[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

THE CONSTITUTION OF THE DICHLOROHYDROXY-ETHYLIDENE-BIS-NITRO-ANILINES

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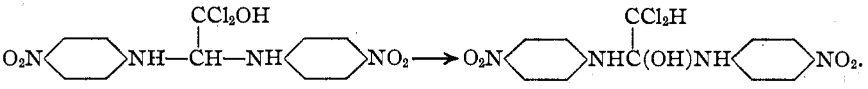
In an attempt to reduce the 3 isomeric Schiff's bases obtained by the condensation of chloral and the nitro-anilines Wheeler and Glenn[2] noted that treatment of these bases with alcoholic potash produced a brilliant red compound. The red compound, however, on purification became yellow and analysis showed that 1 chlorine atom had been replaced by an hydroxyl group, according to the equation: $CCl_3CH(NHC_6H_4NO_2)_2 + KOH = CCl_2OHCH(NHC_6H_4NO_2)_2 + KCl$. Sodium methylate gave a product containing the methoxy group in place of a chlorine atom and more recently Wheeler and Smith[3] prepared the ethoxy derivative, improved the general method of preparation by using acetone as the solvent for the reaction mixture and extended the reaction to *o*-nitro-aniline. The group now included the hydroxy, methoxy and ethoxy derivatives of the *o*- and *p*-nitro-anilines. No derivatives were obtainable from the Schiff base obtained from *m*-nitro-aniline.

Having lately some doubt as to the correctness of our idea in attaching the hydroxyl group to the carbon atom to which 2 chlorine atoms are already joined, we undertook a special study to determine the location of the hydroxyl group as well as the methoxy and ethoxy groups. No compounds are known that contain the hydroxyl group and chlorine attached to the same carbon atom. Such compounds, if formed, usually break up with the elimination of hydrogen chloride. In the compounds under review it seemed likely that the hydroxyl group had wandered to the α-carbon atom, producing a tertiary alcoholic group, thus,



We can readily imagine that the hydroxyl group momentarily takes the place of 1 of the 3 chlorine atoms attached to the β-carbon atom and then wanders to the α-carbon atom in order to form the more stable compound. In order to determine the position of the hydroxyl group the compound was decomposed with alkali. *p*-Nitro-aniline was readily identified among the decomposition products but no other compound of significance could

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[1] This paper constitutes Part I of a thesis submitted in June, 1923, to the Faculty of the University of North Carolina by Samuel C. Smith in candidacy for the degree of Doctor of Philosophy.

[2] Wheeler and Glenn, *J. Elisha Mitchell Sci. Soc.*, **19,** 63 (1903).

[3] Wheeler and Smith, THIS JOURNAL, **41,** 1862 (1919).

be isolated. Concd. sulfuric acid gave a very small quantity of a liquid of strange odor. This liquid was not investigated. Fruitful results however were obtained when the substance was treated with hot 30% sulfuric acid. The compound dissolved and when the solution cooled crystals were deposited which after purification melted at 127°. Neutralization of the mother liquor with sodium hydroxide caused the precipitation of *p*-nitro-aniline, melting at 147°. The course of the reaction appeared to be: $O_2NC_6H_4NHC(OH)(CCl_2H)NHC_6H_4NO_2 \longrightarrow H_2SO_4 \longrightarrow O_2NC_6H_4NHCOCCl_2H(p) + O_2NC_6H_4NH_2(p)$. The first product should be *p*-nitrodichloro-acetanilide. We could find no such anilide described in the literature, dichloro-acetanilide being the nearest to it. The preparation of the latter compound from dichloro-acetic acid and aniline requires the presence of phosphorus pentoxide.[4] Using this method with dichloro-acetic acid and *p*-nitro-aniline we obtained *p*-nitrodichloro-acetanilide which proved to be identical in physical and chemical properties with the decomposition product described above.

In view of the fact that this bis-nitro-aniline, as well as all of the others, splits easily, cleanly and quickly with dil. acid, giving in every case a product containing oxygen attached to the α-carbon atom, it seems clear that in these derivatives of Schiff's bases the hydroxyl and alkoxy groups are attached to the carbon atom which is joined to the nitrogen atoms. Since the acid decomposition of the alkoxy derivatives yields *p*-nitro-aniline (or *ortho*) and not the alkylated nitro-anilines, the reaction must be written:[5] $CCl_2HCOCH_3(NHC_6H_4NO_2)_2 + H_2SO_4 = CCl_2HCONH-C_6H_4NO_2 + NH_2C_6H_4NO_2 + CH_3HSO_4$.

Experimental Part

p-Nitrodichloro-acetanilide, $CCl_2HCONHC_6H_4NO_2$.

(a) **By Acid Decomposition of Dichlorohydroxy-ethylidene-bis-*p*-nitro-aniline.**—Ten g. of the hydroxyethylidene compound (m. p., 178°) was dissolved in 40 cc. of the 30% sulfuric acid and then heated for 2 minutes with a direct flame. The solution was then diluted with an equal volume of water and allowed to cool thoroughly. A heavy deposition of crystals of the anilide occurred. These melted at 124° and weighed 80% of the calculated amount. Recrystallization was best effected with 50% alcohol, 80% of the crude product being recovered in a pure condition. This new acetanilide forms pale yellow needles; m. p., 127°; $CCl_2HCOH(NHC_6H_4NO_2)_2 + H_2SO_4 = CCl_2HCONHC_6H_4NO_2 + NO_2C_6H_4NH_2.H_2SO_4$. *p*-Nitrodichloro-acetanilide is unstable toward alkalies but very stable in the presence of acids. It may be dissolved in acids, including nitric, and is unchanged on reprecipitation. It is insoluble in water and soluble in acetone, alcohol, benzene and chloroform.

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[4] Cech, *Ber.*, **10**, 1265 (1877).

[5] If phosphorous pentoxide is omitted in the reaction between dichloro-acetic acid and *o*-toluidine, the product contains 3 chlorine atoms and, therefore, is not dichloro-*o*-toluidide. This surprising result led to a study of the reaction between dichloro-acetic acid and a number of aromatic amines. Part II of Mr. Smith's thesis will deal with this unusual reaction. It will be published shortly. A. S. W.

Analysis. Subs., 0.3167: AgCl, 0.3694. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249) Cl, 28.51. Found: 28.85.

p-Nitro-aniline, the second product of the reaction, was readily isolated from the mother liquor by the addition of an excess of alkali, as yellow needles; m. p., 147°.

(b) **By Acid Decomposition of Dichloromethoxy-ethylidene-bis-*p*-nitro-aniline.**—The methoxy derivative (m. p., 177°) was treated in the same manner with hot 30% sulfuric acid. The insoluble product, after recrystallization from 50% alcohol, melted at 127° and consisted of yellow needles.

Analysis. Subs., 0.2556: AgCl, 0.2941. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249): Cl, 28.51. Found: 28.46.

$CCl_2HCOCH_3(NHC_6H_4NO_2)_2 + H_2SO_4 = CCl_2HCONHC_6H_4NO_2 + NO_2C_6H_4NH_2 + CH_3HSO_4$.

(c) **By Acid Decomposition of Dichloro-ethoxy-ethylidene-bis-*p*-nitro-aniline.**—The ethoxy derivative (m. p., 147°) was treated with sulfuric acid in the same manner and the same product, melting at 127°, was obtained.

Analysis. Subs., 0.2542: AgCl, 0.2919. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249): Cl, 28.51. Found: 28.41.

(d) **By the Action of Dichloro-acetic Acid on *p*-Nitro-aniline.**—To 5.0 g. of *p*-nitro-aniline was added 5.0 g. of phosphorus pentoxide and 5.0 g. of dichloro-acetic acid. The mixture was heated under a reflux condenser for 10 minutes. Cold water was added and the whole was well shaken. The crystalline product was separated and recrystallized from 50% alcohol as light yellow needles; m. p., 127°.

Analysis. Subs., 0.1422: AgCl, 0.1632. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249): Cl, 28.51. Found: 28.34.

o-Nitrodichloro-acetanilide, $CCl_2HCONHC_6H_4NO_2$

(a) **By Acid Decomposition of Dichlorohydroxy-ethylidene-bis-*o*-nitro-aniline.**—Five g. of the hydroxy derivative (m. p., 143°) was dissolved in 20 cc. of hot 30% sulfuric acid and heated for 2 minutes. An equal volume of water was added; as the solution cooled a liquid separated. When this was removed from the acid solution and washed well, it solidified. When an attempt was made to recrystallize it from alcohol, it separated again as an oil. However, it was obtained in crystallized condition by solution in alcohol, 70% strength, at 70° and cooling, as bright yellow plates; m. p., 70–72°.

Analysis. Subs., 0.0748: AgCl, 0.0866. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249): Cl, 28.51. Found: 28.64.

The compound is insoluble in water but soluble in acetone, alcohol, ether, benzene and chloroform. The yield was 70%. The *ortho* compound was also obtained by the action of hot sulfuric acid on the methoxy and ethoxy derivatives of *o*-nitro-aniline. In each case the product melted at 70–72° and crystallized in bright yellow plates.

(b) **By the Action of Dichloro-acetic Acid on *o*-Nitro-aniline.**—Five g. of *o*-nitro-aniline was mixed with 5.0 g. of phosphorus pentoxide and 5.0 g. of dichloro-acetic acid. Much heat was generated. The mixture was heated for a few minutes longer, and then poured into 200 cc. of cold water, whereupon a heavy oil separated, which, after it had stood overnight, solidified; yield, 6 g. It forms yellow plates; m. p., 70–72°.

m-Nitrodichloro-acetanilide, $CCl_2HCONHC_6H_4NO_2$

Since trichloro-ethylidene-bis-*m*-nitro-aniline gives no hydroxy or alkoxy derivatives with basic reagents[6] we could only use the direct method for preparing the *meta* compound. Equal amounts of *m*-nitro-aniline, phosphorus pentoxide and dichloro-acetic

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[6] Ref. 3, p. 1864.

acid were heated together. The product separated as an oil when the mixture was poured into water, but it solidified after standing a day. The crude product was light brown and melted at 65°. Purification by alcohol raised the melting point to 103°. It crystallizes in almost colorless needles, that are soluble in acetone, alcohol, ether, benzene or chloroform.

Analysis. Subs., 0.1591: AgCl, 0.1849. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249): Cl, 28.51. Found: 28.75.

Summary

1. The three new nitrodichloro-acetanilides were prepared.

2. The *p*-compound appeared as a decomposition product when dichloro-hydroxy-ethylidene-bis-*p*-nitro-aniline was treated with hot dil. sulfuric acid. Its production established the location of the hydroxyl group on the α-carbon. The methoxy and ethoxy derivatives gave the same anilide.

3. The *o*-nitrodichloro-acetanilide was similarly obtained.

4. The *ortho* and *para* compounds were also obtained by the action of dichloro-acetic acid on the nitro-anilines in the presence of phosphorus pentoxide.

5. The *meta* isomer could be obtained only by the direct method since the hydroxy and alkoxy derivatives of trichloro-ethylidene-bis-*m*-nitro-aniline cannot be prepared

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MERCURATED 1-METHYL-1,2-DIHYDRO-BENZOFURANS

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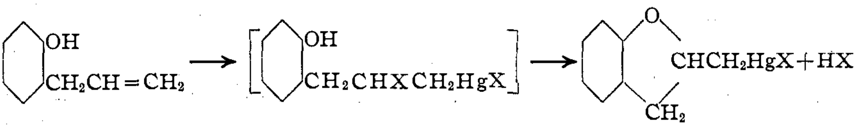
In a recent paper by Roger Adams, F. L. Roman and W. N. Sperry,[2] involving a discussion of the structure of compounds produced from olefins and mercury salts, it was shown that mercury salts and *o*-allylphenol reacted readily to give mercurated 1-methyl-1,2-dihydro-benzofurans according to the following equation.



A study of the preparation of the corresponding compounds from mercury salts and substituted *o*-allylphenols, and a study of their chemical reactions had been made. In view of the fact that the mercurated 1-methyl-1,2-dihydro-benzofurans, in contrast to the compounds from mercuric salts

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[1] This communication is an abstract of a thesis submitted by L. E. Mills in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Adams, Roman and Sperry, THIS JOURNAL, **44**, 1781 (1922).