27. Magnetic-Field Effect in Aromatic Dediazoniation[1])

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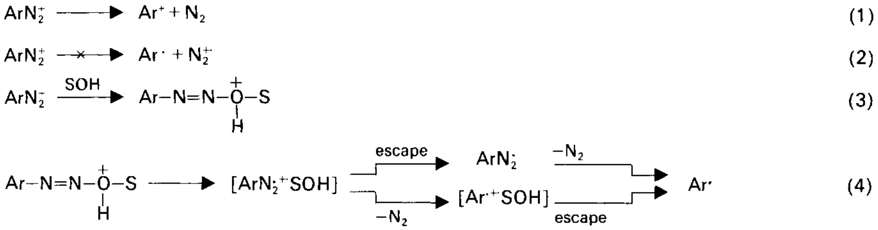
Homolytic dediazoniation of tribromo- and trichloro-benzenediazonium tetrafluoroborates in highly ionizing, low-nucleophilicity solvents (trifluoroethanol and trifluoromethanesulfonic acid (TfOH) exhibits a strong magnetic-field dependency of dediazoniation products; a more facile singlet-to-triplet intersystem crossing results in increased radical-escape products at higher magnetic fields.

Introduction. – Solvent nucleophilicity and the electron demand at N(*β*) provide two important channels for controlling the mechanism of aromatic dediazoniation [1].

Heterolytic dediazoniation (Ar^+ formation; *Eqn. 1*) is usually observed in low-nucleophilicity, highly ionizing solvents (CF_3CH_2OH, $(CF_3)_2CHOH$, and protic superacids) and when electron-donating substituents are present on the aryl ring [2] [3] (*Scheme 1*). Homolysis ($Ar^{\cdot}$ formation), on the other hand, becomes dominant in the more nucleophilic solvents (MeOH, DMSO, NO_2^-/buffer, and hexamethylphosphoric triamide) and in the presence of electron-withdrawing substituents, which increase the electron demand at the N-atom [4] [1].

Scheme 1. *Heterolytic and Homolytic Dediazoniation*



Despite several multinuclear CIDNP studies (^1H, ^{13}C, and ^{15}N) [5–7] on homolytic dediazoniation probing radical intermediates, to our knowledge, homolytic dediazoniation has never been subjected to an extensive magnetic-field (MF) study. Homolytic chemistry in a magnetic field provides an opportunity to alter the course of a chemical reaction (rate and products) through entropic factors ($k = A\, e^{-E/RT}$). Intersystem crossing (ISC) may be promoted or hindered by an external magnetic field, depending on the mechanism of spin interactions. This in turn controls the relative efficiency of escape

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vs. cage products [8–13]. Four distinct classes of MF dependency of ISC are known [8]. In principle, for a singlet pair it is possible to observe more cage or more escape products. For a triplet pair, where ISC (T → S) cannot compete with diffusion, a micellar environment (super cage) may be used to hinder diffusion and hence form a higher percentage of cage products. Pioneering work by *Turro et al.* [11] in this area has provided a number of examples including application in radical polymerization [14].

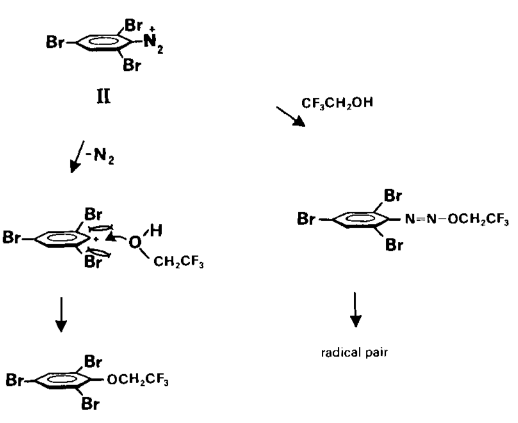
A direct homolysis of ArN$_2^+$ (*Eqn. 2*) requires the formation of the highly unstable N$_2$ radical cation and is energetically unfavorable. Based on a body of experimental evidence [1], it is believed that nucleophilic attack by solvent on N(β) occurs first (*Eqn. 3*). Homolysis is then followed (an inner-sphere ET) to form a singlet radical pair ArN$_2^\cdot$ $^{+\cdot}$SOH in the solvent cage (diazenyl radical and the radical cation of the solvent; *Eqn. 4*). The diazenyl radical [ArN$_2^\cdot$ $^{+\cdot}$SOH] could undergo loss of N$_2$ within the cage to give [Ar$^\cdot$ $^{+\cdot}$SOH] as a second geminate pair or might dissociate only following escape, to give Ar$^\cdot$ and N$_2$ (*Scheme 1*).

If the dissociation of ArN$_2^\cdot$ to Ar$^\cdot$ occurs only after diffusion escape, then the percentage of arene product should, in principle, not depend on the magnetic field (no radical pair). Similarly, the formation of ArN$_2^\cdot$ from ArN$_2^+$X$^-$ and its collapse to Ar$^\cdot$ by any process other than a radical-pair mechanism should result in an MF-independent process.

Results and Discussion. – Product analysis of dediazoniation in CF$_3$CH$_2$OH shows *exclusive* heterolytic dediazoniation for a variety of substituted benzenediazonium ions including 4-ClC$_6$H$_4$N$_2^+$. Tribromo- and trichlorobenzenediazonium ions **I** and **II**, respectively, are, however, exceptional cases, for which product analysis of the dediazoniation showed the presence of the corresponding arenes, indicative of homolysis and H$^\cdot$ abstraction [2]. This change in the mechanism as a function of steric factors can be explained in terms of steric inhibition to solvolysis for a heterolytic pathway which renders attack on N(β), homolysis, and subsequent H$^\cdot$ abstraction energetically more favorable (*Scheme 2*).

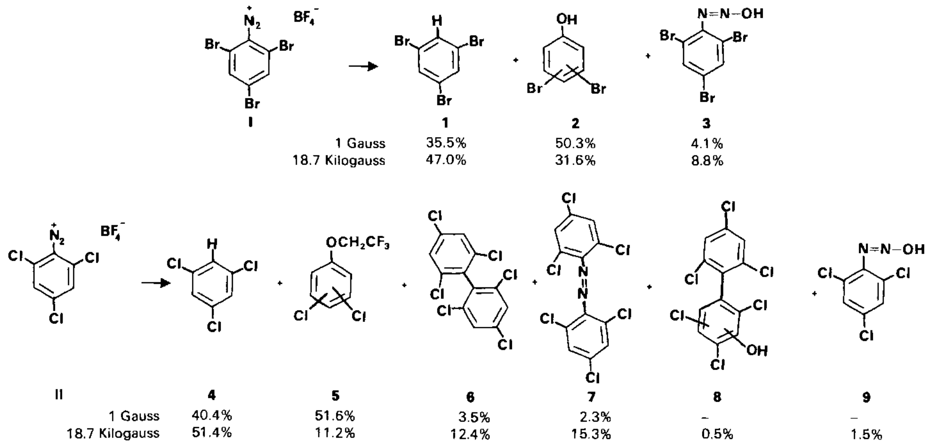
Using CF$_3$CH$_2$OH and trifluoromethanesulfonic acid (TfOH) as solvents, we studied the ambient dediazoniation of the purified tetrafluoroborate salts **I** and **II** at 1 G (earth's magnetic field) and at 18.7 KG (in the probe of an 80-MHz NMR instrument) under

Scheme 2. *Steric Inhibition to Solvolysis in a Heterolytic Pathway*



identical conditions of concentration, reaction times, and temperature under a dry N_2 atmosphere. The reaction mixtures were quenched after 24 h at 34° and subjected to capillary GC and GC/MS analysis. Noticeable differences in product distributions (GC %) were observed as a function of field. Dediazoniation of **I** in CF_3CH_2OH at 1 G resulted in two major and one minor products, *i.e.* tribromobenzene **1**, dibromo-hydroxybenzene **2**, and tribromophenyl diazohydroxide **3**[3]. The same experiment conducted at 18.7 KG showed that products **1** and **3** increased, whereas **2** decreased (*Scheme 3*). With

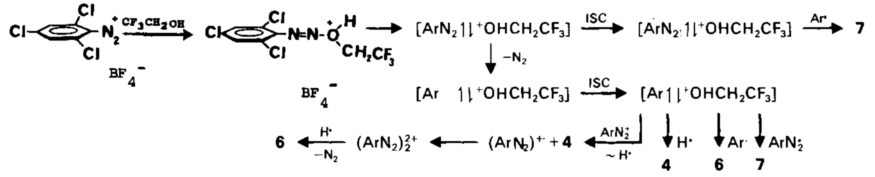
Scheme 3. *Dediazoniation of* **I** and **II** *in* CF_3CH_2OH



II, two major and two minor products were formed at 1G, *i.e.* trichlorobenzene **4**, dichloro(trifluoroethoxy)benzene **5**, hexachlorobiphenyl **6**, and its corresponding diazo compound **7** (*Scheme 3*). The 18.7-KG experiment showed that, except for **5**, all other products increased at higher magnetic field. In addition, two new, very minor products were observed which were *tentatively* identified as hexachlorohydroxybiphenyl **8** and the diazohydroxide **9**.

Our proposed homolytic dediazoniation mechanism is shown in *Scheme 4*. Nucleophilic attack on N(*β*) by the solvent results in an oxonium ion. Upon homolysis, a singlet radical pair is generated. Loss of N_2 results in a second singlet pair. ISC (S→T) is facilitated in the magnetic field and results in a more efficient escape of both the diazenyl

Scheme 4. *Proposed Homolytic Dediazoniation Mechanism in* CF_3CH_2OH



Ar = 2,4,6-Trichlorophenyl

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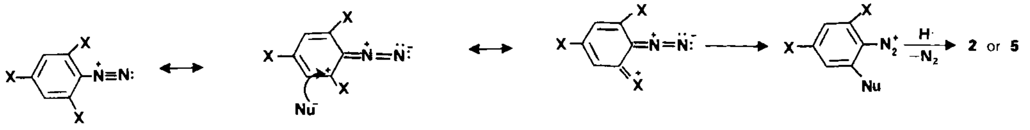
[3] Our GC/MS assignment of this minor product should be considered tentative, as RN=NOH is expected to have limited thermal stability.

radical and the aryl radical from the solvent cage. Upon diffusion, these radicals can react with each other, dimerize, or abstract H-atoms. CF_3CH_2OH provides a convenient source of $H^{\cdot}$, and substantial amounts of the arene **4** are thus formed[4].

We propose that the formation of products **2** and **5** illustrates the ambident character of the diazonium ions [15] and provides new examples for substitution of a nucleofugal leaving group prior to homolytic dediazoniation and $H^{\cdot}$ abstraction (*Scheme 5*)[5]. Since at a higher magnetic field, a more favored ISC (S → T) leads to a substantial increase in the escape products, in a relative sense, substitution of the nucleofugal leaving group becomes a minor pathway.

Scheme 5. *Ambident Character of Diazonium Ion: Substitution of Nucleofugal Leaving Group*



Dediazoniation of **I** in TfOH at 1 G resulted in two major products identified by GC/MS as tribromobenzene (25%) and a tetrabromobenzene isomer (41%). The magnetic-field experiment (18.7 KG) did not show a noticeable increase in the arene content! With **II**, however, the percentage of arene almost doubled (1 G, 6.8%; 18.7 KG, 13%). It should be noted that dediazoniation in TfOH is complicated by an apparent acid-catalyzed bromine disproportionation, following dediazoniation and arene formation. It is, nevertheless, clear that ISC (S → T) is again facilitated.

Formation of arene requires an $H^{\cdot}$. Unlike CF_3CH_2OH, TfOH is not a suitable $H^{\cdot}$ donor. Moreover, the highly non-nucleophilic nature of the triflate anion [18] makes the attack on N(*β*) unlikely. For the first step, a TfOH-catalyzed outer-sphere ET mechanism involving the gegenion (BF_4^-) may be considered. To test the validity of an 'anion-induced' ET process in homolytic dediazoniation of tribromobenzenediazonium cation, we prepared salts with different gegenions ($X = Cl^-$, CF_3COO^-, and TfO^-) having varied oxidation potentials. Dediazoniation was studied in TfOH in the probe of a 60-MHz NMR instrument (14 KG), under identical conditions (25°, 24 h). The amount (GC %) of tribromobenzene was found to be indeed gegenion-dependent; with the Cl^- salt, 34.3% of **1** was present, whereas with the CF_3COO^- and TfO^- salts, the amount of **1** was reduced to 20 and 4.4%, respectively.

In conclusion, our MF-dependency studies provide strong support for a radical-pair mechanism in homolytic dediazoniation of **I** and **II**. Our work is being extended to other diazonium ions and solvents and to dediazoniation at much higher magnetic fields, with particular interest in borderline mechanistic cases (involving both $Ar^{\cdot}$ and Ar^+), where dediazoniation in a magnetic field might alter the mechanistic course. We are also studying the effect of micelles and crown ethers on the S → T process, in the hope that a less favorable diffusion [19] may result in direct observation of the oxonium-ion intermediate.

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[4] A minor pathway involving $H^{\cdot}$ transfer from ArN_2^+ could also lead to **4**. Dimerization of the resulting radical cation followed by dediazoniation and $H^{\cdot}$ abstraction could lead to **6** (*Scheme 4*).

[5] The ambident character of benzenediazonium ions was elegantly demonstrated by *Olah* and coworkers through ^{13}C-NMR studies [16] as well as by-product analysis after dediazoniation in pyridine/HF [17].

Experimental Part

General. The diazonium salts **I** and **II** were freshly prepared by conventional diazotization ($NaNO_2/HBF_4$) and precipitation from $MeCN/Et_2O$ (IR: 2360 and 2313 cm^{-1} ($N\equiv N$)). The Cl^-, CF_3COO^-, and TfO^- salts were similarly prepared by conventional diazotization with $NaNO_2/HCl$, $NaNO_2/CF_3COOH$, and $NaNO_2/TfOH$, resp., and by careful precipitation from $MeCN/Et_2O$. The characteristic $\tilde{\nu}$ ($N\equiv N$) of the diazonium salts showed gegenion dependency: 2271 ($Br_3C_6H_2N_2^+Cl^-$), 2280 ($Br_3C_6H_2N_2^+CF_3COO^-$), 2281 ($Br_3C_6H_2N_2^+TfO^-$), 2280 ($Cl_3C_6H_2N_2^+Cl^-$, 2243 ($Cl_3C_6H_2N_2^+CF_3COO^-$), 2299 cm^{-1} ($Cl_3C_6H_2N_2^+TfO^-$). GC Analyses: *HP-5809A* instrument, 25-m fused-silica *(OV101)* and 5-m *HP* methylsilicon gum capillary columns. GC/MS Analyses (*m/z* (%)): *Finnigan-Mat-4500* instrument.

1-G Experiments. The diazonium salt (0.015 g) was charged into 10-ml flask equiped with magnetic stirrer bar, a drying tube, and a N_2 inlet[6]). CF_3CH_2OH (0.5 ml) or TfOH (*ca.* 0.5 ml) was slowly added to give a homogeneous soln. which was allowed to react for 24 h at 24°, prior to workup and GC analysis.

Magnetic-Field Experiments. The salt was charged into a pre-dried 5-mm NMR tube to which 0.5 ml of CF_3CH_2OH or TfOH was slowly added *via* a pipet or a syringe under N_2 (vortex mixing). TfOH addition was always done with pre-cooling of both the diazonium salt and the superacid to avoid local overheating.

2,4,6-Tribromobenzenediazohydroxide (**3**): GC/MS: 357 (30, $[M + H]^+$), 359 (83), 361 (80), 363 (29), 327 (32, $[M + H - NO]^+$, $ArNH_2^+$), 329 (100), 331 (98), 333 (32), 311 (12, $Br_3C_6H_2^+$), 313 (30), 315 (29), 317 (9), 299 (17), 301 (45), 303 (45), 305 (13), 232 (30, $[311 - Br]^+$), 234 (60), 236 (31), 153 (45, $[232 - Br]^+$), 155 (47), 74 (86).

2,4,6-Trichlorobenzenediazohydroxide (**9**): GC/MS: 225 (35, $[M + H]^+$), 227 (35), 229 (9), 195 (62, $[M + H - NO]^+$, $ArNH_2^+$), 197 (58), 199 (20) 179 (15, $Cl_3C_6H_2^+$), 181 (13), 183 (4), 167 (27), 169 (22), 171 (8), 143 (22), 145 (14), 147 (6), 109 (32), 84 (75), 49 (100).

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[6]) The 1-G experiments were run in a thermostatic bath in the dark, in order to ascertain identical conditions as for the experiments carried out at higher fields in the NMR probe.