Summary

By electron diffraction investigation of the gases the structures of certain methyl compounds have been determined. Four tetramethyls with tetrahedral symmetry have the following bond distances: Si–C = 1.93 ± 0.03 Å., Ge–C = 1.98 ± 0.03 Å., Sn–C = 2.18 ± 0.03 Å., Pb–C = 2.29 ± 0.05 Å. Nitrogen trimethyl has a bond angle of 108 ± 4° with N–C = 1.47 ± 0.02 Å. In sulfur dimethyl and mercury dimethyl the interatomic distances are S–C = 1.82 ± 0.03 Å. and Hg–C = 2.20 ± 0.10 Å., respectively. These distances agree with the sums of covalent radii given by Pauling and Huggins.

In a discussion of previous data for the chlorides it is shown that relative electronegativities (or the existence of electric moments in the bonds) are not responsible for the shortening observed in some of the chlorides. This effect is instead probably due to the contribution of structures having double electron pair bonds. Further investigation is required to explain the observed deviations in the chlorides.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF H. S. NEWCOMB COLLEGE, TULANE UNIVERSITY]

Diazotization of Weakly Basic and Insoluble Amines. The Use of Pyridine, Quinoline and Isoquinoline as Solvents for the Amines

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A series of experiments in this Laboratory on the diazotization of 4-aminobiphenyl with the use of pyridine as a solvent for the amine[2] led the authors to an investigation of the use of pyridine as a solvent for other weakly basic and insoluble amines. The success of this work led to experimentation on the use of quinoline and isoquinoline as solvents.

The use of pyridine as a solvent for the difficultly diazotizable amines has been described by Krishna and Bhatia,[3] who reported the successful diazotization of tribromoaniline, 2,6-dichloro-4-nitroaniline, dibromo-*p*-aminobenzoic acid and dibromo-*p*-aminobenzaldehyde.

The experimental work described in this paper substantiates the conclusion so often expressed that the diazotization proceeds only with the substituted ammonium salt and never with the free amine.[4,5] As groups which decrease the basicity of the amine replace the hydrogen atoms in the benzene ring, the concentration of the ammonium salt in the aqueous solution is correspondingly decreased. In order to prevent this hydrolytic action, Schoutissen[5] found that it was necessary to use a large excess of strong mineral acid or a solvent which reduces the dissociating effect of water. With the use of pyridine, quinoline and isoquinoline as solvents for the weakly basic and insoluble amines, it is possible to introduce the amine into the diazotizing mixture, namely, sulfuric acid and sodium nitrite, so that the amine is evenly distributed throughout the mixture in a very finely divided condition. The amine solution is added slowly to the cold nitrosylsulfuric acid. The solvent seems to hold the amine in solution until the sulfate is formed, which in turn reacts with the nitrous acid that is liberated by the action of the solvent on the nitrosylsulfuric acid. It is to be noted, however, that even though all other quantities and factors are the same, complete diazotization of the amine is not obtained in a reasonable length of time unless the amine is entirely dissolved in the liquid that is being used as the solvent.

The excess of mineral acid that is necessary depends upon the solubility of the amine and the nature, number and position of the groups that are present in the benzene ring. A study of the acid concentrations used in the diazotization of the substituted amines, showed that when a relatively small volume of organic solvent was used, the more dilute acid solution is satisfactory except for 4,6-dibromo-2-nitroaniline and picramide. If, however, a much larger volume of solvent is necessary to dissolve the amine, then the stronger acid solution must be

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[1] The material of this paper is from the thesis of Gertrude Van Zandt, presented in partial fulfilment of the requirements for the degree of M.S. at Tulane University, June, 1935.

[2] Carolyn Samuel, Master's Thesis, Tulane University, June, 1934.

[3] Proc. 15th Indian Sci. Cong., 152 (1928).

[4] Witt, *Ber.*, **42**, 2953 (1909).

[5] Schoutissen, THIS JOURNAL, **55**, 4531 (1933).

used, although the final concentration of the diluted acid is approximately the same. The effect of solubility is illustrated by the diazotization of 2,6-dibromo-4-nitroaniline. The amine is very soluble in quinoline and is easily diazotized with the use of this solvent. When pyridine is used as the solvent, a large volume is necessary to dissolve the amine and complete diazotization results only when a stronger acid concentration is used. It was not found possible to use dilute hydrochloric acid described by Krishna and Bhatia[3] as being satisfactory for the diazotization of difficultly diazotizable amines, when pyridine was used as the solvent for the amines. Pyridine reacts vigorously with concentrated hydrochloric acid, and weaker solutions of hydrochloric acid do not furnish the concentration of mineral acid that is necessary for the diazotization of the very weakly basic amines. For this reason, sulfuric acid has been used almost exclusively and has been found to furnish sufficient acid concentration even for the diazotization of the least basic amine, picramide.

Even though sulfuric acid is the best mineral acid to furnish the necessary acid concentration, Schoutissen[5] showed by experiment that the sulfuric acid, used alone, combines with all the nitrous acid. In order to release the nitrous acid from the nitrosylsulfuric acid, he used phosphoric acid. Glacial acetic acid was used for the same purpose by Misslin[6] in the diazotization of picramide. The addition of pyridine, quinoline or isoquinoline to a solution of nitrosylsulfuric acid was found to release the nitrous acid. Thus besides acting as a solvent for the difficultly soluble amines, these tertiary amines, which do not reduce the concentration of the sulfuric acid appreciably, have another function, that of releasing the nitrous acid from the nitrosylsulfuric acid.

Even though the three solvents have the same function in the diazotization process, each has its advantages. Much heat is generated when pyridine is added to nitrosylsulfuric acid, and it is sometimes difficult to keep the temperature as low as necessary, while little heat is evolved when quinoline or isoquinoline is used. On the other hand, pyridine shows almost no tendency to hold the azo compound formed in a coupling process in solution, while quinoline and isoquinoline do hold the coupled product in solution, especially when a proportionately large volume of the solvent has been used. Moreover, quinoline and isoquinoline cannot be used with those amines the diazonium salts of which couple with β-naphthol in alkaline solution, since they separate out as oils.

Further work on the diazotization of amines with the use of these solvents followed by the Sandmeyer reaction is in progress.

Experimental Part

1. Diazotization with Pyridine

2,6-Dichloro-4-nitroaniline.—Three grams of sodium nitrite was added to a solution of 30 cc. of concentrated sulfuric acid and 15 cc. of water, which had been cooled to 10°. To this was slowly added 4.14 g. of 2,6-dichloro-4-nitroaniline dissolved in 15 cc. of pyridine. During the addition, the mixture was stirred mechanically and the temperature was maintained below 10°. The diazonium salt solution was stirred for a half hour after the amine-pyridine solution had been added. Twice the volume (120 cc.) of ice water was then added. Finally 2 g. of urea was added to remove excess nitrous acid, and the solution was stirred until foaming had ceased. The diazonium salt solution was filtered to remove a slight residue that seemed to result on the addition of the urea. To the clear solution 2.88 g. of β-naphthol dissolved in 10 cc. of pyridine was added, and coupling took place at once. The mixture was allowed to stand for an hour, and was then diluted with 200 cc. of water. The coupled product was filtered, washed with water and digested with 150 cc. of 25% alcohol on a water-bath for a half hour to remove adhering pyridine. The yield was quantitative. Recrystallization of 2,6-dichloro-4-nitrobenzene-azo-β-naphthol from toluene gave deep red needles, m. p. 219°.

3-Nitro-4-aminobiphenyl.—The 3-nitro-4-aminobiphenyl, m. p. 165.5°, was prepared by the nitration of 4-aminobiphenyl, obtained from Eastman Kodak Co.; 4.04 g. of 3-nitro-4-aminobiphenyl dissolved in 20 cc. of pyridine was added slowly to a cold mixture of 3 g. of sodium nitrite in a solution of 30 cc. of concd. sulfuric acid and 15 cc. of water. The diazotization was carried out in the usual way. Coupling took place immediately on the addition of 2.88 g. of β-naphthol dissolved in 10 cc. of pyridine to the clear diazonium salt solution. The coupled product was filtered, washed and digested with 25% alcohol. The 2-nitro-4-phenylbenzene-azo-β-naphthol formed fine red-brown crystals from toluene, m. p. 228°.

Anal. Calcd. for $C_{22}H_{15}O_3N_3$: N, 11.38. Found: N, 10.22, 10.06.

Picramide, 2,4,6-Trinitroaniline.—A solution of 60 cc. of concd. sulfuric acid and 21 cc. of water was cooled to 10° and 3 g. of sodium nitrite was added. This mixture was heated on a water-bath until it became clear (70°) and was then cooled to 0°; 4.56 g. of picramide dissolved in 30 cc. of pyridine was added during an hour and a half to the nitrosylsulfuric acid solution. During the addition, the mixture was stirred mechanically and the temperature kept below 10°. The diazonium solution was allowed to stand for two hours. To the concentrated solution 2 g. of urea was added. Very little foaming resulted, and it was not necessary to filter the clear solution. A solution of

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(6) Misslin, *Helv. Chim. Acta*, **3**, 626 (1920); *C. A.*, **15**, 61 (1921).

2.88 g. of β-naphthol in 10 cc. of pyridine was then added, and coupling took place immediately. The coupled product was allowed to stand for an hour, diluted with 300 cc. of water and filtered. It was washed and digested with 25% alcohol; yield quantitative. Recrystallization of 2,4,6-trinitrobenzene-azo-β-naphthol from toluene gave a brick-red powder, m. p. 147°.

3-Aminophenanthrene in Sulfuric Acid.—1.93 g. of 3-aminophenanthrene (a gift from Professor W. E. Bachmann of the University of Michigan), m. p. 87.5°, dissolved in 10 cc. of pyridine was added slowly to a cold solution of 15 cc. of concd. sulfuric acid and 7 cc. of water containing 1.5 g. of sodium nitrite. The diazonium salt solution was diluted with 50 cc. of ice water and treated with 1 g. of urea. To this was added 1.44 g. of β-naphthol dissolved in 5 cc. of pyridine. Coupling took place when the solution was made alkaline with sodium hydroxide. The coupled product was filtered and washed with water. The yield of the crude product was quantitative. The phenanthrene-azo-β-naphthol recrystallized from toluene gave fine, dark red crystals, m. p. 249°.

Diazotization of 3-Aminophenanthrene in Hydrobromic Acid.—A solution of 1.93 g. of 3-aminophenanthrene in 5 cc. of pyridine was added alternately with a solution of 1.5 g. of sodium nitrite in 4 cc. of water to 18 cc. of 40% hydrobromic acid, cooled below 4°. The diazotized solution was diluted with 50 cc. of ice water and treated with 1 g. of urea. It was now added to a solution of 1.44 g. of β-naphthol in sodium hydroxide. The yield of the crude product was quantitative. The recrystallized product melted at 249°.

2. Diazotization with Quinoline[7]

4,6-Dibromo-2-nitroaniline.—A solution of 5.91 g. of 4,6-dibromo-2-nitroaniline in 15 cc. of quinoline was diazotized in a reaction mixture of 3 g. of sodium nitrite in 40 cc. of concd. sulfuric acid and 15 cc. of water. Coupling took place when to the clear diazonium salt solution a solution of 2.88 g. of β-naphthol in 10 cc. of quinoline was added. The coupled product was filtered, washed and digested with 25% alcohol. The yield was quantitative. Recrystallization of the 4,6-dibromo-2-nitrobenzene-azo-β-naphthol from toluene gave red crystals, m. p. 250°.

Anal. Calcd. for $C_{16}H_9O_3N_3Br_2$: N, 9.32. Found: N, 9.46, 9.30.

3. Diazotization with Isoquinoline

Picramide.—A mixture prepared by adding 3 g. of sodium nitrite to a cold solution of 60 cc. of concd. sulfuric acid and 21 cc. of water was heated on a water-bath to 70° until clear; 4.56 g. of picramide dissolved in 50 cc. of isoquinoline on a water-bath was added as a thick suspension to the nitrosylsulfuric acid. The mixture was stirred mechanically and the reaction carried out at room temperature. The solution was diluted with a mixture of 30 cc. of concd. sulfuric acid and 35 cc. of water and allowed to stand for an hour with stirring. Two grams of urea was added. After the foaming had ceased, the solution was clear. Water was then added until a precipitate began to form. A solution of 2.88 g. of β-naphthol in 10 cc. of isoquinoline was then added. The mixture was allowed to stand, then diluted with water. The product was filtered, washed and digested with 25% alcohol. The yield was not quantitative, apparently because the isoquinoline held some of the coupled product in solution. Recrystallization from toluene gave 2,4,6-trinitrobenzene-azo-β-naphthol as a red powder, m. p. 147°.

Summary

1. A new method for the diazotization of weakly basic and insoluble amines has been devised with the use of pyridine, quinoline and isoquinoline as solvents for the amines. The diazotization of 2,6-dichloro-4-nitroaniline, 2,4-dinitroaniline, 3-nitro-4-aminobiphenyl, 2,4,6-tribromoaniline, 2,6-dibromo-4-nitroaniline, 4,6-dibromo-2-nitroaniline, 3-aminophenanthrene and 2,4,6-trinitroaniline has been carried out with the use of these solvents.

2. Complete diazotization is not obtained in a reasonable length of time unless the amine is entirely dissolved in the liquid that is being used as the solvent.

3. Two new compounds have been prepared: 2-nitro-4-phenyl-benzene-azo-β-naphthol, m. p. 228° and 4,6-dibromo-2-nitrobenzene-azo-β-naphthol, m. p. 250°.

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[7] Contributed by the Barrett Co.