[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Hypophosphorous Acid Deamination of Diazonium Salts in Deuterium Oxide

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In an earlier communication[1] it was reported that the deamination of *m*-nitrobenzenediazonium chloride by hypophosphorous acid[2] in water–deuterium oxide solution introduced no deuterium into the aromatic nucleus. This conclusion was based upon an analysis by infrared spectroscopy which we believed to be sensitive to 0.2–0.4 excess atom per cent. deuterium. Subsequent work has revealed that this conclusion was wrong. Deuterium is introduced into the aromatic ring and in agreement with other studies on the comparative rate of transfer of hydrogen atoms and deuterium atoms,[3] we find that the rate at which deuterium is introduced into the aromatic ring is $^1/_2$ to $^1/_6$ as fast as the rate at which hydrogen is introduced. In this communication our experiments are described together with some observations pertinent to the understanding of hypophosphorous acid deaminations.

Experimental[4]

Preparation of *m*-Deuteronitrobenzene.—To a hot solution of 50 g. (2.5 moles) of deuterium oxide,[5] 25 ml. of concentrated hydrochloric acid (0.31 mole of hydrogen chloride, 1.02 moles water) and 27.6 g. (0.2 mole) of *m*-nitroaniline was added 55 ml. of concentrated hydrochloric acid and the mixture was then cooled to −5 to 0°. While at this temperature, a solution of 14.4 g. (0.2 mole) of 97% sodium nitrite in 35 ml. (1.95 moles) of water was added dropwise over a period of an hour. The mixture was then filtered and the filtrate was again cooled in ice-salt to −5°.

To the filtered diazonium solution was added a pre-cooled solution of 50.0 g. (2.5 moles) of deuterium oxide and 66.0 g. (1.0 mole) of anhydrous hypophosphorous acid.[6] (This solution was allowed to stand at room temperature for twenty-four hours before use.) After addition was complete, stirring was continued for another hour at −5 to 0° and the reaction mixture was then placed in a refrigerator for twenty-four hours.

The reaction mixture was then extracted with ether, the ether extracts were evaporated and after adding 400 ml. of water, the residue was steam distilled. The distillate was then extracted with two 50-ml. portions of ether and the extracts were dried over anhydrous magnesium sulfate. Distillation gave 10–11.7 g. (41.48%) of a mixture of nitrobenzene and *m*-deuteronitrobenzene, b. p. 203–205°. Analysis for deuterium by a mass spectrometer[7] indicated the presence of 2.55 excess atom per cent. deuterium. Infrared analysis carried out with a Perkin–Elmer Model 12B spectrophotometer showed the infrared absorption curve of this sample to be identical with that of ordinary nitrobenzene in the region 2000–2300 cm.$^{-1}$.[8]

The experimental conditions which are described above are the best which we were able to obtain from a series of ten preliminary experiments carried out with water rather than deuterium oxide.

Preparation of *m*-Deuteroaniline Hydrochloride.—A solution of 12.3 g. (0.1 mole) of the mixture of nitrobenzene and *m*-deuteronitrobenzene in 100 ml. of alcohol and 10.7 ml. (0.11 mole) of concentrated hydrochloric acid was hydrogenated at 1–3 atmospheres over 1 g. of 10% palladium-on-carbon catalyst.[9] After reduction was complete, the catalyst was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The yield of the mixture of aniline hydrochloride and *m*-deuteroaniline hydrochloride, m. p. 196–198°, was 98%. Analysis for deuterium by a mass spectrometer[7] indicated the presence of 1.62 excess atom per cent. deuterium. Since the value calculated on the basis of no hydrogen–deuterium exchange during the hydrogenation is 1.60, it is evident no exchange took place. The infrared absorption curve of this sample in the region 2000–2300 cm.$^{-1}$ was identical with that of aniline hydrochloride.[8]

Preparation of Deuterobenzene.—The reaction was carried out by the procedure used for the preparation of *m*-deuteronitrobenzene except that 3.7 g. (0.04 mole) of aniline was substituted for 27.6 g. (0.2 mole) of *m*-nitroaniline and the other quantities of reagents were decreased accordingly (1 to 5 ratio). The product was isolated by heating the reaction mixture to 120° and collecting the benzene and deuterobenzene which distilled. After adding a few pellets of calcium chloride and decanting the dry liquid, 1.3 g. (41%) of a mixture of benzene and deuterobenzene was obtained. Analysis for deuterium by a mass spectrometer[7] indicated the presence of 1.84 excess atom per cent. deuterium. From infrared curves similar to those illustrated in Fig. 1 it could be estimated that the sample contained 1.8–2.0 excess atom per cent. deuterium.[8]

Isolation of Biphenyl and *p*-Terphenyl.—In another identical run carried out with aniline (18.6 g., 0.2 mole), the deuterium oxide dilutions were made with a solution of water–deuterium oxide containing 40.1% deuterium. After distillation of the benzene was complete, it was noticed that a tan solid was left in the reaction flask. This was extracted with ether and the ether was removed on a steam-bath. Water was then added to the residue and the mixture was steam distilled. An orange solid collected in the distillation flask. The steam volatile portion was collected on a filter and dried (1.8 g.). Upon recrystallization from alcohol 1.4 g. (9.1%) of a light colored solid, m. p. 69–70°, was obtained. It showed no mixed melting point depression with an authentic sample of biphenyl. The non-volatile tan residue was recrystallized from alcohol, m. p. 204–206°. A mixed melting point with an authentic sample of *p*-terphenyl[10] showed no depression. The yield of recrystallized material was 0.4 g. (2.6%). Analysis for deuterium by a mass spectrometer[7] indicated the presence of 0.34 excess per cent. deuterium in the biphenyl and 0.27 excess per cent. deuterium in the *p*-terphenyl.

Effect of Reagents upon the Formation of Biphenyl and *p*-Terphenyl During Deamination.—The reactions sum-

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[1] Alexander and Burge, THIS JOURNAL, **70**, 876 (1948).

[2] For a review of the deamination of diazonium salts with hypophosphorous acid see Kornblum in Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 262.

[3] For a recent study and a number of leading references see Westheimer and Nicolaides, THIS JOURNAL, **71**, 25 (1949).

[4] All melting points and boiling points are uncorrected.

[5] Obtained on allocation from the U. S. Atomic Energy Commission.

[6] Prepared by heating 50% aqueous hypophosphorous acid *in vacuo* at 30° until no more water could be removed.

[7] We are indebted to Dr. D. Rittenberg, College of Physicians and Surgeons, Columbia University, for all of the deuterium analyses mentioned in this paper which were carried out with a mass spectrometer.

[8] We are indebted to Dr. Foil A. Miller and Mrs. J. L. Johnson for the determination and interpretation of the infrared curves shown in this paper.

[9] Mozingo, "Organic Syntheses," Vol. **26**, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 78.

[10] Prepared by the method of Grieve and Hey, *J. Chem. Soc.*, **110** (1938).

marized in Table I were carried out as follows: A solution of benzenediazonium chloride (1.0 mole) was prepared in the manner already described and cooled to 0° in ice-salt. In those runs in which benzene and biphenyl were employed, these reagents (0.2 mole) were introduced at this point and the mixture was stirred vigorously. Hypophosphorous acid (50%) was then added dropwise in the amounts shown. After addition was complete, stirring was continued for four hours at 0° and the mixture then shaken mechanically for sixteen hours at room temperature. When the reaction was carried out in the presence of benzene, an additional portion of benzene (0.2 mole) was added before the shaking operation was commenced.

TABLE I

EFFECT OF ADDED BENZENE OR BIPHENYL UPON THE BY-PRODUCTS IN THE DEAMINATION REACTION (0.2-MOLE RUN)

Variation	By-products, g. Biphenyl	*p*-Terphenyl
1.0 mole H_3PO_2 (standard)	1.4	0.4
3.0 moles H_3PO_2[a]	0.9	.3
0.4 mole C_6H_6 + 1.0 mole H_3PO_2	1.4	.6
30.0 g. (0.2 mole) biphenyl + 1.0 mole H_3PO_2	30.0	.4

[a] Benzene as obtained in a yield of 55% from this run.

The products of the reaction were isolated by steam distillation. The steam volatile portion of the reaction mixture was collected, dried and weighed as crude biphenyl. It melted in the range of 63–70° and at 69–70° after one recrystallization.

To obtain the non-volatile *p*-terphenyl, the steam distilled reaction mixture was cooled and filtered. After drying, the granular solid melted at 180–200°. This material was considered to be crude *p*-terphenyl. After one recrystallization from alcohol the melting point rose to 204–206°.

Decomposition of Benzenediazonium Chloride in the Presence and Absence of Phosphoric Acid.—A solution of 0.4 mole of benzenediazonium chloride was prepared in the usual manner and split into two portions. Cold phosphoric acid (85%) was added to each in amounts of 38.0 g. (0.33 mole) and 115.0 g. (1.0 mole) and the mixtures were stored in the refrigerator overnight. Another run with benzenediazonium chloride (0.2 mole) was carried out in the same way but no phosphoric acid was added.

The reaction mixtures were then worked up in essentially the same way that has been described. Fractional distillation of the steam volatile portion gave phenol, chlorobenzene and a residue which on recrystallization from 20% aqueous alcohol melted at 138–144°. This material showed no melting point depression with an authentic sample of *p*-hydroxybiphenyl. The results of these runs are summarized in Table II.

TABLE II

DECOMPOSITION OF THE DIAZONIUM SOLUTION WITHOUT ADDED HYPOPHOSPHORUS ACID SOLUTION UNDER CONDITIONS IDENTICAL TO THOSE EMPLOYED FOR DEAMINATION (0.2-MOLE RUN)

Variation	Products,[a] % Chlorobenzene	Phenol	*p*-Hydroxybiphenyl
No H_3PO_2	21.0	56.4	10.0
0.33 mole H_3PO_4 added	16.5	44.6	18.2
1.0 mole H_3PO_4 added	12.5	38.8	15.3

[a] No biphenyl or *p*-terphenyl was isolated.

Results and Discussion

The Preparation and Analysis of Deuterated Aromatic Compounds.—In Fig. 1 is shown a series of infrared absorption curves obtained from known mixtures of benzene and deuterobenzene in the region of the C–D stretching frequency (2200–2300 cm.$^{-1}$ [11]). It is evident that 0.2% excess atom per cent. deuterium could be detected in a sample of benzene containing deuterobenzene. The infrared absorption curve of the nitrobenzene obtained by the reaction of a solution of *m*-nitrobenzenediazonium chloride containing 29.6 excess atom per cent. deuterium with a solution of hypophosphorous acid containing 62.5 excess atom per cent. deuterium, however, was found to be identical with that of ordinary nitrobenzene. Similarly no difference could be detected in the absorption curve of ordinary aniline hydrochloride with that prepared by the catalytic reduction of the sample of nitrobenzene prepared by deamination in deuterium oxide solution. It was on the basis of these analyses that we reported in our earlier communication[1] that no deuterium was introduced into the aromatic ring during the reaction.

As a result of this publication, Dr. D. Rittenberg at the College of Physicians and Surgeons of Columbia University very kindly offered to analyze our samples by a mass spectrometer. This type of analysis for deuterium, he has found, is accurate to better than 0.01 atom per cent. excess deuterium. *His determination showed that our sample of nitrobenzene actually contained 2.55*

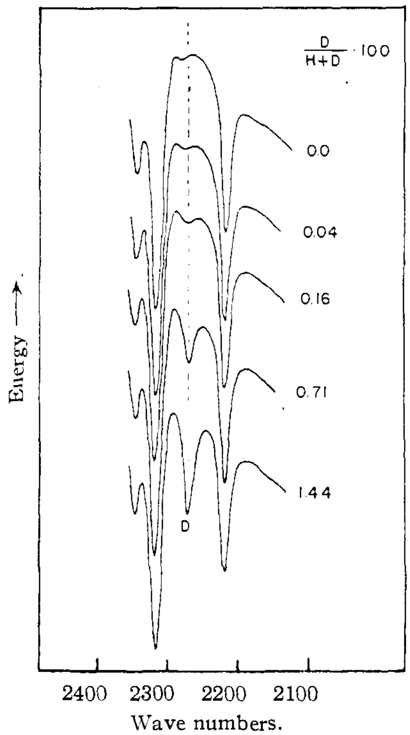

Fig. 1.—Infrared absorption curves obtained from known solutions of deuterobenzene in benzene.

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[11] Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, Inc., New York, N. Y., 1945, p. 364.

excess atom per cent. deuterium and that correspondingly the sample of aniline hydrochloride contained 1.62 excess atom per cent. deuterium. It is evident, therefore, that with nitrobenzene and aniline hydrochloride, the absence of a characteristic infrared absorption in the C–D stretching frequency cannot be taken as evidence for the absence of small amounts of deuterium in the meta position,

It will be observed that in this reaction too[3] deuterium and hydrogen atoms are not introduced into the aromatic ring in a ratio proportional to their concentrations in the reaction mixture. Since the maximum number of hydrogen atoms which could be introduced into the aromatic nucleus is one (*i. e.*, 20% excess atom per cent. deuterium), the nitrobenzene should have contained $20\% \times 29.6\% = 5.92$ excess atom per cent. dueterium calculated from the percentage of deuterium in the diazonium solution, or $20\% \times 62.5\% = 12.50\%$ deuterium calculated on the basis of the deuterium content of the hypophosphorous acid solution added.[12] Similarly, in the deamination of benzenediazonium chloride, the actual percentage of deuterium introduced (1.84) was lower than the values of 4.94 and 10.43 which would have been expected from the deuterium concentration in the diazonium solution and hypophosphorous acid solution, respectively. Hydrogen atoms, therefore, must have been introduced into the aromatic nucleus at a rate 2–6 times as fast as deuterium atoms. Since we do not know whether the hydrogen–deuterium equilibrium is established as fast as or faster than the deamination reaction, it is not possible from these experiments to decide which of the two values more nearly represents the true ratio of the rates of hydrogen and deuterium introduction.

Thus the deamination reaction may be used for the introduction of deuterium into a desired position of an aromatic ring but the efficiency of the reaction is poor. It is improbable that deuterium enters the ring at any other than the desired position since it has been shown that aniline hydrochloride does not undergo deuterium exchange at low temperatures.[13]

By-products in the Deamination Reaction.—In the deamination of benzenediazonium chloride, biphenyl (9.1%) and *p*-terphenyl (2.6%) are formed in addition to benzene (41%). These products must be due to the hypophosphorous acid present since omission of hypophosphorous acid from the reaction mixture leads to the formation of phenol, chlorobenzene and *p*-hydroxybiphenyl, but no biphenyl nor *p*-terphenyl (Table II). The appearance of biphenyl and *p*-terphenyl in the deamination reaction suggests the formation of free radicals, but we cannot be sure that deamination follows a similar path. It is evident that biphenyl and *p*-terphenyl do not arise exclusively by the coupling of phenyl or phenylene free radicals since both the biphenyl and *p*-terphenyl contain deuterium (0.34 and 0.27 excess atom per cent., respectively). Furthermore, we can say that the formation of these products involves one and only one deamination step, Thus if we assume that the ratio of the introduction of deuterium to hydrogen is the same for this reaction as it was for the deamination of aniline (1.84/4.94 or 1.84/10.43) depending upon whether it is calculated from the deuterium content of the diazonium solution or the hypophosphorous acid solution we can calculate that one deamination step in the process should give deuterium percentages of 0.36 or 0.37 for biphenyl and 0.24 or 0.25 for *p*-terphenyl.[14] These values are in fair agreement with those which were actually found.

It is not clear what the actual intermediates are in the formation of biphenyl and *p*-terphenyl. The reaction is reminiscent of the Gomberg–Bachmann synthesis of biaryls[15] in which it is generally accepted that a phenyl free radical attacks an aromatic nucleus.[16] The data in Table I, however, imply that neither benzene nor biphenyl are intermediates in the formation of biphenyl or *p*-terphenyl by deamination. Addition of these reagents to the reaction mixture produced no discernible increase in the amounts of polynuclear hydrocarbons formed.

Summary

1. The deamination of benzenediazonium chloride and *m*-nitrobenzenediazonium chloride with hypophosphorous acid in a solution of water and deuterium oxide can be used for the introduction of a deuterium atom into a benzene ring. The yields are of the order of 40–50% but the efficiency of the reaction is poor since hydrogen is introduced 2–6 times as fast as deuterium.

2. The absence of a characteristic infrared absorption in the C–D stretching frequency (2270 cm.$^{-1}$) cannot be taken as evidence of the absence of small amounts of deuterium in the meta position of nitrobenzene or aniline hydrochloride.

3. In addition to biphenyl, *p*-terphenyl is also formed as a by-product in the deamination of benzene diazonium chloride. These side-products apparently are due to the presence of hypophosphorous acid. When it is omitted from the reaction mixture chlorobenzene, phenol and *p*-

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(12) There can be no doubt that hypophosphorous acid undergoes complete exchange with deuterium oxide. See Erlenmeyer, Schoenauer and Schwarzenbach, *Helv. Chim. Acta*, **20**, 726 (1937); Erlenmeyer and Gärtner, *ibid.*, **17**, 970 (1934); and Franke and Mönch, *Ann.*, **550**, 1 (1941).

(13) Best and Wilson, *J. Chem. Soc.*, 239 (1946); Harada and Titani, *Bull. Chem. Soc., Japan*, **11**, 554 (1934).

(14) In these runs the deuterium concentration in the diazonium solution was 11.6 and 25.0% in the hypophosphorus acid solution. Hence, as a sample calculation, we would expect for *p*-terphenyl ((11.6)(1.84))/((18)(4.94)) = 0.24 excess atom per cent. deuterium based upon the deuterium concentration in the diazonium solution.

(15) Bachmann and Hoffman in Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

(16) For two leading references concerning this problem see Hodgson, *J. Chem. Soc.*, 348 (1948); and Hey and Waters, *ibid.*, 882 (1948).

hydroxybiphenyl are formed but no biphenyl or *p*-terphenyl could be isolated. Neither the manner in which these products are formed nor the nature of the deamination reaction is evident.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Silyl-Amino Boron Compounds[1]

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The existence of aminodiborane[2] and its N-methyl derivatives[3] leads to the question whether it is possible to find many similar derivatives involving a wide variety of types of substituting groups. As a step toward a full exploration of this subject, two new aminodiboranes, containing respectively the $(SiH_3)_2N$ and CH_3NSiH_3 units, have been prepared. As a study contributory to the planning of these preparations, the existence of the corresponding aminoborines and aminoboron dichlorides was investigated.

The preparation of such compounds requires a method somewhat different from the aminolytic processes used for the methyl derivatives, for there are no primary nor secondary amines in which the SiH_3 group is bonded to N. It is known, however, that the SiH_3 groups in tris-silylamine are quite labile, as in the fast reaction $(SiH_3)_3N + 4\ HCl \rightarrow 3\ SiH_3Cl + NH_4Cl$.[4] It thus becomes a reasonable prediction that electron receptors such as boron trichloride will react with $(SiH_3)_3N$ in much the same manner as HCl does. Accordingly, it was found that the reaction $(SiH_3)_3N + BCl_3 \rightarrow SiH_3Cl + (SiH_3)_2NBCl_2$ occurs cleanly at −78°, with indications of an intermediate addition compound such as $(SiH_3)_3NBCl_3$. The new compound N,N-bis-silyl-aminoboron dichloride is like the known $(CH_3)_2NBCl_2$[5] in several respects, including volatility and polymerization.

A somewhat similar experiment showed that the compound $(SiH_3)_3NBF_3$ forms reversibly in the temperature range −78 to −40°, but decomposes irreversibly at higher temperatures. This preliminary work was not so cleanly quantitative as that with boron trichloride, but it served to show the weakness of $(SiH_3)_3N$ as an electron donor.

A parallel reaction between tris-silylamine and diborane does not occur, evidently because the former is such a weak electron donor that it is not possible to form the intermediate complex $(SiH_3)_3NBH_3$, analogous to the very stable $(CH_3)_3NBH_3$.[6] Hence in order to produce the new compound $(SiH_3)_2NBH_2$ it was necessary to render the borine group more electron-receptive, by substitution of a more electronegative atom for one hydrogen. This was accomplished by the use of bromodiborane, the BH_2Br part of which was consumed by the reaction $2(SiH_3)_3N + 2B_2H_5Br \rightarrow 2SiH_3Br + B_2H_6 + 2(SiH_3)_2NBH_2$.

The resulting new volatile compound, bis-silyl-aminoborine, appears partly as a monomer and partly as a dimer from which the monomer cannot be regenerated. The monomeric form reacts with diborane below room temperature, to produce the new compound $(SiH_3)_2NB_2H_5$. This substance, N,N-bis-silyl-aminodiborane, is almost as volatile as the corresponding dimethyl compound but differs in its spontaneous inflammability and in the ease of its decomposition to form diborane and polymers of $(SiH_3)_2NBH_2$.

Methyl-bis-silylamine, $CH_3N(SiH_3)_2$,[7] behaves like $(SiH_3)_3N$ in a parallel series of reactions, but the products differ considerably from expectations based purely on analogy. The reaction with boron trichloride at −78° stops at the stage shown by the equation $CH_3N(SiH_3)_2 + BCl_3 \rightarrow SiH_3Cl + (CH_3NSiH_3)BCl_2$, but at higher temperatures a second stage is rapidly completed according to the equation $3(CH_3NSiH_3)BCl_2 \rightarrow 3SiH_3Cl + (CH_3NBCl)_3$. The resulting trimer appears to be N,N′,N″-trimethyl-B,B′,B″-trichloroborazole, a new compound which is formed quantitatively by this process.

The first step of the reaction of methyl-bis-silylamine with bromodiborane at −78° probably is $2CH_3N(SiH_3)_2 + 2B_2H_5Br \rightarrow 2SiH_3Br + B_2H_6 + 2(CH_3NSiH_3)BH_2$, but if so the hypothetical N-methyl-N-silylaminoborine is rapidly removed by at least three reactions at −78°: a polymerization–decomposition yielding major proportions of silane, a split yielding a trace of N,N′,-N″-trimethylborazole, and the addition of diborane to form the relatively stable new compound $(CH_3NSiH_3)B_2H_5$, N-methyl-N-silylaminodiborane. This spontaneously inflammable liquid is a little more volatile than $(SiH_3)_2NB_2H_5$ but less so than $(CH_3)_2NB_2H_5$. Its decomposition (slow at room temperature but rapid at 50°) yields diborane and the products ascribed to the hypothetical $(CH_3NSiH_3)BH_2$.

Like bromodiborane, dimethylboron bromide reacts with tris-silylamine to liberate bromosilane.

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[1] Presented in part in the Symposium on Structural Problems in Inorganic Chemistry at the 115th (San Francisco) National Meeting of the American Chemical Society, March, 1949.

[2] Schlesinger, Ritter and Burg, THIS JOURNAL, **60**, 2297 (1938).

[3] Burg and Randolph, *ibid.*, **71**, 3451 (1949).

[4] Stock and Somieski, *Ber.*, **54B**, 743 (1921).

[5] Wiberg and Schuster, *Z. anorg. allgem. Chem.*, **213**, 77 (1933).

[6] Burg and Schlesinger, THIS JOURNAL, **59**, 785 (1937).

[7] Emeléus and Miller, *J. Chem. Soc.*, 819 (1939).