem.*, **145**, 301 (1936).

(2) Reddelien, *Ann.*, **388**, 194 (1912); cf. Vörländer, Fischer and Wille, *Ber.*, **62**, 2836 (1929).

(3) Fröschl, *Monatsh.*, **59**, 275 (1932).

hydrochloride (1.6 g.) were heated for one and one-half hours under carbon dioxide at 175°. The aniline was then removed by distillation under atmospheric pressure, and the remaining tar refluxed with 100 cc. of glacial acetic acid for one hour. On cooling, 4 g. of solid separated, which gave 2.8 g. of pure material after four recrystallizations from a mixture of equal parts of glacial acetic acid and acetic anhydride; yield 18%. In preparations in which impure  $\alpha$ -acetylnaphthalene (contaminated with the  $\beta$ -isomer) was used, only tars separated from the acetic acid solution on cooling. However, it was found that an attempt to purify the acetic acid solution by boiling with decolorizing carbon caused the adsorption of the 1,3,5-tri- $\alpha$ -naphthylbenzene on the carbon, from which it could be recovered in a relatively pure condition by extraction with a glacial acetic acid-acetic anhydride mixture. The substance crystallizes in white, flat needles with rounded ends; m. p. 190.5–191°; it gives no color with concentrated sulfuric acid.

*Anal.* Calcd. for C<sub>38</sub>H<sub>24</sub>: C, 94.69; H, 5.31; mol. wt., 456. Found: C, 94.61; H, 5.40; mol. wt. (Rast), 466, 450.

**1,3,5 - Tri -  $\beta$  - naphthylbenzene.**— $\beta$ -Acetylnaphthalene (Eastman Kodak Co.) (19.2 g., 0.113 mole), aniline (15.6 g.) and aniline hydrochloride (1.2 g.) were heated for four and one-half hours under carbon dioxide at 175°. After the reaction mixture had stood in the ice box for one day, 5.5 g. of crystalline material had separated. Three recrystallizations from toluene gave 3.4 g. of pure substance; yield 20%; white needles; m. p. 234–235°; gives no color with cold concentrated sulfuric acid; less soluble than tri- $\alpha$ -naphthylbenzene in common solvents.

*Anal.* Calcd. for C<sub>38</sub>H<sub>24</sub>: C, 94.69; H, 5.31; mol. wt., 456. Found: C, 94.58; H, 5.38; mol. wt. (Rast), 462, 468.

### Summary

1,3,5-Tri-*p*-diphenylbenzene, 1,3,5-tri- $\alpha$ -naphthylbenzene and 1,3,5-tri- $\beta$ -naphthylbenzene have been prepared from *p*-acetyldiphenyl,  $\alpha$ -acetylnaphthalene and  $\beta$ -acetylnaphthalene, respectively, by the action of aniline and aniline hydrochloride.

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