[CONTRIBUTION FROM PURDUE UNIVERSITY]

VII. THE CONDENSATION OF ARYL DIAZONIUM SALTS AND/ OR HYDROXIDES WITH SECONDARY NITRO ALKANES[1]

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HISTORICAL SURVEY

The fact that aromatic diazonium salts condense with nitro alkanes was first discovered in 1875 by Meyer and Ambühl (15). They allowed benzenediazonium sulfate to react with sodium nitroethane, obtaining an orange solid which they formulated as $C_6H_5N{:}NCH(NO_2)CH_3$ and found to possess acid properties. In attempting to prove the structure of this compound Meyer and Ambühl (16) reported a yellow transparent oil, $C_6H_5N{:}NC(NO_2)(CH_3)_2$, from the reaction of benzenediazonium nitrate on the potassium salt of 2-nitropropane. All attempts to isolate and purify this derivative were unsuccessful, hence there is no positive proof that this compound was obtained even in an impure form.

The same year (1875) Friese (10), working in Meyer's laboratory, reported the formation of nitroformazyl, $C_6H_5NHN{:}C(NO_2)N{:}NC_6H_5$, from benzenediazonium hydroxide and nitromethane. In the eighteen years that followed, Meyer and his students continued their study of the condensation of aromatic diazonium salts with 1-nitro alkanes (17), 3-nitropropene (1), and 1,3-dinitropropane (14). Duden in 1893 (9) reported a condensation with the potassium salt of dinitromethane.

Bamberger and his students, for a period of eight years starting in 1894, condensed 1-nitro alkanes with aromatic diazonium salts (2, 3, 4, 5, 6). Similar work was done by Hantzsch and Kissel on nitroethane (11, 12).

Ponzio and collaborators studied condensations of aromatic diazonium salts with aromatic dinitromethanes (19, 20, 26), with diphenylnitromethane (25), and with trinitromethane (28, 29). This group of workers did much to investigate the reactions and behavior of these compounds (21, 22, 23, 26, 27, 28, 29).

Later investigators have condensed aromatic diazonium salts with nitro alcohols (13), with trichloro-1-nitro-2-acetoxy alkanes (8), with methyl 2,4-dinitrophenylacetate (18), and with 1,5-dinitropentane (30).

THEORETICAL

In carrying out this reaction, the diazonium chloride is prepared in the usual manner in excess acid. It is then neutralized cold with a slight excess of base, and finally coupled with a salt of a secondary nitro alkane. The reaction

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between benzenediazonium chloride and the sodium salt of 2-nitropropane may be shown by:

$$C_6H_5N(\vdots N)^+\ {}^-Cl + (CH_3)_2C{:}N(\rightarrow O)ONa \xrightarrow{OH^-} C_6H_5N{:}NC(NO_2)(CH_3)_2 + NaCl.$$

Highly colored compounds result from these condensations. When the aryldiazonium chloride contains one or more auxochrome groups, the final compound is found to serve for dyeing silk, wool, or other animal fibers. When the coupling reaction is carried out in fibers of cotton or rayon, a fast color is obtained.

Not all of the compounds prepared by this condensation are stable and a number of them decompose even when cold. This behavior has been reported also by Ponzio and co-workers (22, 26) for the condensation product from any *para* substituted diazonium salt. They found that the *para* substituted derivatives, in dry organic solvents, gave first a benzoylarylnitrosohydrazine, $C_6H_5C({:}O)$-$N(NO_2)N(NO)C_6H_4X$, and then, in moist ether, benzoylazophenyl compounds of the type $C_6H_5C({:}O)N{:}NC_6H_4X$, which resulted from loss of three atoms of oxygen and two atoms of nitrogen (possibly as NO and NO_2).

It has been proved by Ponzio and others (7, 24, 25) that a nitro group in a few cases shifts from the aliphatic carbon atom to the *para* position of the benzene nucleus in the condensation.

In the normal coupling reaction, Ponzio (19) found that, starting with benzenediazonium acetate, sodium acetate, and the potassium salt of phenyldinitromethane, the expected salt was the first product formed. In dry benzene, chloroform, or carbon disulfide, this product was found to be transformed in the cold into the isomeric benzoylphenylnitronitrosohydrazine, $C_6H_5C({:}O)N(NO_2)$-$N(NO)C_6H_5$, while in the presence of water, ethyl alcohol, diethyl ether, or acetone it was found to go over into another isomer, phenylazophenyldinitromethane, $C_6H_5C(NO_2)_2N{:}NC_6H_5$.

It is apparent from the work in this laboratory that the compounds prepared from 2-nitropropane, which are more symmetrical, are more stable than those prepared from 2-nitrobutane. The compounds synthesized from 2-nitrobutane, however, have additional interest in that optical isomers are theoretically possible. No attempt has been made to separate the expected optical isomers.

The advantages of these condensation products over those prepared from primary nitroalkanes are quite important. They are more easily prepared and purified, since only one main organic product is formed. In primary nitro alkane condensations, one or two equivalents of the diazonium salt may be allowed to react to give compounds of various types such as $ArN{:}NCH(NO_2)R$; $ArNHN{:}C(NO_2)R$; and $(ArN{:}N)_2C(NO_2)R$. With nitromethane the products would be even more complicated. The compounds prepared from secondary nitro alkanes, moreover, have a stabler chromophoric group than those prepared from primary nitro alkanes, as evidenced by a 1-nitro alkane condensation product equilibrium:

$$ArN{:}NCH(NO_2)\cdot R \rightleftarrows ArNHN{:}C(NO_2)R.$$

In addition to the destruction of the desired azo linkage by the shift of a hydrogen atom, the resulting aryl hydrazone formed is much more subject to degradation under hydrolytic conditions. No such shift is possible in the condensation product from a secondary nitro paraffin.

TABLE I

AZONITRO ALKANES

COMPOUNDS	NITROGEN		COLOR	M.P., °C.
	Calc'd	Found		
1. 2-(Phenylazo)-2-nitropropane	21.7	21.6 ± .1	Yellow-red oil	(b.p. 98/0.7 mm.)
2. 2-(2-Nitrophenylazo)-2-nitropropane	23.5	23.3 ± .1	Dark brown	56.9
3. 2-(3-Nitrophenylazo)-2-nitropropane	23.5	23.6 ± .3	Yellow	71.2–72.2
4. 2-(3-Nitrophenylazo)-2-nitrobutane	22.2	22.1 ± .1	Yellow	63.3–63.7
5. 2-(2-Methyl-5-nitrophenylazo)-2-nitropropane	22.2	22.3 ± .1	Red-yellow	70.1
6. 2-(2-Methyl-5-nitrophenylazo)-2-nitrobutane	21.0	21.1 ± .2	Yellow	48.9
7. 2-(4-Acetamidophenylazo)-2-nitropropane	22.4	22.3 ± .1	Yellow	125.3–125.8
8. 2-(4-Chlorophenylazo)-2-nitropropane	18.5	18.5 ± .2	Red-brown	67.8
9. 2-(4-Bromophenylazo)-2-nitropropane	15.4	15.4 ± .1	Brown-orange	90–91
10. 2-(2,5-Dichlorophenylazo)-2-nitropropane	16.1	16.2 ± .2	Yellow	57–58
11. 2-(2,5-Dichlorophenylazo)-2-nitrobutane	15.3	15.5 ± .2	Yellow	40–40.3
12. 2-(2,4,6-Tribromophenylazo)-2-nitropropane	9.8	9.9 ± .2	Yellow	58.1
13. 2-(2,4,6-Tribromophenylazo)-2-nitrobutane	9.5	9.6 ± .1	Yellow	57.4–58
14. 2-(4-Methylphenylazo)-2-nitropropane	20.3	20.4 ± .1	Red oil	20 ± 1
15. 2-(2-Carboxyphenylazo)-2-nitropropane	17.7	17.8 ± .1	Orange-yellow	93.2–93.6
16. 2-(4-Carboxyphenylazo)-2-nitropropane	17.7	17.8 ± .3	Yellow	167–169
17. 2-(4-Carboxyphenylazo)-2-nitrobutane	16.7	16.9 ± .2	Yellow	129–130
18. 2-[Phenyl-(1,4-phenylenedisazo)]-2-nitropropane	23.5	23.2 ± .2	Brown	107–108
19. 2-[Phenyl-(1,4-phenylenedisazo)]-2-nitrobutane	22.5	22.2 ± .2	Light brown	80.9–81.4
20. 4,4′-[Bis-2-(2-nitropropaneazo)]-biphenyl	21.9	21.5 ± .2	Brown	162–163.6
21. 2-(2-Naphthylazo)-2-nitropropane	17.3	17.1 ± .3	Purple-brown	67

EXPERIMENTAL

In preparing these azo compounds, the general method is: 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 nitrite in water. The diazotized solution is then neutralized by pouring it with stirring into a suspension of 300 g. of ice in 500 ml. of about 2 *N* sodium hydroxide (41.3 g. of sodium hydroxide in 500 ml. of water). Immediately after neutralization, a previously prepared solution of 0.2 mole of the secondary nitro alkane in 8.0 g. of sodium hydroxide and 250 ml. of water is poured in with stirring. The solution is stirred until the azo compound appears and then filtered cold. The compounds are purified by recrystallization (3 to 5 times) from 95% ethyl alcohol.

Not all of the compounds prepared by this condensation are stable and a number of them decompose when cold, usually with the evolution of gas and heat.

A wide variety of condensation products containing sulfonic acid groups were prepared. Nitrogen analyses showed these materials to be slightly contaminated with salts, and they are not included in the table of pure compounds.

A number of compounds were prepared by tetrazotizing an aromatic diamine and coupling with two equivalents of a salt of a secondary nitro alkane. The most readily prepared of these compounds was 4,4′-[bis-2-(2-nitropropaneazo)]biphenyl. The corresponding compound prepared from 2-nitrobutane was not stable to boiling ethanol used as a recrystallization medium. A reddish-brown condensation product prepared by tetrazotizing 2,4-diaminotoluene and coupling with the sodium salt of 2-nitropropane proved rather difficult to purify and did not give close enough nitrogen analyses to be included in the table of pure compounds.

To obtain good yields of these condensation products the actual coupling must take place in a basic medium, using a salt of the nitro alkane, the reaction mixture must be kept ice-cold, and the product isolated as quickly as possible. For alkali-soluble products sufficient time should be allowed for coupling before the products are precipitated cold by the addition of dilute acid.

Duplicate nitrogen determinations (Dumas) were made on samples carefully dried for several weeks in a desiccator over anhydrous magnesium perchlorate. These nitrogen determinations and the method of synthesis offer adequate proof for the azo-linkage in these compounds, since two known chemicals were being condensed.

SUMMARY

1. Twenty new compounds have been prepared by condensing aryl diazonium salts with nitro alkanes, and their properties recorded. These are found in Table I.

2. These compounds offer advantages over the already known primary nitro alkane condensation products in ease of purification and stability of the chromophoric azo linkage.

3. The condensation products formed with 2-nitropropane are more stable in general than those prepared from 2-nitrobutane. This may be attributed to the greater symmetry of the compounds prepared from 2-nitropropane.

4. To obtain good yields of the condensation product, the actual coupling must take place in a basic medium using a salt of the nitro compound; the reaction mixture should be kept ice-cold and the product isolated as soon as the reaction is complete.

5. For alkali-soluble products, sufficient time must be allowed for coupling before the products are precipitated in the cold by addition of dilute acid.

6. If the original aromatic amine contains acidic auxochromic groups the

condensation product is found to dye wool and silk directly. Success in dyeing has also been obtained by carrying out the coupling reaction in the fibers of the cloth.

7. This coupling reaction should make many new and interesting compounds available to serve as dyes or organic intermediates for further synthesis.

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