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STUDIES IN THE DIARYL ACYL HYDRAZINE SERIES. I

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The diaryl acyl hydrazines of the type $ArNCOCH_3NHAr$ have been hitherto little investigated. The only previously known members of this series are mono-acetylhydrazobenzene,[1] mono-acetylbenzene-hydrazo-*p*-toluene,[2] and mono-acetylhydrazo-*p*-toluene.[1]

The acetylation of aromatic hydrazo compounds, by means of which the members of this group may be prepared, was undertaken by us to gain some knowledge of the relative reactivities of the N atoms of the hydrazo linking in unsymmetrical members of the series, of the type Ar′NHNHAr. The behavior of hydrazo compounds on rearrangement in acid solution has been thoroughly investigated[3] with reference to the effect of the presence of the more common substituent groups in the aryl nuclei. The effect of such structural modifications upon the hydrazine residue, however, has not previously been studied; it has been found possible by us to detect such changes by treatment with acetic anhydride, which had previously been shown, in the cases cited above, to yield mono-acetyl derivatives readily. We have therefore prepared and studied several of the mono-acetyl derivatives of the unsymmetrical hydrazobenzenes from this point of view.

The structures of these compounds were determined by reduction with phenylhydrazine. The present paper describes the preparation and identification of these compounds; an alternative method of identification involving oxidation of the acetyl derivatives, with the description of some new members of this series, and the bearing of this research upon the rearrangement of hydrazo compounds in acid solution, will be presented in a later communication. Of the compounds described here it was found that each of the following yields two isomeric mono-acetyl derivatives in approximately equal amounts: benzene-hydrazo-*p*-toluene, *p*-chlorohydrazobenzene and *p*-bromohydrazobenzene. Benzene-hydrazo-*o*-toluene yields a single mono-acetyl derivative. It is of interest to note also that we have observed in this series the kind of isomerism shown by monobenzoylhydrazobenzene, and described by Freundler.[4] Mono-acetyl-*p*-bromohydrazobenzene was isolated in three forms, one of which changed gradually into one of the others during several weeks.

The reduction of the mono-acetylhydrazo compounds by phenylhydrazine severs the nitrogen atoms of the hydrazo linking, yielding the corre-

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[1] Stern, *Ber.*, **17**, 380 (1884); Goldschmidt and Euler, *ibid.*, **55**, 616 (1922).

[2] Jacobson and Lischke, *Ann.*, **303**, 370 (1898).

[3] Jacobson, *ibid.*, **428**, 90–99 (1922).

[4] Freundler, *Compt. rend.*, **136**, 1554 (1903).

sponding amine and anilide. The reduction products are easily separated by treatment with dilute acetic acid, in which the amine dissolves while the amide remains undissolved. This reduction method has been applied successfully to the mono-acetyl derivatives of hydrazobenzene and benzene-hydrazo-*o*-toluene, and to one of each of the two isomeric mono-acetyl derivatives of benzene-hydrazo-*p*-toluene, *p*-chlorohydrazobenzene and *p*-bromohydrazobenzene.

In our early.experiments attempts were made to follow the reduction and judge of its completeness by measuring the volume of nitrogen evolved during the reaction, since phenylhydrazine on oxidation yields nitrogen as shown by the equation

$$C_6H_5NHNH_2 \longrightarrow C_6H_6 + N_2 + 2H$$

The volume of nitrogen evolved was in most cases less than the theoretical. Further addition of phenylhydrazine to the partly reduced acetylhydrazo compound resulted in the evolution of more nitrogen, even after an amount far in excess of the theoretical one mole had been added. Ammonia was also detected among the gaseous products of the reaction. These facts made it evident that the phenylhydrazine, in addition to its reaction with the acetylhydrazo compound, was undergoing self-oxidation–reduction

$$2C_6H_5NHNH_2 \longrightarrow C_6H_6 + N_2 + NH_3 + C_6H_5NH_2$$

Considering that phenylhydrazine boils at 242° with only slight decomposition, it seemed remarkable that decomposition should take place so readily at the temperature of these experiments (160–180°). In one experiment the rate of evolution of the nitrogen was measured and was found to increase rapidly for a time, as the reduction of the acetyl hydrazo compound progressed. It was evident that one of the reaction products catalyzed the self-oxidation–reduction of phenylhydrazine. A study of the behavior of phenylhydrazine at 160° in the presence of acetanilide and at 185° in the presence of acet-*m*-toluidide showed that both of these substances bring about rapid decomposition of the phenylhydrazine, while undergoing no change themselves. A similar effect has been reported by Just,[5] who observed that sulfanilic acid accelerated the self-oxidation–reduction of phenylhydrazine. A procedure, to be described in the experimental part, was finally developed whereby complete reduction of the hydrazo compound may be recognized.

For convenience in describing the acetylhydrazo compounds in the experimental part, the nitrogen atoms of the hydrazo linking will be designated as N and N′, N referring to the nitrogen atom attached directly to the unsubstituted benzene nucleus.

Experimental Part

The unsymmetrical hydrazo compounds were prepared by reduction of the corre-

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[5] Just, *Ber.*, **19**, 1207 (1886).

sponding azo compounds, the latter having been obtained by Wieland's[6] modification of Baeyer's[7] method. Treatment of the hydrazo compounds with acetic anhydride resulted in the mono-acetyl derivatives. The general procedures, which were substantially the same in all cases, will be briefly outlined.

Preparation of the Azo Compounds.—Equimolar amounts of nitrosobenzene and the appropriate amine were condensed according to Wieland's procedure. In practically all cases nearly pure crystalline products were readily obtained in yields of about 80% of the theoretical: **benzene-azo-*p*-toluene,** m. p. 71–72°, in agreement with Mills;[8] **benzene-azo-*o*-toluene,** b. p. 156–158° (corr.) at 4 mm. (Jacobson[9] reported this substance as a liquid at ordinary temperature); ***p*-chloro-azobenzene,** m. p. 88°, in agreement with Heumann and Mentha;[10] ***p*-bromo-azobenzene,** m. p. 88°, in agreement with Jacobson and Grosse.[11]

Preparation of the Hydrazo Compounds.—The azo compounds were reduced with zinc dust and glacial acetic acid in boiling alcohol. This method was found to be more convenient than that of Jacobson and Lischke[2] in which reduction was accomplished with zinc dust and sodium hydroxide solution. The procedure in a typical experiment was as follows. Glacial acetic acid was added dropwise to a mixture of zinc dust and a 10–15% solution of the azo compound in boiling 95% alcohol until the solution became colorless. The solution was filtered hot and the filtrate cooled rapidly in an ice-bath. In some cases the hydrazo compound crystallized from the cold solution; in others, it was necessary to add ice water slowly to the alcoholic solution to bring about precipitation. The crystals were filtered and allowed to dry. The solvent evaporates rapidly from the crystalline products obtained in this way and the danger of air oxidation to the azo compound is thus greatly minimized. The products obtained by this procedure were colorless and apparently quite free from the azo compounds: **benzene-hydrazo-*p*-toluene,** m. p. 87–88° (Jacobson and Lischke[2] give 86–87°); **benzene-hydrazo-*o*-toluene** m. p. 101–102°, in agreement with Jacobson;[9] ***p*-chlorohydrazobenzene,** m. p. 90–91° (Heumann and Mentha[10] report 89–90°); ***p*-bromohydrazobenzene,** m. p. 115° in agreement with Janowsky and Erb.[12]

Acetylation of the Hydrazo Compounds.—The procedure described by Stern[13] was employed. One part of the hydrazo compounds was dissolved in about three parts of freshly distilled acetic anhydride, and the mixture allowed to stand for several hours, usually overnight. The resulting solution was then added to about five parts of water and well shaken. The acetyl derivatives separated either as crystalline solids or as viscous oils which slowly solidified on standing. It was found that the structurally isomeric acetyl derivatives, when formed, could be separated by recrystallization from 95% alcohol. One of the isomers in each case was found to crystallize from the hot solution on cooling, while the second could be isolated by slow spontaneous evaporation of the mother liquor. As a class these compounds are colorless crystalline solids, rather soluble in alcohol, ether, chloroform and boiling benzene, and sparingly soluble in water and in ligroin.

N'-Acetylbenzene-hydrazo-*p*-toluene, m. p. 140–141° (corr.) in agreement with Jacobson and Lischke.[2]

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[6] Wieland, *Ber.*, **48,** 1107 (1915).

[7] Baeyer, *ibid.*, **7,** 1639 (1874).

[8] Mills, *J. Chem. Soc.*, **67,** 930 (1895).

[9] Jacobson, *Ber.*, **28,** 2544 (1895).

[10] Heumann and Mentha, *ibid.*, **19,** 1687 (1886).

[11] Jacobson and Grosse, *Ann.*, **303,** 320 (1898).

[12] Janowsky and Erb, *Ber.*, **20,** 358 (1887).

[13] Stern, *ibid.*, **17,** 380 (1884).

N-Acetylbenzene-hydrazo-*p*-toluene, needles, m. p. 124°.

Anal. Calcd. for $C_{15}H_{16}ON_2$: N, 11.66. Found (micro-Dumas): N, 11.75.

N-Acetylbenzene-hydrazo-*o*-toluene, m. p. 78°.

Anal. Calcd. for $C_{15}H_{16}ON_2$: N, 11.66. Found (micro-Dumas): N, 11.47.

N-Acetyl-*p*-chlorohydrazobenzene, m. p. 123–124°.

Anal. Calcd. for $C_{14}H_{13}ON_2Cl$: N, 10.74. Found (micro-Dumas): N, 10.62.

N′-Acetyl-*p*-chlorohydrazobenzene, m. p. 111–112°.

Anal. Calcd. for $C_{14}H_{13}ON_2Cl$: N, 10.74. Found (micro-Dumas): N, 10.82.

N′-Acetyl-*p*-bromohydrazobenzene, m. p. 83°, prisms from 90–120° ligroin.

Anal. Calcd. for $C_{14}H_{13}ON_2Br$: N, 9.18. Found (micro-Dumas): N, 8.97.

N-Acetyl-*p*-bromohydrazobenzene, rosets of prismatic crystals from alcohol, m. p. 117–118°.

Anal. Calcd. for $C_{14}H_{13}ON_2Br$: N, 9.18. Found (micro-Dumas): N, 9.42.

Isomeric Form of N-Acetyl-*p*-bromohydrazobenzene.—In the course of one experiment, N-acetyl-*p*-bromohydrazobenzene was recrystallized from alcohol containing about 10% of benzene. In addition to the N-acetyl derivative already described, a second product consisting of large cubical crystals was deposited on spontaneous evaporation of a part of the mother liquor. This substance melted at 88–89°. It was analyzed directly after isolation.

Anal. Calcd. for $C_{14}H_{13}ON_2Br$: N, 9.18. Found (micro-Dumas): N, 9.70.

After standing for two or three months in a closed vessel, the cubical crystals were found to have crumbled slowly to a white opaque powder. The latter melted at 117–118° and was identical with the stable N-isomer.

Identification of the Acetyl Derivatives.—A small amount (3–5 g.) of the acetyl derivative was heated with an equimolar amount of phenylhydrazine at 180° until the evolution of nitrogen and ammonia had ceased. This usually required about six hours. The mixture was then dissolved in 2–3 cc. of glacial acetic acid with slight warming and then treated with 5 cc. of water. The amide was precipitated as an oil which slowly solidified. The solid mass was then recrystallized from benzene or toluene. In those cases where isomeric compounds were obtained, one of the isomers only was identified by this procedure. The identity of the second isomer was established from the following considerations: (1) its non-identity with the first, (2) analysis, (3) transformation to the azo compound by hydrolysis of the acetyl group followed by oxidation with hydrogen peroxide. The following members of the above series were identified by phenylhydrazine reduction: N′-acetylbenzene-hydrazo-*p*-toluene, N-acetylbenzene-hydrazo-*o*-toluene, N′-acetyl-*p*-chlorohydrazobenzene and N′-acetyl-*p*-bromohydrazobenzene.

Effect of Anilides on the Self-oxidation–Reduction of Phenylhydrazine.—The reduction of N-acetylbenzene-hydrazo-*o*-toluene was conducted in one experiment to secure an approximate measure of the rate of evolution of nitrogen; 0.566 g. of the substance and 0.25 g. of phenylhydrazine were heated at 175–180° and the nitrogen evolved was collected over dilute hydrochloric acid in an inverted graduated cylinder. The volumes (cc.) evolved during successive five-minute intervals were (uncorr.): 5.0, 9.5, 12.5, 10.0, 7.0, 6.0, 4.0. The rapid increase in rate during the first fifteen minutes suggested the following experiments on the effect of acetanilide and acet-*m*-toluidide in the self-oxidation–reduction of phenylhydrazine.

(a) **Acetanilide.**—1.35 g. of acetanilide and 1.08 g. of phenylhydrazine were heated at 185° and the evolved gases collected over water in a graduated cylinder. The presence of ammonia in the gaseous products was detected by its odor and action on litmus, and a layer of benzene appeared on the surface of the water in the graduated cylinder. After the reaction had ceased, 110 cc. of nitrogen (corrected for temperature, pressure, water vapor and benzene vapor) had been collected. This corresponds almost exactly to the volume of nitrogen theoretically obtainable by the self-oxidation–reduction of phenylhydrazine (112 cc.). The reaction mixture solidified on cooling. The crystals after washing with benzene melted at 114–115° and were shown to be acetanilide by comparison with an authentic sample of the latter.

(b) **Acet-*m*-toluidide.**—0.822 gram of acet-*m*-toluidide and 0.608 g. of phenylhydrazine were heated at 150–160°, as in (a). The nitrogen evolved measured 63 cc. (corr.); the theoretical nitrogen volume is 63 cc. The reaction mixture was dissolved in 1 cc. of glacial acetic acid and the solution slowly diluted with 5 cc. of water. An oil separated which was washed with hot water and allowed to cool. It was then seeded with a small crystal of acet-*m*-toluidide and allowed to stand for twenty-four hours. The oil solidified completely; the crystals were pressed dry on filter papers and found to melt at 67–68°. The crystalline product was acet-*m*-toluidide which underwent no change during the reaction.

Modified Procedure for Reduction with Phenylhydrazine.—The point at which the reduction of the acetylhydrazo compound with phenylhydrazine is complete was determined in the case of a mono-acetylbenzene-hydrazo-*m*-toluene (not described in this communication) in the following manner: 1.33 g. (1 mol) of acetylhydrazo compound and 1.8 g. (3 mols) of phenylhydrazine were heated at 160° until gases ceased to be evolved. Then 0.16 g. of phenylhydrazine was added, the mixture again heated and the evolved nitrogen collected and measured. It was found that 25 cc. (corr.) was evolved; 0.16 g. of phenylhydrazine should yield 16.6 cc. when undergoing complete self-oxidation–reduction; the reduction of the acetyl hydrazo compound was therefore incomplete. An additional 0.16 g. of phenylhydrazine was added, the heating continued at 160°, and the volume of nitrogen again measured. This time 17.1 cc. (corr.) was collected, indicating that the reduction was practically complete, inasmuch as the newly added phenylhydrazine underwent only self-oxidation–reduction.

Summary

1. Several new diaryl acyl hydrazines have been prepared.

2. A method for their identification has been described.

3. The self-oxidation–reduction of phenylhydrazine has been shown to be accelerated by acetanilide and acet-*m*-toluidide.

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