[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Condensations. XV.[1] The Electronic Mechanism of the Diazo Coupling Reaction[2]

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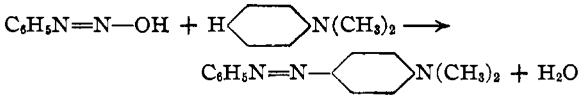
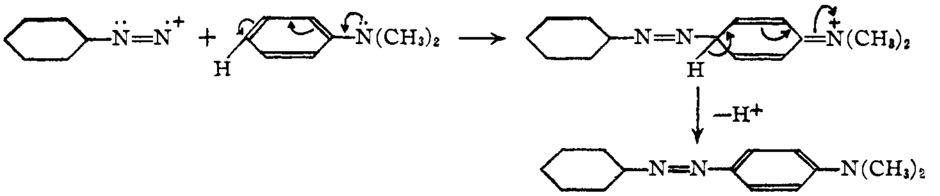
The diazo coupling reaction, which in most cases is effected in basic or weakly acidic solution, is generally considered to involve the condensation of the diazo hydroxide rather than the diazonium ion,[3] the following equation appearing frequently in the literature.[4]



The view that the diazo hydroxide condenses appears to be supported by the well-known fact that in the presence of alkali benzenediazonium chloride is converted into the alkali diazotate. Also, this view appears to be consistent with the kinetics of the diazo coupling reaction with phenols.[5] On the basis of electronic theories,[6] however, one should expect that the positively charged diazonium ion rather than the molecular diazo hydroxide would be the active condensing agent, since the former can serve as the active electron-accepting component. The diazonium ion may be represented in two resonance forms, (a) $C_6H_5-\overset{+}{N}\equiv\ddot{N}$ and (b) $C_6H_5-\ddot{N}=\ddot{N}^+$. Although resonance form (a) probably contributes largely to the structure of the ion, it may be assumed that at the approach of an electron-donating molecule, for example, dimethylaniline, the diazonium ion acquires the structure of resonance form (b) which contains the active nitrogen atom with only a sextet of electrons. The most obvious electronic mechanism may be represented as follows



This view[3] accounts for the fact that electron-attracting groups (like the nitro group) in the diazonium ion favor the coupling reaction, since the presence of the electron-attracting groups should cause resonance form (b) to contribute relatively more to the structure of the ion.

The fact that bases facilitate the coupling reaction is also in agreement with the view that the diazonium ion condenses, since the addition of a base to the medium converts the dimethylanilinium ion (present in the acidic medium in which the diazonium ion is prepared) into the free amine which is a stronger electron-donating reagent. Likewise, phenol is converted by a base into the more active electron-donating reagent, the phenoxide ion. It is possible that in certain cases the base might facilitate the coupling by removing the proton in the second step of the mechanism represented above; the two steps of the above mechanism may occur simultaneously. Of course the addition of hydroxyl ion (or other base) to the medium would also convert a portion of the diazonium ion into the diazo hydroxide, this reaction competing with the desired nitrogen–carbon condensation of the diazonium ion with the dimethylaniline; but in the presence of the proton donors that are commonly present in the coupling medium (aqueous solution), the diazo hydroxide would be in equilibrium with diazonium ion, the latter being stabilized through resonance. These changes may be represented as indicated.[6a]

Evidence has been obtained that, at least in anhydrous media, the diazonium ion couples. In dry pyridine, phenyldiazonium chloride couples readily with either β-naphthol or sodium β-naphthoxide to form 1-benzeneazo-napththol-2. These results show that the diazonium ion is capable of coupling. The argument that there

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[1] Paper XIV of this series, THIS JOURNAL, **62**, 2611 (1940).

[2] This investigation was supported by a grant from the Duke University Research Council.

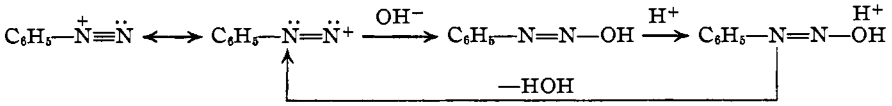
[3] Recently, Hammett in his excellent book on physical organic chemistry considers that the diazonium ion undergoes the coupling reaction; see Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 314.

[4] Theories involving various intermediates have been postulated on the basis that the diazo hydroxide condenses. See especially, Saunders, "The Aromatic Diazo Compounds and their Technical Applications," Edward Arnold and Co., London, England, 1936, p. 118; Walker, *J. Soc. Dyers and Colourists*, **39**, 293 (1923).

[5] Conant and Peterson, THIS JOURNAL, **52**, 1220 (1930).

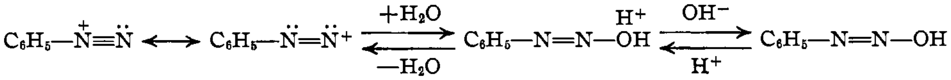
[6] For a discussion of the electronic theory of carbon–carbon condensations see Hauser and Breslow, *ibid.*, **62**, 2389 (1940).

[6a] The double-headed arrow is used to illustrate resonance forms: see especially Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.



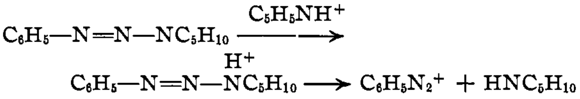
$$\begin{tikzcd}[column sep=small] C_6H_5\text{—}\overset{+}{N}\equiv\ddot{N} \arrow[r, leftrightarrow] & C_6H_5\text{—}\ddot{N}=\ddot{N}^+ \arrow[r, "OH^-"] & C_6H_5\text{—}N=N\text{—}OH \arrow[r, "H^+"] & C_6H_5\text{—}N=N\text{—}\overset{H^+}{OH} \arrow[ll, bend left, "\text{—}HOH"] \end{tikzcd}$$

or



$$C_6H_5\text{—}\overset{+}{N}\equiv\ddot{N} \longleftrightarrow C_6H_5\text{—}\ddot{N}=\ddot{N}^+ \xrightleftharpoons[\text{—}H_2O]{+H_2O} C_6H_5\text{—}N=N\text{—}\overset{H^+}{OH} \xrightleftharpoons[H^+]{OH^-} C_6H_5\text{—}N=N\text{—}OH$$

might be formed first a molecular oxy-azo compound (analogous to diazo hydroxide in aqueous solution) which then couples with unchanged β-naphthol appears to be invalidated by the fact that under comparable conditions the analogous nitrogen-azo compound, benzene diazopiperidide,[7] fails to couple with β-naphthol or its anion. These results become even more convincing when one considers that the addition of pyridinium chloride to the solution of benzene diazopiperidide and β-naphthol (or sodium β-naphthoxide) brings about some coupling almost immediately. The addition of the pyridinium ion effects the decomposition of the benzene diazopiperidide to form piperidine and the benzenediazonium ion, the latter coupling with the β-naphthol.[8] The decomposition of the diazopiperidide in the presence of pyridinium ion may be represented as follows



$$C_6H_5\text{—}N=N\text{—}NC_5H_{10} \xrightarrow{C_5H_5NH^+}$$

$$C_6H_5\text{—}N=N\text{—}\overset{H^+}{N}C_5H_{10} \longrightarrow C_6H_5N_2^+ + HNC_5H_{10}$$

It should be mentioned also that, when sufficient triethylamine is present in the pyridine solution of benzene diazopiperidide and β-naphthol, the addition of pyridinium ion fails to bring about coupling. Apparently the triethylammonium ion and also β-naphthol are not sufficiently strong proton donors to decompose the diazopiperidide.

In the accompanying paper, Bartlett and Wistar[9] point out that the earlier kinetic results with phenols[5] are not inconsistent with the view that the diazonium ion condenses. From a study of the kinetics of the reaction with certain amines these workers conclude that the diazonium ion and not the diazo hydroxide couples.

Experimental[10]

Preparation and Purification of Materials.—Amyl nitrite was prepared according to the method of Noyes.[11] It was dried over "Drierite" but was not distilled.

Phenyldiazonium chloride was prepared from aniline hydrochloride (Eastman Kodak Co.) and amyl nitrite essentially according to the method described by Gattermann and Wieland.[12] In order to obtain a product free from aniline hydrochloride, an excess of amyl nitrite was used. The phenyldiazonium chloride was dried overnight in a vacuum desiccator before using.

Benzene diazopiperidide (yellow crystals) was prepared according to the method of Holleman and Beekman,[13] recrystallized three times from alcohol at room temperature and dried *in vacuo;* m. p. 42.0–42.5°.

β-Naphthol (Eastman) was recrystallized from a mixture of benzene and ligroin (b. p. 70–90°) and dried; m. p. 122.5–123.0°. Pyridine (Eastman) was dried over Drierite and distilled through a Widmer column; b. p. 114–115°.

Coupling of Phenyldiazonium Chloride with β-Naphthol.—Phenyldiazonium chloride, prepared from 3.5 g. (0.027 mole) of aniline hydrochloride as described above, was suspended in 25 cc. of pyridine and the mixture chilled in an ice-bath. To this was added drop by drop with stirring a solution of 3.6 g. (0.025 mole) of β-naphthol in 25 cc. of pyridine. The mixture was stirred in the ice-bath for an hour and then for an additional half-hour at room temperature. The solution was colored a deep red, very little precipitate being present. The solution was poured into a mixture of 50 cc. of concentrated hydrochloric acid and about 300 g. of ice. The resulting mixture was diluted with water to about 600 cc. and filtered. The red precipitate obtained was recrystallized from hot alcohol and was identified as 1-benzeneazonaphthol-2 (2.5 g.) by its melting point, 131.5–133°. The melting point recorded in the literature for this compound is 134°.[14] The acidic filtrate was extracted with ether, the ether dried and evaporated and the residue recrystallized from alcohol-water; 0.6 g. of β-naphthol, m. p. 121–122.5°, was obtained.

The yield of 1-benzeneazo-naphthol-2 was 40.3% of the theoretical amount; based on the β-naphthol used minus that recovered, the yield was 48.5%.

Coupling of Phenyldiazonium Chloride with Sodium β-Naphthoxide.—Sodium β-naphthoxide was prepared from 3.6 g. (0.025 mole) of β-naphthol in 50 cc. of dry ether and excess sodium. The clear ethereal solution was decanted from the excess sodium and added drop by drop to a chilled suspension of phenyldiazonium chloride (prepared from 3.5 g. of aniline hydrochloride) in 25 cc. of pyridine. The mixture was stirred at 0° for one hour and then poured into a mixture of 50 cc. of concentrated hydrochloric acid and 300 g. of ice. The red precipitate was filtered off and

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[7] Since oxy-azo compounds are difficult to isolate in the pure condition, the nitrogen-azo compound has been used.

[8] The results of Goldschmidt on the diazoamino rearrangement in an aniline–anilinium chloride medium may be explained in a similar manner: see Goldschmidt, *Z. Elektrochem.*, **36**, 662 (1930).

[9] Bartlett and Wistar, THIS JOURNAL, **63**, 413 (1941).

[10] All melting and boiling points are corrected.

[11] Noyes, THIS JOURNAL, **55**, 3888 (1933).

[12] Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Co., New York, N. Y., 24th ed., 1937, p. 286.

[13] Holleman and Beekman, *Rec. trav. chim.*, **23**, 226 (1904).

[14] Ciusa and Pestalozza, *Gazz. chim. ital.*, **41**, I, 394 (1911).

recrystallized from hot alcohol; in this way 2.4 g. of 1-benzeneazo-naphthol-2, m. p. 132–133.5°, was obtained. The acidic filtrate was extracted with ether, the ethereal solution extracted with dilute sodium hydroxide and then dried. The ether was evaporated and the residue recrystallized twice from hot alcohol, 0.5 g. of 1-benzeneazo-naphthol-2, m. p. 132–133°, being obtained.

The total yield of 1-benzeneazo-naphthol-2 was 2.9 g. (46.8% of the theoretical amount based on the β-naphthol used as starting material).

Benzene Diazopiperidine and β-Naphthol.—Benzene diazopiperidide (4.7 g., 0.025 mole) and β-naphthol (3.6 g., 0.025 mole) were dissolved at room temperature in 75 cc. of dry pyridine saturated with pyridinium chloride (solution was approximately 0.33 *N* with respect to hydrogen chloride). A blank solution was prepared at the same time, using pyridine but no pyridinium chloride. Within a few minutes the solution containing pyridinium chloride had a definite red tinge as compared to the blank, the color deepening on standing. At the end of fifty hours no noticeable color change was observed in the blank when compared with a freshly prepared solution (both yellow). It was found that the addition of 0.001 g. of 1-benzeneazo-naphthol-2 to 5 cc. of the freshly prepared solution gave a definite red color.

Since a preliminary experiment showed that coupling took place on attempting to isolate the dye, the yield obtained from the pyridinium chloride solution was determined colorimetrically. By comparison with a standard solution containing an equivalent amount of benzene diazopiperidide and 1.00% of 1-benzeneazo-naphthol-2, the reaction mixture was found to contain 0.41 g. (6.6% of the theoretical amount) of coupling product at the end of fifty hours.

To determine whether an acid weaker than pyridinium chloride would effect coupling, 10.0 cc. of the blank was treated with 1.0 cc. of triethylamine (large excess) and 2.0 cc. of pyridinium chloride. No coupling took place within fourteen hours, the solution remaining yellow.

To determine the effect of decreasing the acidity of the medium, 25.0 cc. of the run which had stood for twenty-five hours was treated with 0.69 cc. of triethylamine (0.0025 mole of pyridinium chloride remaining uncombined). The solution, containing a precipitate presumably of triethylammonium chloride, was allowed to stand an additional twenty-five hours, making the total time the same as that for the run. Colorimetric analysis showed the presence of 0.55 g. of coupling product (8.9% of the theoretical amount). A decrease in acidity therefore increased the yield. The pyridine–pyridinium ion ratio which would give the maximum yield has not been determined.

To ensure that the color of the solutions was due to 1-benzeneazo-naphthol-2, this compound was isolated in another experiment in which a lower concentration of pyridinium chloride was used than in the experiment described above. The product was isolated in the following manner. After standing at room temperature for twenty-four hours, the red solution was poured into a mixture of concentrated hydrochloric acid and ice and the acid solution heated to boiling to destroy the diazonium salt. The mixture was cooled, filtered and the product, after recrystallization from hot alcohol, melted at 133–134°. The yield of 1-benzeneazo-naphthol-2 was 16% of the theoretical amount. Part of the coupling product, however, was probably formed during the working-up process, since a freshly prepared pyridine solution (yellow in color) of benzene diazopiperidide and β-naphthol worked up in the same manner gave a 2% yield of the dye.

Benzene Diazopiperidide and Sodium β-Naphthoxide.—Sodium β-naphthoxide was prepared from 1.4 g. (0.01 mole) of β-naphthol in 20 cc. of dry ether and excess sodium in an atmosphere of nitrogen. The clear yellow solution was added to a solution of 1.9 g. (0.01 mole) of benzene diazopiperidide in 30 cc. of pyridine. The solution turned deep blue (probably because of the action of oxygen on the sodium β-naphthoxide). At the end of fifteen hours the solution was colored green, but no red tinge was observable. The addition of 0.001 g. of 1-benzeneazo-naphthol-2 to 5 cc. of the solution gave a noticeable red color.

The solution was saturated with dry hydrogen chloride. It immediately turned orange and gradually red on standing.

Summary

1. Evidence is presented that the diazo coupling reaction involves the condensation of the diazonium ion rather than the diazo hydroxide as generally assumed.

2. In anhydrous pyridine phenyldiazonium chloride couples with β-naphthol or sodium β-naphthoxide to form 1-benzeneazo-naphthol-2. Benzene diazopiperidide couples with β-naphthol or its anion only in the presence of proton donors of sufficient strength.

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