THE REDUCTION OF 1,2,3-BENZOTRIAZOLE AND ITS *N*-METHYL DERIVATIVES BY SODIUM IN LIQUID AMMONIA

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INTRODUCTION

In the course of a series of experiments on the salt-forming power of the 1,2,3-triazoles, 1,2,3-benzotriazole was treated with sodium in liquid ammonia. It was thought that the hydrogen of the heterocyclic nucleus would be displaced by sodium with the formation of hydrogen gas. Experiments demonstrated, however, that sodium reacts with 1,2,3-benzotriazole in a 1:1 ratio without the liberation of hydrogen. Subsequent experiments indicated that the benzene nucleus is hydrogenated probably to a dihydro-1,2,3,-benzotriazole so that the reaction may be formulated



Moreover, sodium is entirely ineffective in converting a larger portion of the 1,2,3-benzotriazole to the dihydro compound. Here is a definite case where "nascent" (presumably atomic) hydrogen is a more effective reducing (hydrogenating) agent than the ammonated electron $(Na + xNH_3 \rightleftharpoons Na^+ + \epsilon^- \cdot xNH_3)^1$

The literature records cases (1) where the theoretical amount of hydrogen has not been obtained in the reaction of an ammonia solution of sodium with compounds containing replaceable hydrogen,² and (2) where it has been postulated that nascent hydrogen is responsible, in whole or in part, for the products obtained by sodium reductions in ammonia.³ In most instances of this kind, complete quantitative data is unavailable, and in

¹ For a review of solutions of metals in liquid ammonia see FERNELIUS AND WATT, Chem. Reviews, **20**, 195–258 (1937).

² FERNELIUS AND WATT, loc. cit., pp. 217, 222, 246.

³ Fernelius and Watt, *loc. cit.*, pp. 232, 240, 244–5.

no instance has such a reaction been studied thoroughly. Wooster and Godfrey⁴ have observed that the system Na—NH₃—H₂O reduces toluene whereas the systems Na—NH₃ and Na—NH₃—H₄⁺ are totally ineffective. Consequently, they recommend that water not be used to destroy the excess of sodium customarily employed for reductions in liquid ammonia but instead that ammonium salts or an ammonolysis catalyst (e.g., iron) be used. The results of the work described here leave some doubt as to the reliability of this suggestion.

Other investigators⁵ have shown that an ammonia solution of nitroguanidine is readily reduced to aminoguanidine by sodium in the presence of ammonium chloride whereas sodium alone yields an indefinite mixture. It is not clear from the published reports whether the failure to obtain 100 per cent. yields of aminoguanidine is to be attributed to side reactions or to the generation of *insufficient* hydrogen to effect complete reduction. To settle the question it would be necessary to determine what fraction of the total hydrogen generated is retained by the compound undergoing reduction.

EXPERIMENTAL

Preparation of 1,2,3-benzotriazole.—This substance was prepared by a slight modification of the method described by Fieser and Martin.⁶ The acetyl derivative of 1,2,3-benzotriazole was conveniently deacetylated by solution in liquid ammonia at -33° . After evaporation of the ammonia, the residue was dissolved in water, the solution was neutralized with acetic acid, and the benzotriazole allowed to crystallize; m.p. 98.5°. The average yield was 95%, starting with the purified acetate.

Anal. Calc'd for C₆H₅N₈: N, 35.3. Found: N, 35.2, 35.3.

Preparation of the N-methyl derivatives.—The 1- and 2-methyl derivatives of benzotriazole were prepared by the methylation of benzotriazole with dimethyl sulfate and sodium hydroxide according to the method of Krollpfeiffer, Rosenberg and Mühlhausen⁷ and also by methylation with diazomethane in ethyl alcohol. The yield in the first method was approximately 37% of 1-methyl-1,2,3-benzotriazole (m.p. 65°) and 25% of 2-methyl-2,1,3-benzotriazole, $(105-7^{\circ}/15 \text{ mm.})$. The second method resulted in a 15% yield of the 1-methyl and a 51% yield of the 2-methyl derivative.

Apparatus.—The apparatus used in this work was a modified form of the closed system described by Johnson and Fernelius⁸ which provided for (1) condensation of ammonia (usually about 150 ml.), (2) stirring of the solution by means of a current of gaseous ammonia, (3) addition of a known weight of sample, (4) alternate addition of weighable quantities of alkali metal and ammonium salt without opening

⁴ WOOSTER AND GODFREY, J. Am. Chem. Soc., 59, 596 (1937).

⁵ FULLER, LIEBER, AND SMITH, J. Am. Chem. Soc., 59, 1150 (1937).

⁶ FIESER, AND MARTIN, *ibid.*, 57, 1838 (1935).

⁷ KROLLPFEIFFER, ROSENBERG, AND MÜHLHAUSEN, Ann., 515, 124 (1935).

⁸ JOHNSON AND FERNELIUS, J. Chem. Educ., 6, 444-447 (1929).

of the system to the air, (δ) quantitative collection of gases evolved during reaction, and (δ) complete removal of ammonia prior to the working up of the product.

1,2,3-Benzotriazole and sodium.—1,2,3-Benzotriazole dissolved in liquid ammonia (very soluble) reacted rapidly with sodium without the evolution of gas. The solution remained clear until approximately 0.82 gram atom of sodium had been added when it became yellow. This color intensified upon further reaction and was orange-yellow near the end-point (dark-green, due to the blue color of dissolved sodium). The average of five runs gave a ratio of 1.05:1.00 for gram atoms of sodium/ moles of triazole. Excess of sodium over this ratio resulted in no further reaction over a period of four hours.

The yellow product remaining after evaporation of the ammonia was readily soluble in water. Upon neutralization with hydrochloric acid a yellow-brown precipitate formed, which darkened rapidly in contact with air. Further addition of acid dissolved the precipitate to form a dark-red solution. With small quantities of material it was not possible to isolate a pure compound, but with 0.1 mole of triazole a dark-red precipitate was obtained by working at 0° with the minimum amount of water and treatment with aqua regia. After filtering and thorough washing with ether, the red material melted sharply at 137–137.6°. It was extremely soluble in water, ethanol, and acetone, but only slightly soluble in ether, ligroïn, and chloroform. Yield: 5 g. from 10 g. (0.083 moles) of 1,2,3-benzotriazole.⁹

Exhaustive ether extraction of the solution remaining after the precipitation of the above material together with the washings, yielded a residue which upon solution in hot water, charcoal clarification, and crystallization melted at 98.5° and showed no depression in melting point when mixed with 1,2,3-benzotriazole. Yield: 4.768 g., or 47.5% of the original triazole.

1,2,3-Benzotriazole, sodium, and ammonium bromide.—After addition of sodium to a solution of 1,2,3-benzotriazole until the end-point was reached, the reaction mixture was treated alternately with sodium and ammonium bromide until a considerable quantity of hydrogen gas had been liberated (this usually represented a fivefold excess of sodium over the amount required for the initial end-point). During the early stages of the titration, the neutral solution was yellow. This color, which could be discharged by excess ammonium bromide, disappeared entirely near the end of the reaction. The weight of ammonium bromide required to just discharge the blue color of the excess sodium was exactly equivalent to this excess but the amount of gaseous hydrogen collected was always less than that which would be equivalent to the excess sodium:

| Gram atoms Na | 0.0858 | 0.0909 | 0.1017 |
|-------------------------------------|--------|--------|--------|
| Moles triazole | 0.0142 | 0.0152 | 0.0171 |
| Gram atoms H ₂ collected | 0.0286 | 0.0272 | 0.0322 |
| Gram atoms H ₂ taken up | 0.0430 | 0.0485 | 0.0524 |
| Gram atoms N ₂ collected | | 0.0034 | 0.0029 |
| H/mole | 3.01 | 3.19 | 3.06 |

It was found advisable to add a considerable excess of ammonium bromide at the *end* of the reaction so that the aqueous solution later obtained would not be strongly basic.

The presence of o-phenylenediamine in the reaction products was shown by forming, in separate runs, the phenazine derivative with phenanthraquinone and

 9 FIELDS (unpublished observations) has studied a number of reactions of this substance with the object of determining its structure. Since permanganate oxidation yields the 4,5-dicarboxylic acid of 1,2,3-triazole, it is very doubtful that the triazole nucleus has been hydrogenated.

the dibenzenesulfonyl derivative with benzenesulfonyl chloride. The dibenzo [a, c] phenazine melted at 204-6°. The dibenzenesulfonyl derivative melted at 190-191.5°. Neither derivative showed any depression of melting point with authentic samples. In further runs, the dibenzoyl derivative was prepared, d. 305°; yields 48%, 43%.

Sodium 1,2,3-benzotriazolate, sodium, and ammonium bromide.—The soluble sodium salt of 1,2,3-benzotriazole was prepared by the reaction between excess sodium amide and the triazole. This salt did not discharge the color of a sodium solution even on long standing. On alternately treating such solutions with ammonium bromide and sodium the following results were obtained:

| Gram atoms Na | 0.1420 | 0.1546 |
|-------------------------------------|--------|--------|
| Moles triazole | 0.0161 | 0.0176 |
| Gram atoms H ₂ collected | 0.0489 | 0.0544 |
| Gram atoms H ₂ taken up | 0.0931 | 0.1002 |
| H/mole | 5.78 | 5.69 |
| Yield: N, N'-Dibenzoyl-o-phenylene | | |
| | | |

| Gram atoms K | 0.1113 | 0.1003 |
|---|---------|---------|
| Moles triazole | 0.0154 | 0.0139 |
| Gram atoms H ₂ collected | 0.0717 | 0.0631 |
| Gram atoms H ₂ taken up | 0.0242 | 0.0233 |
| H/mole | 1.57 | 1.67 |
| Yield: N, N' -dibenzoyl-o-phenylene diamine | 0.14 g. | 0.21 g. |
| | | |

2-Methyl-1,2,3-benzotriazole, sodium, and ammonium bromide.—A liquid ammonia solution of the 2-methyltriazole did not decolorize sodium. Ammonium bromide and sodium were then added alternately until a considerable volume of hydrogen had been collected. No gas was liberated until 5.65 equivalents had been generated. During the early stages of the titration, the neutral solution was yellow. This color which could be discharged by excess ammonium bromide disappeared entirely near the end of the reaction.

| Gram atoms Na | 0.1061 | 0.0979 |
|-------------------------------------|---------------|---------------|
| Moles triazole | 0.0149 | 0.0125 |
| Gram atoms H ₂ collected | 0.0185 | 0.0254 |
| Gram atoms H ₂ taken up | 0.0876 | 0.0725 |
| H/mole | 5.87 | 5.80 |
| Yield: dibenzo [a,c] phenazine | 2.98 g. (73%) | 3.06 g. (89%) |

1-Methyl-1, 3, 3-benzotriazole, sodium, and ammonium bromide. A suspension of the 1-methyltriazole did not discharge the color of dissolved sodium. The mixture was then treated alternately with ammonium bromide and sodium until a considerable volume of gas had been collected. The solution at the end-point was red-orange.

| Gram atoms Na | 0.0675 | 0.0927 |
|-------------------------------------|--------|--------|
| Moles triazole | 0.0113 | 0.0104 |
| Gram atoms H ₂ collected | 0.0159 | 0.0400 |
| Gram atoms H ₂ taken up | 0.0516 | 0.0527 |
| Gram atoms N ₂ collected | 0.0079 | 0.0096 |
| H/mole | 4.56 | 5.06 |

The product from reaction 1 was converted to the dibenzoyl derivative (light-tan) and recrystallized three times from 95% ethanol (white), m.p. 152.8-153.8°.

Anal.* Calc'd for $C_{21}H_{18}N_2O_2$: C, 76.3; H, 5.5; N, 8.5

Found: C, 75.9; 75.9; H, 5.4, 5.5; N, 9.0, 9.3.

The product from reaction 2 was converted to the dibenzenesulfonyl derivative and recrystallized four times from 95% ethanol (colorless needles), m.p. 156-157°.† Anal.‡ Calc'd for C₁₉H₁₈S₂O₄N₂: C, 56.7; H, 4.5.

Found: C, 57.2, 57.1; H, 4.4, 4.5.

DISCUSSION

The reactions described above demonstrate that hydrogen is not evolved in the reaction between a liquid-ammonia solution of 1,2,3-benzotriazole and sodium. Half of the 1,2,3-benzotriazole may be recovered at the end of the reaction; the other half is apparently reduced to an unstable dihydrobenzotriazole.¹⁰



The above mixture of salts, sodium 1,2,3-benzotriazolate alone, and the 1- and 2-methyl derivatives of benzotriazole are not affected by a sodium solution.

The generation of hydrogen by the interaction of sodium and the ammonium ion,

$$\mathrm{NH}_{4}^{+} + \epsilon^{-} \rightarrow \mathrm{NH}_{3} + \mathrm{H},$$

reduces sodium 1,2,3-benzotriazolate and the 2-methyl derivative to o-phenylenediamine,



* Microanalysis by H. S. Clark.

 \dagger Apparently the dibenzoyl and dibenzenesulfonyl derivatives of N-methyl-ophenylene diamine have not been described in the literature.

[‡] Microanalysis by J. H. Walker.

¹⁰ FRIES, GUTERBOCK, AND KÜHN, Ann., **511**, 214 (1934), state (without giving experimental details) that they have investigated the catalytic hydrogenation of 1,2,3-benzotriazole. With a palladium or platinum catalyst they obtained tetra-hydro-1,2,3-benzotriazole; with a nickel catalyst, o-phenylenediamine and ammonia.

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Although the uptake of hydrogen approaches six atoms in both cases, this value was never realized in practice probably because (1) the hydrogenation is accompanied by some splitting of the ring as evidenced by the presence of nitrogen in the gases collected and (2) the hydrogenation of the last portion of the triazoles is inefficient because of the low concentration. Since the uptake of hydrogen in the case of an equimolecular mixture of the sodium salts of 1,2,3-benzotriazole and its dihydro derivative is only slightly in excess of 3 atoms, it appears that the dihydro compound resists further reduction.

The hydrogenation of 1-methyl-1,2,3-benzotriazole is complicated by its insolubility and the marked splitting of the ring. In practice an uptake of 5 atoms of hydrogen has been obtained, but not 6 as would be expected,



The hydrogenation of 1,2,3-benzotriazole in basic solution where the hydrogen is liberated by the reaction,

 $K \rightleftharpoons K^+ + \epsilon^-; NH_3 + \epsilon^- \xrightarrow{Fe \text{ catalyst}} NH_2^- + H,$

is by no means as effective as hydrogenation with sodium and ammonium ion. This difference may be due to (1) the greater basicity of the solution, (2) the fact that hydrogen is liberated only at the surface of the iron, or (3) the possibility that iron promotes the combination of hydrogen atoms, $2 H \rightarrow H_2$. There seems to be no obvious reason why the hydrogen liberated from 1,2,3-benzotriazole and that from the ammonium ion should reduce the benzene ring in the first case and the heterocyclic ring in the latter.

Reduction by electrons vs. hydrogenation.—There are two widely accepted theories as to the mechanism of the reduction of organic substances by active metals. One view regards the active hydrogen formed by the reactions of the metal with a solvent as the effective agent. According to the other view organometallic compounds are first formed which are solvolyzed giving rise to the hydrogenated product.¹¹ Studies in liquid ammonia have brought to light a number of instances of this latter type of reduction. It is now evident that active hydrogen may also play an important rôle and that the effects of the two mechanisms may be separately evaluated, at least for the substances involved in these studies. The question is really one of the relative ease of addition of electrons and of hydrogen atoms. The triazole nucleus is stable toward electrons but is broken down by hydrogen atoms.

Destruction of excess sodium following a reduction.—The usual practice in using an ammonia solution of sodium as a reducing agent is that of adding an excess of metal and later destroying this excess by treatment with water or an ammonium salt. Since reduction may take place both before and after the addition of ammonium salt, it is desirable to know which is involved, or if both are. In case active hydrogen is effective, yields may be increased, or more extensive reduction obtained by providing those conditions which will yield an ample amount of such hydrogen. As an example, dibenzothiophene is converted to the dihydro derivative by sodium in liquid ammonia,¹² but is more completely reduced with excess sodium and ammonium bromide.¹³

The subject of reductions in ammonia presents another aspect. Suppose one wishes to obtain only the reduction due to the electron and not that due to active hydrogen. Suppose, further that it is desirable for speed, completeness, etc. to have an excess of sodium present initially. If the use of water, ammonium salts, and even ammonolysis catalysts, introduces complications, how may this excess metal be destroyed without liberating hydrogen or introducing other complications? Sodium nitrate reacts with three atoms of sodium without the evolution of any gas.¹⁴ The probable reaction is:

 $NaNO_3 + 3Na + NH_3 \rightarrow Na_2NO_2 + NaOH + NaNH_2$ ¹⁵

Preliminary studies indicate that sodium nitrate may be used safely and effectively to destroy excess sodium, provided the disodium nitrite so formed, is decomposed by ammonium salts before the evaporation of the ammonia. Advantage may also be taken of the fact that mercury, in

¹¹ For literature references see WOOSTER AND GODFREY, J. Am. Chem. Soc., 59, 596 (1937).

¹² Gilman and Jacoby, J. Org. Chem., **3**, 116 (1938).

¹³ CAPPEL AND FERNELIUS, unpublished observations.

¹⁴ BURGESS AND HOLDEN, J. Am. Chem. Soc., 59, 461 (1937).

¹⁵ For formation and properties of Na₂NO₂ see MAXTED, J. Chem. Soc., **111**, 1016 (1917); ZINTL AND KOHN, Ber., **61**, 189 (1928).

contact with an ammonia solution of a metal, removes the metal from ammonia. $^{16}\,$

Further studies on the relative reducing tendencies of the electron and active hydrogen are in progress.

We are indebted to Mr. Karl E. Blumenberg for help with the gas analyses involved in this work.

SUMMARY

1. 1,2,3-Benzotriazole reacts with sodium in ammonia solution to form equimolecular quantities of the sodium salts of 1,2,3-benzotriazole and its dihydro derivative. Active hydrogen $(NH_4^+ + \epsilon^-)$ reduces the former salt to *o*-phenylenediamine but not the latter.

2. An ammonia solution of sodium does not react with 1-methyl- or 2-methylbenzotriazole, nor with the sodium salts of 1,2,3-benzo- and dihydro-1,2,3-benzotriazole.

3. Active hydrogen (NH₄⁺ + ϵ^{-}) reduces 2-methyl-2,1,3-benzotriazole to *o*-phenylenediamine and 1-methyl-1,2,3-benzotriazole to *N*-methyl-*o*-phenylenediamine.

4. Hydrogen generated by the interaction of potassium and liquid ammonia in the presence of iron is relatively ineffective in reducing potassium, 1,2,3-benzotriazolate to o-phenylenediamine.

5. The bearing of these results on the general subject of reductions in liquid ammonia is discussed.

¹⁶ BERGSTROM, J. Am. Chem. Soc., 45, 2791 (1923).