

The Reaction of Certain Nitro Alcohols with Aromatic Diazonium Bases and/or Salts*

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Historical Survey

In 1890 Demuth and Meyer (2) allowed 2-nitroethanol to react with benzenediazonium chloride and obtained an orange-red substance which melted at 104°C. A repetition of the work confirmed their result with the exception that the substance melted at 108°C. The freshly prepared product was colorless, but turned yellow on standing. The mechanism may be explained by the Bülow reaction with hydrazones (1), the product being nitroformaldehydephenylhydrazone, $(\text{NO}_2)\text{HC}=\text{N}-\text{NH}-\text{C}_6\text{H}_5$.

The hydrazone formula for the product of coupling nitro- and similar reactive compounds with benzenediazonium chloride was suggested in 1888 by Victor Meyer (7).

In 1897 Pauwels (9) coupled the sodium salt of 2-nitro-1-pentanol with benzenediazonium chloride and obtained the hydrazone. The same product was obtained directly by the sodium salt of nitrobutane.

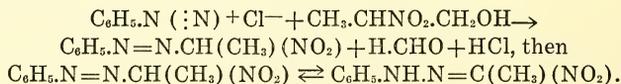
In 1895 Henry (4) treated the sodium salt of nitroisopropyl alcohol with benzenediazonium chloride and produced the phenylhydrazone, $\text{Me}.\text{CH}(\text{OH}).\text{C}(\text{NO}_2)=\text{N}-\text{NH}.\text{C}_6\text{H}_5$. Also from 1-nitro-2-butanol, he obtained a phenylhydrazone, $\text{Et}.\text{CH}(\text{OH}).\text{C}(\text{NO}_2)=\text{N}-\text{NH}.\text{C}_6\text{H}_5$. He also chlorinated 1-nitro-2-pentanol directly and obtained 1-chloro-1-nitro-2-pentanol. This was coupled with benzenediazonium chloride and yielded the phenylhydrazone as brilliant red needles, m.p. 92-94°C.

In 1896 Henry (5) coupled, 3,3,3-trichloro-1-nitro-2-pentanol with benzenediazonium chloride in an aqueous solution immediately after addition of sodium hydroxide. This yielded a phenylhydrazone, m.p. 129°C.

In 1901 Mousset (8) coupled the sodium salt of 1-nitro-2-hexanol with benzenediazonium chloride and obtained a phenylhydrazone with m.p. 108-111°C. The chloro-derivative was obtained as an oil.

In 1913 Rosenmund (10) coupled the sodium salt of 2-nitro-1-phenylethanol with benzenediazonium chloride and obtained the phenylhydrazone as fine red needles with m.p. 126°C.

In 1930 Jones and Kenner (6) prepared ω -nitroacetaldehydephenylhydrazone from 2-nitro-1-propanol and benzenediazonium chloride, (yellow plates, m.p. 149°C), according to the equations:

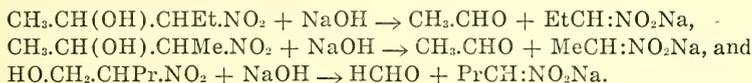


* An abstract of a thesis submitted to the Faculty of Purdue University in partial fulfillment of the requirements of the degree of Master of Science, February, 1944, by Carl I. Gochenour.

They also observed that with an increase in the complexity of the groups X and Y, the stability of the compound $X.CH(OH).CHY.NO_2$ toward alkali diminishes, as in the case of the aldols. For instance, whereas the hydroxymethyl derivatives prepared from nitroethane, 1-nitropropane, and 1-nitrobutane are convertible into their sodium salts, analysis of those compounds prepared from the hydroxyethyl derivative undergo decomposition by alkali. Feasley and the senior author studied the condensation of aromatic diazonium compounds with the nitroalkanes in 1942.

Theoretical

A study was made of the reaction between aromatic diazonium salts and certain nitroalcohols, as 2-nitro-1-butanol, 3-nitro-2-pentanol, 3-nitro-2-butanol, and 2-nitro-1-pentanol. The diazonium chloride was prepared in the usual manner in an excess of acid. It was neutralized with a slight excess of base in the cold and coupled with the salt of a nitroalcohol. It was observed that 3-nitro-2-pentanol, 3-nitro-2-butanol, and 2-nitro-1-pentanol are decomposed by alkali in accordance with the equations:

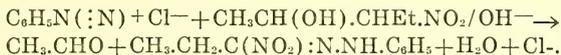


Under the same conditions, however, the desired sodium salt was obtained from 2-nitro-1-butanol:



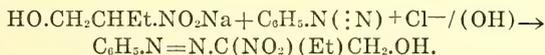
These observations confirm the report of Jones and Kenner (6).

Those alcohols which decompose in alkali form a hydrazone when coupled with an aromatic diazonium salt. The reaction between 3-nitro-2-pentanol and benzenediazonium chloride may be shown by:



The reaction was confirmed by reacting benzenediazonium chloride with 1-nitropropane. The same product was obtained by treating benzenediazonium chloride with 1-nitropropane, as evidenced by the same color, same crystalline structure, and identical melting points.

The reaction between the sodium salt of 2-nitro-1-butanol and benzenediazonium chloride may be shown by:



If, however, this product is not removed immediately from the alkaline solution by precipitation with hydrochloric acid, it will lose formaldehyde and form the hydrazone. Pauwels (9) formed the hydrazone from this reaction after letting the product stand for several days. In our studies this product was immediately removed from the alkaline solution in order to obtain the azo linkage instead of hydrazone formation. The linkage was confirmed by analysis for nitrogen by the Dumas method.

Most of the products prepared were not stable even though they were recrystallized several times from 95 per cent ethanol. Although they did not decompose rapidly, over a period of several weeks, they gave a dark oil. The nature of the decomposed material was not investigated.

Another phase of this work was the determination of the pH of the solution in which the coupling takes place. An attempt was made to correlate the yield and alkalinity of the coupling solution. The amine used in this investigation was *p*-chloroaniline. The yield of product obtained was a direct function, within certain limits, of the alkalinity with the minimum pH being about 10.8.

Experimental

In preparing these compounds a solution of the aromatic amine (0.2 mole) in 60 ml. of concentrated hydrochloric acid (sp. gr. 1.19) and 125 ml. of water is diazotized by the dropwise addition of 15 g. of sodium nitrate in water. The diazotized solution is then neutralized by pouring it with stirring into a suspension of 500 g. of ice in 500 ml. of 2*N* sodium hydroxide (41.3 g. of sodium hydroxide in 500 ml. of water). Immediately after neutralization in an excess of sodium hydroxide, a previously prepared solution of 0.2 mole of the nitro alcohol in 8.0 g. of sodium hydroxide and 250 ml. of water is poured in with stirring. The solution is stirred until coupling is completed and is then filtered in the cold to remove traces of unreacted diazotized material. The filtrate is immediately acidified with concentrated hydrochloric acid (sp. gr. 1.19) and the product is filtered. The compounds are purified by recrystallization several times from 95 per cent ethanol.

The physical properties of the compounds that have been highly purified and proven by chemical analysis for nitrogen are given in Table I.

Correlation Between pH Values and Yields

In determining the pH of the coupling liquor at which maximum yields are obtained, a stick-antimony electrode (11) was used.

The coupling was conducted by using diazotized *p*-chloroaniline and the sodium salt of 2-nitro-1-butanol. The same procedure was used throughout this series of experiments. The only variation was the amount of base used for the coupling medium. The results that were obtained are given in Table II.

These data indicate that the alkalinity of the coupling solution is a major factor for coupling compounds of this type.

Summary

1. Most nitroalcohols decompose in an alkaline medium and form hydrazones upon coupling with aromatic diazonium salts.
2. 2-Nitro-1-butanol will couple with aromatic diazonium salts without decomposition.
3. The yield, obtained from an amine and nitroalcohol which couple without decomposition, is greater in an alkaline medium.

TABLE I. Compounds Prepared, Purified, and Analyzed

Com- pounds	Exp. No.	Mol. Wt.	% Calc.	N ₂ found	Color	M.P. °C
1.	R.3	282	19.97	19.98	red	119-120
2.	R.11	301.9	13.9	14.0	orange	112.5-113.5
3.	R.12	257.46	16.31	16.64	orange	107.5-108
4.	R.15	257.46	16.31	16.75	red	78-79
5.	R.16	291.92	14.40	14.39	amber	93-94
6.	R.17	301.9	13.9	14.00	brown	84
7.	R.18	237	17.72	18.2	red	87-88
8.	S.3	252	22.22	22.23	red	117-118
9.	S.11	271.9	15.39	15.38	red	110-111
10.	S.12	227.46	18.46	17.98	red	106.5-107.5
11.	X.16	257.92	16.28	16.52	salmon	108-109
12.	Q.18	221	19.00	18.89	red	71-72

The twelve compounds referred to in the table are: (1) 2-nitro-2-(3-nitro-5-methylphenylazo)-1-butanol (2) 2-nitro-2-(4-bromophenylazo)-1-butanol (3) 2-nitro-2-(4-chlorophenylazo)-1-butanol (4) 2-nitro-2-(2-chlorophenylazo)-1-butanol (5) 2-nitro-2-(2,5-dichlorophenylazo)-1-butanol (6) 2-nitro-2-(2-bromophenylazo)-1-butanol (7) 2-nitro-2-(4-methylphenylazo)-1-butanol (8) 1-nitropropionaldehyde-(4-nitro-2-methylphenylhydrazone) (9) 1-nitropropionaldehyde-(4-bromophenylhydrazone) (10) 1-nitropropionaldehyde-(4-chlorophenylhydrazone) (11) 1-nitroacetaldehyde-(2, 5-dichlorophenylhydrazone) (12) 1-butyraldehyde-(4-methylphenylhydrazone).

TABLE II. Correlation Between pH and Yield

EMF	pH	% Yield	EMF	pH	% Yield
.6020	11.0	3.1	.7222	13.0	45.7
.6342	11.5	14.0	.7517	13.5	53.2
.6640	12.0	24.0	.7616	13.7	55.0
.6952	12.6	34.9	.7742	13.9	55.6

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