10 ml. anhydrous ether and 3 ml. purified pyridine cooled in an ice bath, was slowly added with shaking, 2 g. thionyl chloride. The reaction mixture was allowed to warm to room temperature and then stand for 16 hr. It was then poured onto cracked ice and the mixture extracted with ether. The ether extract, after having been washed several times with water and then dried over sodium sulfate, was concentrated *in vacuo* to remove the ether.

An infrared spectrum of the total crude product revealed that the hydroxyl group, which appeared in the adduct at 3580 cm.$^{-1}$ as a sharp and intense bond, was completely lacking, thus indicating the completeness of the dehydration reaction.

The ultraviolet spectrum run on an ethanol solution whose concentration was $1.2 \times 10^{-3}M$, showed only end absorption above 220 mμ.

EMORY UNIVERSITY, GA.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE U. S. NAVAL ORDNANCE TEST STATION]

Preparation and Oxidation of 1,2-Diamino-1,2-dimethylguanidine

WILLIAM R. McBRIDE, WILLIAM G. FINNEGAN, AND RONALD A. HENRY

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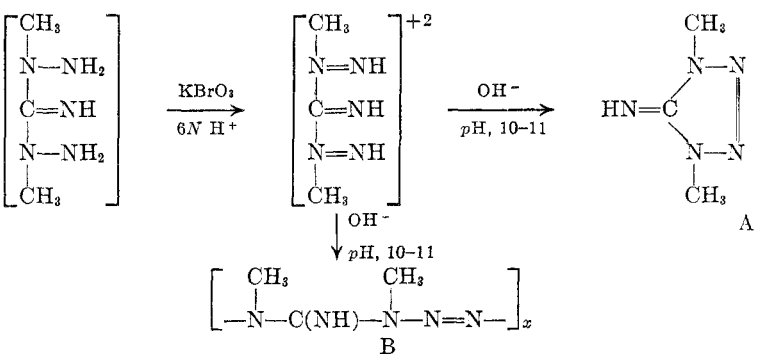
1,2-Diamino-1,2-dimethylguanidine has been synthesized and oxidized with bromate in acidic medium to 1,4-dimethyl-5-iminotetrazole.

It has recently been demonstrated[1] that the oxidation of 1,1-dialkylhydrazines with bromate or iodate in strongly acidic medium involves a two electron change and yields diazo-like intermediates, $[R_2N{=}NH]^+$, of varying stability. These intermediates are irreversibly converted to tetraalkyltetrazenes in basic medium. This sequence of reactions has now been applied to 1,2-diamino-1,2-dimethylguanidine. The coupling of the diazo-like intermediate can occur either intramolecularly to give the known 1,4-dimethyl-5-iminotetrazole[2] or intermolecularly to give a water-soluble polytetrazene.



Experimentally the substituted tetrazole (A) was recovered as its phenylthiourea derivative in 35–37% yield. The synthesis of the 1,4-dimethyl-5-iminotetrazole in this manner is further proof that the previously assigned positions[2] for the methyl groups are correct. In addition, this method offers a new route to this class of tetrazole compounds.

Since the phenylthiourea derivative of the 1,4-dimethyl-5-iminotetrazole is readily formed and is sparingly soluble, the results from this method of isolation should be a good indication of the total amount of tetrazole present in solution. However, a comparison of the molar absorbancy indices (A_M) for 1,4-dimethyl-5-iminotetrazole and the oxidized species from 1,2-diamino-1,2-dimethylguanidinium nitrate (A_M = 1980 and *ca.* 1750, respectively, at 258 mμ in basic aqueous solution) indicates that conversion to tetrazole or compounds with a similar nitrogen resonance system should be about 90%. This spectrophotometric procedure would probably not discriminate between the nitrogen system in the tetrazole and that found either in a polytetrazene (B) or conceivably in a 10-membered ring compound resulting from a dimerization of the diazo-like intermediate. Hence, the difference between the 36% and the 90% is best attributed to polytetrazene although it has not been isolated.

One other product that might result indirectly during the oxidation of 1,2-diamino-1,2-dimethylguanidine is 1,4-dimethyl-5-tetrazolone (from the hydrolysis of the corresponding imino-compound). This possibility is largely excluded, however, by the following: 1,4-Dimethyl-5-tetrazolone in aqueous solution has a maximum absorption at 223 mμ (A_M = 3185), which is similar to that for 1,4-dimethyl-5-iminotetrazole in acidic medium, but which is otherwise essentially independent of *p*H.

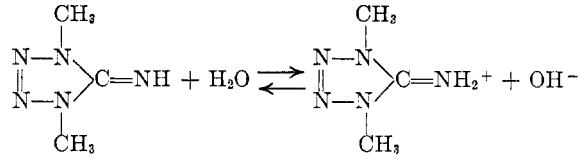
(1) W. R. McBride and H. W. Kruse, Abstracts 129th National Meeting, AMERICAN CHEMICAL SOCIETY, 6Q, Dallas, April 1956. *J. Am. Chem. Soc.*, **79**, 572 (1957).

(2) R. A. Henry, W. G. Finnegan, and E. Lieber, *J. Am. Chem. Soc.*, **76**, 2894 (1954).

As stated earlier, when the solution arising from the oxidation is made basic, the absorption at 258 mμ corresponds to 90% conversion to 1,4-dimethyl-5-iminotetrazole or compounds with similar resonance systems. Hence, the amount of tetrazolone formed is at best only about 10%. Hattori, *et al.*,[3] previously used the similarity in the characteristic absorptions of 1,3-dimethyl-5-tetrazolone (256 mμ, A_M = 2030) and of 1,3-dimethyl-5-iminotetrazole (256 mμ, A_M = 2670) as indirect evidence to support the former structure.

In contrast to the relative instability of the diazo-like intermediate formed by the oxidation of the 1,1-dialkylhydrazines in acid media,[1] the corresponding intermediate obtained from the 1,2-diamino-1,2-dimethylguanidine was stable and showed no evidence of decomposition, either titrimetrically (a further consumption of iodate as the solution aged) or spectrophotometrically. With the 1,1-dialkylhydrazines the decomposition of the diazo-like intermediate could be followed by both procedures. Furthermore, in contrast to the behavior of the diazo-like intermediate from a 1,1-dialkylhydrazine, the intermediate formed in the oxidation of 1,2-diamino-1,2-dimethylguanidine does not appear to be reduced by stannous chloride in acid medium to the starting hydrazine. 1,4-Dimethyl-5-iminotetrazole is not reduced to the starting diaminoguanidine derivative by stannous chloride in concentrated hydrochloric acid at 60–70° during 1.5 hr. These facts might be interpreted to mean that in the oxidation of 1,2-diamino-1,2-dimethylguanidine the proposed diazo-like compound either is not formed at all or is capable of cyclizing immediately under acidic conditions to the tetrazole derivative. On the other hand, this particular intermediate should be much more stable because of increased resonance than the one from a 1,1-dialkylhydrazine. Furthermore, the equilibrium concentration of the unstable, reactive, unprotonated form in acidic solution should be very much less with the derivative from the 1,2-diamino-1,2-dimethylguanidine. The existence of the diazo-like intermediate from a 1,1-dialkylhydrazine can easily be demonstrated spectrophotometrically. However, since the region in which both the proposed intermediate and the 1,4-dimethyl-5-iminotetrazole should absorb is opaque in the acidic oxidation medium, it is not possible to resolve this problem unambiguously by the spectrophotometric method.

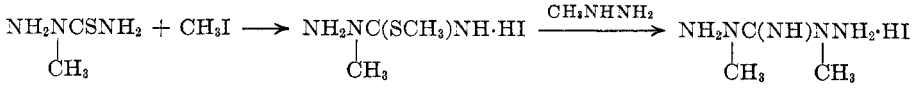
In connection with the spectrophotometric studies, it was noted that the ultraviolet absorption spectrum of 1,4-dimethyl-5-iminotetrazole was dependent on *p*H. A single absorption maximum occurs at 258 mμ (A_M = 1980) in aqueous solutions of *p*H 10 or higher. In aqueous hydrochloric acid solutions with a *p*H of 6 or less the 258 mμ peak disappears and is replaced by an absorption maximum at 220 mμ (A_M = 2194). The hydrochloride salt in absolute ethanol has an absorption at 221 mμ identical to that in the acidic, aqueous solution. Previous workers[2,4] overlooked this effect of *p*H and described only a single absorption maximum; consequently the reported molar absorbancy indices are probably in error since the particular solutions examined would contain an appreciable concentration of each of the two absorbing forms. For example, the molar absorbancy index reported by Murphy and Picard[4] for 1,4-dimethyl-5-iminotetrazole in 95% ethanol (A_M = 1750 at 260 mμ) is probably low since no allowance has been made for the following equilibrium:



Only at high *p*H's (above 10) where the equilibrium lies predominantly on the left, will the absorption spectrum be almost exclusively that due to the free imino form. Although the conclusion of Murphy and Picard that the amino- and imino- forms of substituted 5-aminotetrazoles can be distinguished by the differences in their absorption maxima is correct, in acidic solution 1,4-dimethyl-5-iminotetrazole is distinguished from the other 5-aminotetrazole derivatives only by the intensity of absorption and not by the peak displacement, as these authors suggest.

1,1-Dialkylhydrazines can be oxidized directly to tetrazenes by iodine[1,5] in neutral or slightly basic solution. However, the oxidation of 1,2-diamino-1,2-dimethylguanidine in a solution of sodium bicarbonate with iodine involves a total electron change of about eight rather than the desired four. Considerable gas is evolved with this reaction in contrast to essentially no gas liberated during the oxidation with iodate or bromate in acid solution; and no tetrazole derivative can be recovered. This result appears to be independent of the order of addition.

The 1,2-diamino-1,2-dimethylguanidine used in the oxidation experiments was prepared by the following reaction sequence:



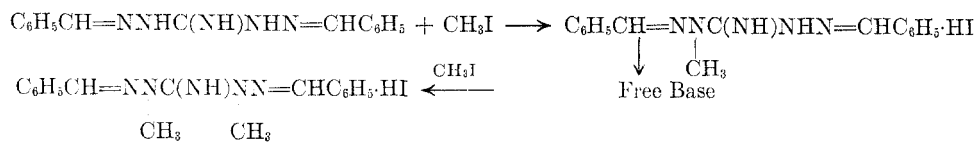
The corresponding dibenzal derivative can be made by a two-step methylation of dibenzaldiami-

(3) K. Hattori, E. Lieber, and J. P. Horwitz, *J. Am. Chem. Soc.*, **78**, 411 (1956).

(4) D. B. Murphy and J. P. Picard, *J. Org. Chem.*, **19**, 1807 1954).

(5) Rowe and Audrieth, *J. Am. Chem. Soc.*, **78**, 563 (1956).

noguanidine in a process analogous to that used for synthesizing benzal 1-amino-1-methylguanidinium iodide:[6]



Since the second methylation appears to be considerably more difficult than the first and since separation of unreacted dibenzal 1,2-diamino-1-methylguanidine from the product is also difficult, this method does not readily or conveniently yield a pure compound.

Attempts to form 1,2-diamino-1,2-dimethylguanidine by the reaction of methylhydrazine and guanidinium nitrate in refluxing aqueous solution led only to low yields of 1-amino-1-methylguanidine; under similar conditions the hydrazinolysis of guanidinium nitrate readily gives triaminoguanidinium nitrate.[7] Similarly, methylhydrazine and aminoguanidinium nitrate reacted very slowly to give small yields of 1,2-diamino-1-methylguanidine, isolated as the picrate of the dibenzal hydrazone. The latter compound was identical with the monomethyl derivative obtained from dibenzaldiaminoguanidine.

The syntheses of several other methylated amino- and diaminoguanidine derivatives are described in the experimental part. Reaction of dimethylamine and S-methylisothiocarbohydrazide hydroiodide in an effort to prepare 1,2-diamino-3,3-dimethylguanidinium iodide yielded triaminoguanidinium iodide as the most easily recoverable product. A similar result was noted when methylhydrazine and S-methylisothiocarbohydrazide hydroiodide were reacted in ethanol.

EXPERIMENTAL[8]

Oxidation of 1,2-diamino-1,2-dimethylguanidine in acid solution. 1,2-Diamino-1,2-dimethylguanidinium nitrate (0.8676 g., 0.00482 mole) was dissolved in 40 ml. of 6*N* hydrochloric acid, cooled to 0–4°, and titrated potentiometrically with a 1.000*N* solution of potassium bromate. The amount of oxidant used corresponded to 0.01900 equivalent, the theoretical requirement was 0.01928 equivalent. The resulting solution was neutralized with a solution of sodium hydroxide to the phenophthalein end point during which time the temperature rose to 15°. The solution was diluted to 100 ml. The molar absorbancy index, A_M, for this solution at 2580 Å was 1727 in units of 1000 cm.²/mol; the pK_b of the oxidation product, as determined spectrophotometrically,[9] was 5.42 at 25°. To 97 ml. of the solution was added 50 ml. of 95% ethanol. The resulting solution was shaken with phenyl isothiocyanate (0.83 g.; 0.0061 mole) and allowed to stand overnight at room temperature; the precipitated solid was removed by filtration, washed several times with pentane, dried, and weighed. The yield was 0.40 g. (34.7%), m.p. 198–202°; a mixed melting point with an authentic sample of the phenylthiourea of 1,4-dimethyl-5-iminotetrazole was 205–207°. The melting point after recrystallization from absolute ethanol was 207–208°.

When the procedure for the initial oxidation with potassium bromate was repeated at room temperature, the yield of the phenylthiourea derivative of 1,4-dimethyl-5-iminotetrazole was 36.7%; the A_M at 2580 Å was 1755.

In the oxidation at 0° an extraneous peak of low intensity which is not accounted for by 1,4-dimethyl-5-iminotetrazole was observed at 277 mμ in a reacidified solution.

1,2-Diamino-1,2-dimethylguanidinium nitrate (0.0686 g. or 0.003807 mole) dissolved in 60 ml. of 6.1*N* hydrochloric acid was rapidly titrated with 0.1000*N* potassium iodate at 25° by the potentiometric procedure. The observed titer was 15.33 ml. (theory 15.23 ml.); after 24 hr. an additional titer of only 0.25 ml. was consumed.

Oxidation of 1,2-diamino-1,2-dimethylguanidine with iodine in neutral solution. A solution of 1 g. of diaminodimethylguanidinium nitrate in 50 ml. of water was added during 2 hr. to 440 ml. of 0.1*N* iodine in potassium iodide (20 g. per l.). Sodium bicarbonate (10 g.) was used to buffer the iodine solution. The reaction mixture was stirred vigorously and the temperature maintained between 0 and 5°. There was a steady evolution of gas. This amount of iodine, which corresponds to twice the theoretical amount required for the desired four electron change, was almost completely reduced. The slight excess of iodine was destroyed with sodium sulfite, the *p*H of the solution was adjusted to 9, and 0.5 ml. of phenyl isothiocyanate in 100 ml. of 95% ethanol added. No thiourea precipitated even after several days at room temperature.

A similar result was observed when the 0.1*N* solution of iodine was added to a buffered solution of the diaminodimethylguanidinium nitrate at 0–3°. Twice the expected quantity of oxidizing agent was required, much gas was evolved, and no phenylthiourea derivative of the 1,4-dimethyl-5-iminotetrazole was recovered.

Ultraviolet absorption data. The ultraviolet absorption spectra were determined with a Cary recording spectrophotometer, model 11MS. The pK_b for 1,4-dimethyl-5-iminotetrazole as determined spectrophotometrically was 5.43 at 25°; the previously reported value determined potentiometrically was 5.32.[2]

The ultraviolet absorption spectrum of 1,3-dimethyl-5-iminotetrazole[2] is also dependent on the *p*H of the solution; for example in an aqueous solution of the hydrochloride at *p*H 1.8 the absorption maximum occurred at 256 mμ (A_M = 2487); at *p*H 12.9, 307 mμ (A_M = 1903). For 1,3-dimethyl-5-iminotetrazole the pK_b was 2.36 at 25° versus a previously reported value[2] of 2.5.

1,2-Diamino-1,2-dimethylguanidine. Methylhydrazine sulfate (72 g.; 0.5 mole) was dissolved in 100 ml. of water and neutralized to a bromophenol blue end point with a 50% solution of sodium hydroxide. Solid sodium thiocyanate (40.5 g.; 0.5 mole) was added and the resulting solution was evaporated to a syrup *in vacuo* on a steam bath. The syrup was extracted three times with 100 ml. portions of boiling 95% ethanol. The ethanol solution of methylhydrazine thiocyanate was evaporated to dryness *in vacuo* on a steam bath and the residue heated to 150° for 30 min. The reaction mixture was then cooled and 100 ml. of ice water added. The precipitated 2-methylthiosemicarbazide was removed by filtration; yield, 37.5 g. Concentration of the filtrate to dry-

(6) Finnegan, Henry, and Smith, *J. Am. Chem. Soc.*, **74**, 2981 (1952).

(7) G. Pellizzari and A. Gaiter, *Gazz. chim. ital.*, **44**, II, 72 (1944).

(8) All melting points are uncorrected.

(9) J. E. DeVries and E. S. Gantz, *J. Am. Chem. Soc.*, **76**, 1008 (1954).

ness, reheating the residue to 150° for 30 min. and dilution with 50 ml. of water yielded an additional 1.1 g. of product. The combined yield of product amounted to 73.5%. One recrystallization from water gave 37.2 g. of product, 166–167.5°, which was adequately pure for the subsequent reactions. Repeated recrystallizations from acetonitrile or from 2-propanol finally gave a material decomposing at 174–176° (very dependent on the rate of heating). The reported[10] melting point of 183–186° was never obtained.

Anal. Calcd. for $C_2H_7N_3S$: N, 39.96. Found: N, 39.86, 39.64.

The benzal thiosemicarbazone after one recrystallization from ethanol melted at 172–174°; reported,[10] 174°.

The 2-methylthiosemicarbazide (37.2 g.; 0.35 mole) was suspended in 150 ml. of absolute ethanol and 60 g. (0.423 mole) of methyl iodide was added. The suspension was kept in a cold water bath for 48 hr., then heated to reflux for 1 hr. The 2-methylthiosemicarbazide gradually dissolved during this time. Removal of the ethanol *in vacuo* left 88 g. of crude 2,S-dimethylisothiosemicarbazide hydroiodide as a thick syrup.

The crude hydroiodide from the preceding reaction was dissolved in 100 ml. of water. To this solution was added 100 ml. of an aqueous solution containing 0.36 mole of methylhydrazine. The reaction mixture was allowed to stand for 48 hr. and then was heated on a steam bath for 4 hr. Methyl mercaptan was evolved copiously. When the solution was concentrated *in vacuo*, 1,2-diamino-1,2-dimethylguanidine hydroiodide (87 g.) was recovered as a syrup. All of the hydroiodide was dissolved in 300 ml. of 60% ethanol, acidified with nitric acid, and converted to the nitrate by reaction with 60 g. (0.353 mole) of silver nitrate in 100 ml. of water. The precipitated silver iodide was removed by filtration and the filtrate was concentrated to dryness under reduced pressure on the steam bath. The residue of 1,2-diamino-1,2-dimethylguanidinium nitrate partially solidified on standing. Crystallization from 100 ml. of boiling acetonitrile yielded 16.23 g. (25.8% based on the methylthiosemicarbazide or 18% over-all) of colorless, coarse crystals, m.p. 82–84°.

Anal. Calcd. for $C_3H_{12}N_6O_3$: C, 20.00; H, 6.72; N, 46.65; mol. wt., 180.19. Found: C, 19.61, 20.25; H, 6.87, 6.94; N, 46.62; mol. wt., 181.1, 179.5.

The *dipicrate* melted at 141–142° after recrystallization from 95% ethanol.

Anal. Calcd. for $C_{15}H_{17}N_{11}O_4$; C, 31.31; H, 2.98; N, 26.78; mol. wt., 575.38. Found: C, 31.92; H, 3.19; N, 27.20; mol. wt., 575.1.

The *monobenzal 1,2-diamino-1,2-dimethylguanidinium nitrate* was obtained as prisms from 2-propanol; m.p. 202–203°.

Anal. Calcd. for $C_{10}H_{16}N_6O_3$: C, 44.77; H, 6.01; N, 31.33. Found: C, 44.81; H, 6.18; N, 31.73.

The *dibenzal 1,2-diamino-1,2-dimethylguanidinium nitrate* crystallizes from 2-propanol-diethyl ether as rosettes of fine, white needles; m.p. 128–129°.

Anal. Calcd. for $C_{17}H_{20}N_6O_3$; C, 57.29; H, 5.66; N, 23.59. Found: C, 57.65; H, 6.19; N, 23.54.

The picrate of the dibenzal derivative melted at 192–193° after recrystallization from ethanol; short needles.

Anal. Calcd. for $C_{23}H_{22}N_8O_7$: C, 52.87, H, 4.25; N, 21.45. Found: C, 52.79; H, 4.97; N, 22.16.

The free base of the dibenzal hydrazone crystallized from cyclohexane as white needles, m.p. 135–136° (still impure). Admixture with a pure sample (m.p. 143–144°) of the dibenzal dimethyl derivative prepared in the following experiment was 142°.

Methylation of dibenzal 1,2-diaminoguanidine. Dibenzal 1,2-diaminoguanidine (67 g.; 0.253 mole) was suspended in 200 ml. of absolute ethanol and 37 g. (0.26 mole) of methyl iodide was added. The mixture was allowed to stand 48 hr. at room temperature, then refluxed for 1 hr. On cooling to 5°, 59.8 g. (0.147 mole, 58.1%) of yellow-orange dibenzal 1,2-diamino-1-methylguanidine hydroiodide precipitated; m.p. 225–227° after recrystallization from ethanol.

Anal. Calcd. for $C_{16}H_{18}IN_5$: C, 47.18; H, 4.45; N, 17.20. Found: C, 47.43; H, 4.95; N, 17.17.

The entire quantity of hydroiodide was suspended in 300 ml. of 95% ethanol, and converted to the free base by adding a solution of 6.2 g. of sodium hydroxide in 10 ml. of water. The mixture was heated to boiling and sufficient ethanol was added at the boiling point to dissolve the free base. Cooling yielded the light yellow *dibenzal 1,2-diamino-1-methylguanidine* (26.19 g.; 63.9%), m.p. 137–138° after an additional recrystallization from methanol.

Anal. Calcd. for $C_{16}H_{17}N_5$: C, 68.79; H, 6.14; N, 25.08. Found: C, 68.45; H, 6.03; N, 24.76.

Dibenzal 1,2-diamino-1-methylguanidinium picrate melted at 229–230° after recrystallization from 95% ethanol. A mixed melting point with benzalaminoguanidinium picrate was 215–220°.

Anal. Calcd. for $C_{22}H_{20}N_8O_7$: C, 51.97; H, 3.97; N, 22.04. Found: C, 52.18; H, 4.09; N, 22.12.

Dibenzal 1,2-diamino-1-methylguanidine (30.6 g., 0.11 mole) was methylated with 15.6 g. (0.11 mole) of methyl iodide in a sealed tube at 100° for 18 hr. Recrystallization from 500 ml. of ethanol yielded 32.7 g. (70.5%) of a yellow-orange product melting from 192–197°. Another recrystallization raised the melting point to 209–215° (dec.).

Anal. Calcd. for $C_{17}H_{20}IN_5$: N, 16.63. Found: N, 16.86.

The picrate after two recrystallizations from 95% ethanol melted at 191–192° (dec.). A mixed melting point with an authentic sample of dibenzal 1,2-diamino-1,2-dimethylguanidinium picrate, m.p. 192–193° (dec.), was 191.5–192.5° (dec.). Thus, one of the products formed by methylation is dibenzal 1,2-diamino-1,2-dimethylguanidine.

The free base was obtained as fine colorless needles by treating the hydroiodide in 95% ethanol with concentrated sodium hydroxide. The melting point after two recrystallizations from ligroin was 143–144°.

Anal. Calcd. for $C_{17}H_{19}N_5$: C, 69.95; H, 6.53; N, 23.88. Found: C, 69.87; H, 6.51; N, 23.67.

Reaction of methylhydrazine and guanidinium nitrate. Method A. A solution consisting of 12.2 g. (0.1 mole) of guanidinium nitrate, 9.6 g. (0.2 mole) of methylhydrazine, and 150 ml. of water was refluxed for 6 hr. and then evaporated to dryness under reduced pressure to remove unreacted methylhydrazine. The residue was redissolved in 100 ml. of water, acidified with 1 ml. of concentrated nitric acid, warmed on the steam bath, and shaken with 10 ml. of benzaldehyde. The product, which still contained excess benzaldehyde, was removed by filtration after being chilled to 5°, washed with much cold water, triturated with diethyl ether, and dried. The yield amounted to 5.6 g.; m.p. 170–200°. Recrystallization from absolute ethanol gave 2.8 g. of benzal 1-amino-1-methylguanidinium nitrate melting at 195–196° (dec.); the mother liquor was retained (*A*). A second recrystallization raised the melting point to 199–200° (dec.).

Anal. Calcd. for $C_9H_{13}N_5O_3$: C, 45.18; H, 5.48; N, 29.28. Found: C, 45.33; H, 5.64; N, 29.57.

The purified hydrazone gave a picrate melting at 215–217°; admixture with an authentic sample of benzal 1-amino-1-methylguanidinium picrate[11] was 217–218°.

When the mother liquor (*A*) was treated with an excess of picric acid, 1.4 g. of the benzal methylaminoguanidinium picrate (m.p. 210–213°) was recovered, together with some guanidinium picrate (m.p. above 300°). No diaminodimethylguanidine was detected in these products.

Increasing the reaction time to 24 hr. did not change significantly the yield of benzal 1-amino-1-methylguanidinium nitrate (5.2 g.; m.p. 198–200°). However, from the mother liquors a small quantity of a second compound was

(10) E. Cattelain, *Compt. rend.*, **209**, 799 (1939).

(11) A. H. Greer and G. B. L. Smith, *J. Am. Chem. Soc.*, **72**, 874 (1950).

recovered as a picrate (0.5 g.). Several recrystallizations from 95% ethanol gave rosettes of thin, yellow needles, 202–203°. Admixture with benzal 1-amino-1-methylguanidinium picrate lowered the melting point to about 180°; with dibenzal 1,2-diamino-1,2-dimethylguanidinium picrate to 160–170°.

Anal. Calcd. for $C_{23}H_{22}N_8O_7$: C, 52.87; H, 4.25; N, 21.45. Found: C, 53.33; H, 4.44; N, 21.21, 21.96.

Method B. Methylhydrazine sulfate (43.2 g.; 0.3 mole) and 11.5 g. of guanidine nitrate (0.094 mole) were dissolved in an ice cold solution of 24 g. of sodium hydroxide (0.6 mole) in 125 ml. of water. This solution was refluxed for 13.5 hr.; ammonia was evolved steadily. After the solution had been evaporated to dryness on the steam bath, the remaining solid was extracted successively with the following portions of boiling 80% ethanol: 100 ml., 50 ml., 50 ml., and 25 ml. The weight of alcohol insoluble residues was 41.5 g. The combined extracts were chilled overnight at 0° to yield 0.55 g. of impure 1-amino-1-methylguanidine sulfate (4.2%). This material was characterized by conversion to the picrate which melted at 230–231° (dec.) after recrystallization from 80% ethanol; a mixed melting point with an authentic sample of 1-amino-1-methylguanidine picrate was the same.

One half of the alcoholic mother liquors was diluted to 125 ml. with 95% ethanol, heated to boiling, and treated with a hot solution of 11 g. of picric acid in 100 ml. of 95% ethanol. An orange microcrystalline salt began to separate almost immediately and was removed by filtration when the temperature of the solution reached 40°; this material (1.7 g.) proved to be guanidine picrate. Further cooling of the filtrate to room temperature yielded 9.0 g. of material, m.p. 165–170°; the filtrate was retained. Fractional crystallization of the 9.0 g. of solid from 110 ml. of 95% ethanol gave 5.3 g. of methylhydrazine picrate, m.p. 166°C (dec.), and 1.2 g. (8.0% on total basis) of 1-amino-1-methylguanidine picrate, m.p. 229–231° (dec.). When the original filtrate was cooled at 0° for 3 weeks, 0.8 g. more of guanidine picrate was recovered. After the guanidine picrate was removed the filtrate was evaporated to 20 ml. and cooled; there was obtained 1.8 g. of material melting at 173–176° (dec.). Recrystallization from 65 ml. of 95% ethanol gave 0,6 g. (4%) of 1-(methylamino)guanidine picrate, m.p. 182–184° (dec.). A mixed melting point with an authentic sample of 1-(methylamino)guanidine picrate[6] was the same; x-ray powder diagrams were also identical. Limited attempts to obtain other pure materials from the mother liquors were not successful.

The other half of the original alcoholic extraction liquors was diluted to 125 ml. with 95% ethanol, heated to boiling, and treated successively with 16 ml. of benzaldehyde and 11.0 g. of picric acid in 100 ml. of hot ethanol. Upon cooling the solution to room temperature fluffy rosettes of yellow needles crystallized. This material was removed and dried; yield 2.6 g. (13.6% on total basis); m.p. 215–217°; a mixed melting point with an authentic sample of benzal 1-amino-1-methylguanidine picrate was 217–218° (dec.). Cooling the mother liquors at 0° for several days gave 9.9 g. of amorphous solid, m.p. 120–130°; the remaining filtrate was discarded. Fractional crystallization from 200 ml. of 95% ethanol gave 2.0 g. of guanidine picrate, 0.1 g. of benzal 1-amino-1-methylguanidine picrate, and the balance essentially monobenzal methylhydrazine picrate. The latter was obtained as orange prisms, m.p. 137.5–138.5° when recrystallized from ethanol.

Anal. Calcd. for $C_{14}H_{13}N_5O_7$: C, 46.28; H, 3.61; N, 19.28. Found: C, 46.42; H, 3.76; N, 19.36.

Reaction of methylhydrazine and aminoguanidine. Aminoguanidinium chloride (11.0 g; 0.1 mole), 4.8 g. (0.1 mole) of methylhydrazine, and 150 ml. of water were heated under reflux for 16 hr. Ammonia was evolved slowly. Concentrated hydrochloric acid was then added until the *p*H was 5. Benzaldehyde (20 ml.) was added with shaking; a precipitate formed immediately and was removed by filtration after the solution had been cooled to 5°. The solid hydrazone was washed several times with cold water, then with diethyl ether. The yield of dried product was 10.8 g. Solution in a minimum volume of hot 95% ethanol and cooling gave 1.0 g. (3.2%) of impure dibenzal 1,2-diamino-1-methylguanidinium chloride, m.p. 190–205°. This salt was converted to the free base, which recrystallized from 95% ethanol as yellow plates, m.p. 139–140°; admixture with the compound made by monomethylating dibenzaldiaminoguanidine did not depress the melting point.

The ethanolic mother liquors were diluted with 100 ml. of ethanol, heated to boiling, and treated with 10 g. of picric acid. Fractional crystallization of the picrates from 95% ethanol finally gave about 4.1 g. (8.0%) of impure dibenzal 1,2-diamino-1-methylguanidinium picrate, m.p. about 220°. Further recrystallizations raised the melting point to 224–227°. A mixed melting point with benzalaminoguanidinium picrate was 215–220°, with dibenzal 1,2-diamino-1-methylguanidinium picrate made by another method was 223–226°. X-ray powder patterns on the two different samples of dibenzal diaminomethylguanidinium picrate were identical. The only other picrate which was recovered in reasonable purity was that from benzalaminoguanidine.

1,2-Diamino-1,3-dimethylguanidine. Twelve grams of 4-methylthiosemicarbazide (m.p. 138–140°) was slurried in 200 ml. of absolute ethanol and treated with 16.5 g. of methyl iodide. The mixture was allowed to stand overnight at room temperature, then refluxed until complete solution was attained, evaporated to one half its volume under reduced pressure, and mixed with 5.3 g. of methylhydrazine in 40 ml. of ethanol. Methyl mercaptan was evolved slowly during several days at room temperature; the solution was refluxed for 1 hr. to complete the reaction before evaporating to dryness. The soft residue was recrystallized from 2-propanol; 17.5 g.; m.p. *ca.* 90°. This once recrystallized product was freed from some triaminoguanidine hydroiodide (0.5 g.; m.p. 225–230°; x-ray powder pattern same as that for an authentic sample) by warming to 60° with 200 ml. of 2-propanol and filtering rapidly. The crystalline hydroiodide obtained by cooling the filtrate was removed and recrystallized another time from 2-propanol; m.p. 91–92°.

Anal. Calcd. for $C_3H_{12}IN_5$: C, 14.70; H, 4.94; N, 28.58. Found: C, 15.12; H, 5.14; N, 28.35.

The dipicrate after two recrystallizations from 95% ethanol and drying at 105° melted at 116.5–118°. The salt obtained directly from the recrystallization and air dried at room temperature is a dihydrate (loss in weight on drying: 6.18%.)

Anal. Calcd. for $C_{15}H_{17}N_{11}O_{14}$ (anhydrous): C, 31.31; H, 2.98; N, 26.78. Found: C, 31.99; H, 3.16; N, 27.11, 26.56.

The picrate of the dibenzal hydrazone separated as rosettes of small, yellow needles after a second recrystallization from ethanol; m.p. 171–172° (dec.).

Anal. Calcd. for $C_{23}H_{22}N_8O_7$: C, 52.87; H, 4.25; N, 21.45. Found: C, 53.30; H, 4.15; N, 21.38, 21.74.

1,2-Diamino-3-methylguanidine. The hydroiodide was obtained in 65% yield by allowing 5.04 g. of S-methylisothiocarbohydrazide hydroiodide[12] and 2.5 g. of 25% aqueous methylamine in 50 ml. of 95% ethanol to stand 1 week at room temperature, then chilling to 5°C. After recrystallization from ethanol the compound decomposed at 238–239°.

Anal. Calcd. for $C_2H_{10}IN_5$: C, 10.40, H, 4.36; I, 54.93; N, 30.31. Found: C, 10.19; H, 4.42; I, 55.31; N, 31.32.

The picrate was obtained as prisms from 95% ethanol; m.p. 167–168°.

Anal. Calcd. for $C_8H_{12}N_8O_7$: C, 28.92; H, 3.64; N, 33.73. Found: C, 29.20; H, 3.51; N, 34.38, 33.59.

1-Amino-1,2,3-trimethylguanidine was formed when methylhydrazine (0.1 mole) and 1,3,S-trimethylisothiourea hydroiodide (0.1 mole) in 80 ml. of water were heated under

(12) E. S. Scott and L. F. Audrieth, *J. Org. Chem.*, 19, 1231 (1954).

reflux until the evolution of methyl mercaptan ceased.

The picrate of the benzal hydrazone melted at 156–156.5° (dec.); orange, flat needles from 95% ethanol.

Anal. Calcd. for $C_{17}H_{19}N_7O_7$: C, 47.11; H, 4.42; N, 22.63. Found: C, 47.15; H, 4.69; N, 21.50.

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China Lake, Calif.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

Experiments with Quinone Imides. III. A Novel Synthesis of 1,4-Diphenylnaphthalene

AHMED MUSTAFA AND MOHAMED KAMEL

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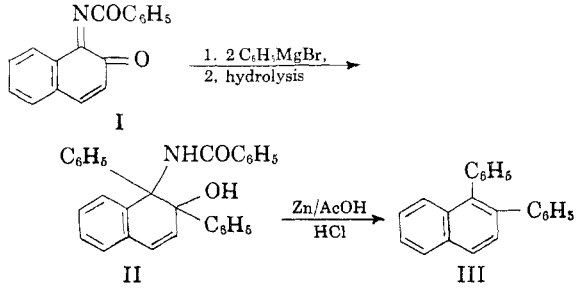
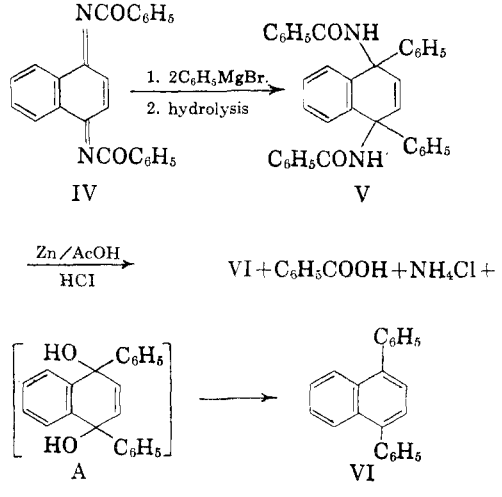
The action of phenylmagnesium bromide on 1,4-naphthoquinone dibenzimide, followed by the treatment of the hydrolyzed Grignard product with zinc dust and acetic and hydrochloric acids establishes a novel synthesis of 1,4-diphenylnaphthalene.

In Part II,[1] Mustafa and Kamel have shown that when 1,2-naphthoquinone-1-benzimide (I) is treated with an excess of phenylmagnesium bromide followed by hydrolysis, 1-benzamido-2-hydroxy-1,2-diphenyl-1,2-dihydronaphthalene (II) is obtained. Compound II, on treatment with zinc dust and acetic and hydrochloric acids gives 1,2-diphenylnaphthalene (III).



We now have investigated the action of phenylmagnesium bromide on a *p*-quinone dibenzimide, namely 1,4-naphthoquinone dibenzimide (IV). Thus, when the pale yellow IV is treated with phenylmagnesium bromide, followed by hydrolysis, a colorless product believed to be 1,4-dibenzamido-1,4-diphenyl-1,4-dihydronaphthalene (V) is obtained.

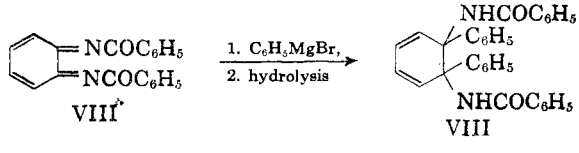
Compound (V) gives correct analytical values: When its solution in glacial acetic acid is treated with a mixture of zinc dust and concentrated hydrochloric acid in the presence of a few drops of platinum chloride, it gives 1,4-diphenylnaphthalene (VI) in good yield, together with ammonium chloride and benzoic acid,[1] probably *via* the intermediate A. The ready transformation of the intermediate (A) to VI may be compared with the ready transformation of 9,10-dihydroxy-9-10-diphenyl-9,10-dihydroanthracene to 9,10-diphenylanthracene



by the action of zinc dust and glacial acetic acid.[2]

The action of phenylmagnesium bromide on IV, followed by the action of Zn/HCl/acetic acid, establishes a novel synthesis of 1,4-diphenylnaphthalene (VI). The new synthesis of VI may be considered as an extension of our previous finding for the synthesis of 1,2-diarynaphthalenes, *e.g.* II.

We also have investigated the action of phenylmagnesium bromide on *o*-quinone dibenzimides, *e.g.*, *o*-benzoquinone dibenzimide (VII). When VII is treated with phenylmagnesium bromide, followed by hydrolysis, a colorless compound, believed to have a structure like VIII and which is under further investigation, is obtained.



On the other hand, when 4-methyl-*o*-benzoqui-

(1) A. Mustafa and M. Kamel, *J. Am. Chem. Soc.*, **77**, 5630 (1955).

(2) A. Haller and A. Guyot, *Compt. rend.*, **138**, 1251 (1904).