DECOMPOSITION AND FORMATION OF ONIUM SALTS AND THE SYNTHESIS
OF HETERO-ORGANIC COMPOUNDS

COMMUNICATION 8. DECOMPOSITION OF BENZENEDIAZONIUM
FLUOBORATE IN PRESENCE OF NITRILES

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We have shown in previous investigations [1, 2] that benzenediazoniurn and diphenyliodonium fluoborates
decompose heterolytically. The heterolytic character of the decomposition of benzenediazonium fluoborate was
proved by observations on the orientation of entering groups both in substitution reactions with benzene derivatives
(the phenyl cation formed by the decomposition of benzenediazonium fluoborate was found to enter the meta posi-
tion with respect to an orienting group of the second kind), and also in addition reactions with unsaturated com-
ounds. In the present investigation we have studied the decomposition of benzenediazonium fluoborate in presence
of nitriles.

It was thought that the phenyl cation formed by the decomposition of benzenediazonium fluoborate would
add at the point of highest electron density in the nitrile molecule — the nitrogen of the nitrile group — with the
formation of anilides, in accordance with the scheme:

\[ \text{RC} = \text{N} + \text{C}_6\text{H}_5^+ + \text{F}^- \rightarrow \text{RCF} = \text{N} \text{C}_6\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{RC(OH)} = \text{N} \text{C}_6\text{H}_5 \]

Also, it could be expected that, as a result of the decomposition of benzenediazonium fluoborate in a med-
ium of benzonitrile (or other aromatic nitrile), 3-biphenylcarbonitrile (or one of its homologs) would be formed by
entry of the phenyl cation into the benzene nucleus in the meta position to the meta-orienting nitrile group.

On the other hand, the possibility could not be excluded that the diazonium form would be converted into
the diazo form under the influence of the free pair of electrons on the nitrogen of the nitrile group, which is what
actually occurs when benzenediazonium fluoborate decomposes in pyridine, in presence of hydroxyl ions, or in
presence of metals:

\[ \text{C}_6\text{H}_5\text{N} = \text{N} + \text{:OH} \rightarrow \text{C}_6\text{H}_5\text{N} \text{H}_2\text{N}^- \rightarrow \text{C}_6\text{H}_5\text{R} = \text{N}^- \]

The decomposition of the diazo form, however, would be homolytic, with formation of an aryl radical; and by re-
action of this aryl radical with the nitrile, not only the anilides, but also other products would be formed, in par-
ticular ketones and, when aromatic nitriles are used, also derivatives of 2- or 4-bipheny1carbonitrile. The phenyl
radical formed by the decomposition of benzenediazohydroxide enters the benzene nucleus in the para position to
the nitrile group with formation of 4-biphenylcarbonitrile [3].

Hanby and Waters [4] found that, in the decomposition of benzenediazonium chloride in acetonitrile, a mixture
of substances was formed — benzene, chlorobenzene, and about 10% of acetanilide — and this was interpreted by them
as proof of the homolytic character of the decomposition of arenediazonium chlorides. When the decomposition was
carried out in propionitrile, Hanby and Waters found only benzene and chlorobenzene in the products and could not
detect any propionanilide. They were unable to identify any reaction products in the decomposition of benzene-
diazonium chloride in a medium of phenylacetonitrile.

In the decomposition of arenediazonium chlorides in aqueous acetone solution in presence of acrylonitrile,
sodium acetate, and a cupric salt, Koelsch [5] obtained 30-40% yields of products of the addition of aryl at the
double bond, namely, nitriles of a-chlorohydrocinnamic acids. This must be considered to prove that the decom-
position of the diazo compounds investigated by Koelsch is homolytic and is followed by addition of an aryl radical
at a double bond. Koelsch did not observe addition of aryl to the nitrogen of acrylonitrile.
We have carried out the decomposition of benzenediazonium fluoborate in the following media: benzonitrile, p-tolunitrile, o-tolunitrile, phenylacetoniuite, acetonitrile, propionitrile, and acrylonitrile. It was found that phenyl added at the nitrogen of the nitrite group with formation of the corresponding anilides, the yields being 40% from benzonitrile, p-tolunitrile, and phenylacetoniuite, 30% from o-tolunitrile and acetonitrile, 15% from propionitrile, and 10% from acrylonitrile. No ketone formation was observed in any of these reactions. In the reactions with aromatic nitriles, phenyl did not enter the aromatic nucleus—no biphenyl derivatives were formed. Also, when the decomposition occurred in a medium of acrylonitrile, no identifiable products arising by the addition of phenyl at the carbon-carbon double bond were obtained. Formation of anilides was accompanied by the polymerization of the nitriles, evidently resulting from the promoting action of boron trifluoride, and in the reactions with benzonitrile and p-tolunitrile the trimers were isolated; in the other reactions the occurrence of polymerization was shown by the formation of high-boiling substances or undistilable (acrylonitrile) resins.

The following facts, therefore, indicate that the mechanism of the reaction that we have investigated is different from that of the reactions of Hanby and Waters, Koelsch, and Gomberg and Bachmann, and that it consists, in fact, of the action of a phenyl cation, formed by the heterolytic decomposition of benzenediazonium fluoborate, on the nitrile: first, the greatly increased yields of anilides in the decomposition of benzenediazonium fluoborate in nitrile media, as compared with the yields obtained by Hanby and Waters in the decomposition of benzenediazonium chloride (for acetonitrile 10 to 30%, for phenylacetoniuite 0 to 40%, and for propionitrile 0 to 14%); second, the absence of ketone formation by the action of radicals on the nitriles; and finally, the formation of essentially different products (comparison of the decomposition of benzenediazonium fluoborate in acrylonitrile and benzonitrile media with the decomposition of arenediazonium chloride in acrylonitrile and benzenediazohydroxide in benzonitrile).

**EXPERIMENTAL**

**Decomposition of Benzenediazonium Fluoborate in a Benzonitrile Medium**

The decomposition was carried out in a four-necked cylindrical flask placed in an oil bath and fitted with mercury-sealed stirrer, reflux condenser, and thermometer. The fourth opening of the flask was used for the addition of the diazonium salt. Benzenediazonium fluoborate was freshly prepared and dried in a desiccator over calcium chloride; 150 g (one molecular proportion) of it was added in small portions over a period of 80 minutes to 225 g (2.8 molecular proportions) of benzonitrile at 70°C. The reaction was exothermic, and after addition of the first portion of diazonium salt the temperature rose to 80°C. Further additions were therefore made without external heating, the rate of addition being adjusted so that the temperature did not rise above 80°C. On the next day the mixture was dissolved in ether, the small amount of boron-containing inorganic precipitate being removed. When washed with 10% NaOH (500 ml), the ether solution yielded a voluminous precipitate, which was filtered off. From this precipitate, boiling ethanol extracted 33.4 g of benzanilide. After recrystallization from alcohol its melting point and the melting point of a mixture with known benzanilide were 163°C. The alcohol-insoluble residue was crystallized from benzene and chloroform, and then melted at 232°C. For kyaphenin (2,4,6-triphenyl-s-triazine) (C₃H₆CN)₃ Scholl and Norr [6] give m.p. 231-232°C.

The ether solution was washed with water and dried with sodium sulfate. The residue remaining after removal of ether was vacuum-distilled.

- **Fraction I.** b.p. 74-76°C (12 mm); 98 g
- **Fraction II.** b.p. 120-167°C (5 mm); 1 g
- **Fraction III.** b.p. 185-205°C (5 mm); 30 g
- **Fraction IV.** b.p. 205-255°C (5 mm); 13 g

Fraction I was benzonitrile; Fraction III solidified completely; Fraction IV was a viscous red oil, which partially solidified on standing. The crystals that formed from Fraction IV were separated from the oil and added to Fraction III. The mixture was crystallized from alcohol, acetone, or benzene, and the melting point of the product, and also of its mixture with known benzanilide, was 163°C. The total yield of benzanilide was 61 g (39%).

**Found %**

| C | 78.94; 79.14; 80.66; 5.52 |
| H | 5.61 |

**C₃H₄ON. Calculated %**

| C | 79.16; 79.18 |
| H | 5.61 |

Solvent was distilled from the mother liquor remaining from the crystallization of benzanilide, and the