167. Dediazoniation of Arenediazonium Ions. Part XXII. Reactions of 2,6-Dialkyl-Substituted Benzenediazonium Ions in Super Acids, Acetonitrile and Acetone[1])

by **Khosrow Laali, Ivanka Szele*** and **Heinrich Zollinger***

Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule (ETH), CH-8092 Zürich

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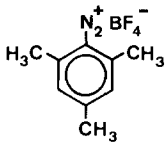
Summary

Reactions of 2,4,6-trimethylbenzenediazonium (**1**), 2,6-diethylbenzenediazonium (**2**) and 2,6-diisopropylbenzenediazonium (**3**) tetrafluoroborates were studied in magic acid, SbF_5/SO_2ClF, acetonitrile and acetone by ^{1}H-NMR and by analysis of the dediazoniation products. The N_α-N_β rearrangement of β-N^{15}-labelled tetrafluoroborates **1–3** was followed by ^{15}N-NMR of the corresponding arylazonaphthols, as well as by MS analysis of the anilines obtained by reduction of the azo compounds. Diazonium salts **2** and **3** were synthesized for the first time and the steric effect of substituents at C(2) and C(6) on the reactions under study is discussed. All the results obtained can be rationalized by heterolytic dediazoniation of diazonium salts **1–3** and product formation from the corresponding aryl cations.

Introduction. – There is a great deal of evidence for the involvement of aryl cations as steady-state intermediates in the dediazoniation of arenediazonium ions in polar solvents of low nucleophilicity [2–8]. The reversibility of the reaction has been demonstrated by the N_α-N_β rearrangement and by the exchange of the diazonio group with molecular nitrogen, both reactions accompanying heterolytic dediazoniation [5–7]. The higher percentage of rearrangement and exchange observed for 2,4,6-trimethylbenzenediazonium ion (**1**) compared with benzene- and *p*-substituted benzenediazonium ions has been interpreted in terms of steric interference of the *o*-methyl groups with the capture of the aryl cation by larger solvent molecules and thus preferential reaction with smaller nitrogen molecules [7]. To test this interpretation it would be interesting to study other sterically hindered 2,6-substituted benzenediazonium ions which dediazoniate heterolytically. Therefore, two as yet unknown diazonium salts, 2,6-diethyl- (**2**) and 2,6-diisopropylbenzenediazonium tetrafluoroborate (**3**) were prepared. The reactions of compounds **1–3** were studied in magic acid (FSO_3H/SbF_5 1:1) and in SbF_5/SO_2ClF, since up to now dediazoniations of arenediazonium ions in such solvents have not

[1]) Part XXI: [1].

been investigated. A detailed product analysis after dediazoniation of **1–3** in magic acid, as well as in acetonitrile and acetone will also be reported.



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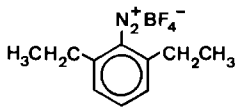

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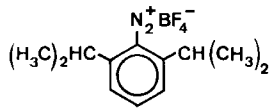

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Results and Discussion. – *Preparation of 2,6-Diethyl-* (**2**) *and 2,6-Diisopropylbenzenediazonium* (**3**) *Tetrafluoroborates.* To the best of our knowledge, with the exception of 2,4,6-trimethylbenzenediazonium salt (**1**), no other stable sterically hindered 2,6-dialkyl substituted benzenediazonium salts are known. Obviously, owing to steric hindrance in these compounds, the subsequent dediazoniation competes successfully with the formation of the diazonium ions from the corresponding anilines. Therefore the investigations describing reactions of such compounds all deal with the *in situ* preparation of the diazonium ions, either by diazotisation of the anilines or by decomposition of the *N*-nitrosoacetanilides [9–12]. However, with careful handling, diazonium salts **2** and **3** can be isolated after diazotisation of the anilines with $NaNO_2$ in aqueous HBF_4 and are reasonably stable in the solid state if stored at $-20°$ (**2**: $\nu_{NN} = 2235\ cm^{-1}$, **3**: $\nu_{NN} = 2230\ cm^{-1}$, both in Nujol). Attempts to isolate 2,6-di-*tert*-butylbenzenediazonium tetrafluoroborate were, however, unsuccessful.

^{1}H-NMR of Diazonium Salts **1**, **2** *and* **3**. Compounds **1**, **2** and **3** proved to be quite stable in magic acid at low temperature. Comparison of the chemical shifts in magic acid/SO_2 with those in neat SO_2 does not give any indication of ring or

Table 1. *Proton Chemical Shifts*[a]) *of 2,4,6-Trimethylbenzenediazonium Tetrafluoroborate* (**1**)

Solvent	4-CH_3	2,6-CH_3	3,5-H
CD_3CN[b])	2.50 (*s*)	2.64 (*s*)	7.40 (*s*)
$(CD_3)_2CO$[c])	2.55 (*s*)	2.80 (*s*)	7.56 (*s*)
SO_2[d])	2.45 (*s*)	2.62 (*s*)	7.32 (*s*)
$FSO_3H \cdot SbF_5$ (1:1)/SO_2[e])	2.80 (*s*)	2.97 (*s*)	7.69 (*s*)
SbF_5/SO_2ClF[f])	2.96 (*s*)	3.06 (*s*)	7.79 (*s*)

[a]) δ-Values, relative to external TMS capillary. [b]) $-3°$. [c]) $-15°$. [d]) $-20°$. [e]) $-20°$. [f]) $-60°$.

Table 2. *Proton Chemical Shifts*[a]) *of 2,6-Diethylbenzenediazonium Tetrafluoroborate* (**2**)

Solvent	CH_3	CH_2	4-H	3,5-H
CD_3CN[b])	1.35 (*t*)	3.02 (*q*)	8.10 (*t*)	7.63 (*d*)
$(CD_3)_2CO$[b])	1.39 (*t*)	3.17 (*q*)	8.14 (*t*)	7.76 (*d*)
SO_2[c])	1.39 (*t*)	3.04 (*q*)	8.04 (*t*)	7.63 (*d*)
$FSO_3H \cdot SbF_5$ (1:1)/SO_2[d])	1.61 (*t*)	3.27 (*q*)	8.28 (*t*)	7.86 (*d*)
SbF_5/SO_2ClF[e])	1.71 (*t*)	3.30 (*q*)	8.38 (*t*)	7.89 (*d*)

[a]) δ-Values, relative to external TMS capillary. All coupling constants 7–8 Hz at 90 MHz. [b]) $-15°$. [c]) $-20°$. [d]) $-70°$. [e]) $-48°$.

Table 3. *Proton Chemical Shifts*[a]) *of 2,6-Diisopropylbenzenediazonium Tetrafluoroborate* (**3**)

Solvent[b])	CH_3	CH	4-H	3,5-H
CD_3CN[c])	1.38 (*d*)	3.29 (*m*)	8.14 (*t*)	7.70 (*d*)
$FSO_3H \cdot SbF_5$ (1:1)/SO_2[d])	1.87 (*d*)	3.68 (*m*)	8.55 (*t*)	8.10 (*d*)
SbF_5/SO_2ClF[e])	1.79 (*d*)	3.69 (*m*)	8.47 (*t*)[f])	8.10 (*d*)[f])

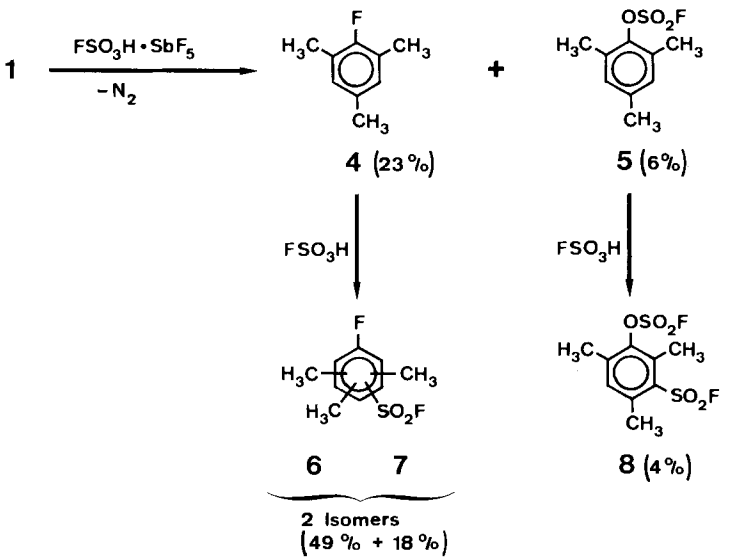
[a]) δ-Values, relative to external TMS capillary. [b]) **3** is poorly soluble in SO_2 at low temperature, while dediazoniation proceeds at higher temperatures, so no spectra in that solvent could be recorded. [c]) $-15°$ (dediazoniation already proceeding). [d]) $-48°$. [e]) $-59°$. [f]) Broad signals.

N-protonation. Only a small solvent effect on the chemical shifts is observed. Compounds **1**, **2** and **3** were also stable in SbF_5/SO_2ClF at low temperature and, except for slight variations due to a small change in the medium, the spectra were the same as those observed in magic acid. Chemical shifts for **1**, **2** and **3** in these solvents and in acetonitrile and acetone are given in *Tables 1–3*.

Dediazoniation of **1**, **2** *and* **3** *in Magic Acid.* The diazonium salts were decomposed in neat magic acid at room temperature (**1**) or at *ca.* 0° (**2** and **3**), and after dediazoniation was complete, the mixtures were quenched with ice/$NaHCO_3$, the products extracted and analyzed by GC/MS.

The dediazoniation products of **1** in magic acid after *ca.* 20 h are shown in *Scheme 1*. The product mixture observed is that expected for a heterolytic dediazoniation. The 2,4,6-trimethylphenyl cation reacts with a fluoride ion (either from the counter-ion or from the solvent) to give fluoromesitylene (**4**), as well as with the fluorosulfate ion to give mesityl fluorosulfate (**5**). Each of these compounds can become fluorosulfonated by fluorosulfuric acid to give the corresponding sulfonyl fluorides **6**, **7** and **8**. Whereas there is only one possible sulfonyl fluoride isomer of fluoromesitylene, GC/MS revealed the presence of two isomers (49%

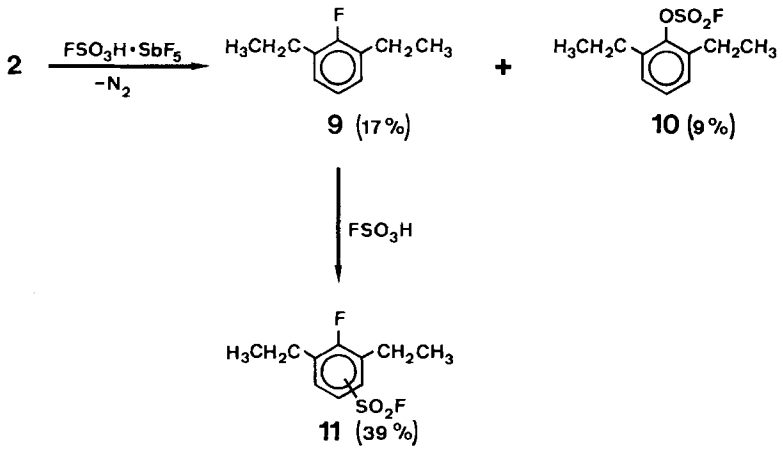
Scheme 1



and 18%, respectively) of the same mass, with a very small difference in retention time and a very similar fragmentation pattern. This is most likely due to isomerisation of fluoromesitylene in magic acid. Isomerisation and disproportionation of alkylaromatic compounds are facile processes which occur with a variety of protic and *Lewis*-acid catalysts [13].

To compare the products of dediazoniation of **1** in magic acid with those of mesitylene (a product of possible homolytic dediazoniation), mesitylene was added to cold magic acid to form a stable cation at low temperature by ring protonation [14] [15]. The temperature was then allowed to rise slowly and the sample was quenched after standing at room temperature for 3 h. The only product (GC/MS) in addition to unreacted mesitylene was mesityl sulfonyl fluoride, a product not observed in the dediazoniation of **1**.

Scheme 2



Dediazoniation of **2** in magic acid was essentially complete after *ca.* 20 min. at 0°, forming a pale brown solution. The products **9**, **10** and **11** *(Scheme 2)* were identified by GC/MS analysis. In addition the gas chromatogram showed several other volatile products, which we could not identify by their MS. Comparison of the dediazoniation products of **1** and **2** in magic acid[2]) shows that both reactions proceed by the same mechanism.

The dediazoniation of **3** in magic acid at 0° proceeded rapidly and was complete in *ca.* 10–15 min. Because of the much greater tendency of the isopropyl groups to isomerise and disproportionate under the influence of acid, the residue obtained after quenching and extraction was polymeric, and none of the expected dediazoniation products could be identified. Evidence for isopropyl disproportionation was obtained by detecting isopropylfluorobenzene and isopropylphenyl fluorosulfate (*ca.* 4 : 1), in addition to three minor unidentified compounds in the volatile mixture.

[2]) There is only a minor difference in that in the reaction of **2** no sulfonation product of the fluorosulfate ester **10**, corresponding to **8** in the reaction of **1** was detected, and that only one isomer of the sulfonyl fluoride **11** was observed.

Dediazoniation of **1**, **2** *and* **3** *in [D_6]Acetone (Table 4).* From the kinetics of dediazoniation of benzenediazonium tetrafluoroborate in acetone and in other aprotic polar solvents, it was concluded that the reaction proceeds by a heterolytic dediazoniation mechanism [16]. However, to the best of our knowledge, no product analysis in acetone is known.

The reaction of **1**, **2** and **3** in [D_6]acetone was followed by ^{1}H-NMR. The dediazoniation of **1** is fairly slow. After 16 h at room temperature the extent of dediazoniation was estimated to be 68%. When the reaction was complete, a GC/MS analysis of the mixture showed fluoromesitylene (**4**) and 2,4,6-trimethylphenol as the only aromatic products, in addition to three non-aromatic products involving the solvent[3]).

The ^{1}H-NMR spectra of **2** in [D_6]acetone were recorded starting at $-15°$, where almost no dediazoniation product could be detected. The spectrum at $-4°$ shows very little dediazoniation, whereas the spectrum at $+20°$ shows clearly additional upfield signals of the dediazoniation products. 60% dediazoniation was estimated. After complete dediazoniation in addition to 1,3-diethyl-2-fluorobenzene (**9**) and 2,6-diethylphenol (**12**) *(cf. Scheme 4)*, a small amount of an [D_3]acetylphenol derivative, probably arising by acetylation by the solvent in the presence of the acid formed on dediazoniation[4]) was detected (GC/MS). No acetylated fluoroarene was detected *(Table 4).*

Table 4. *Dediazoniation Products*[a]) *of Diazonium Tetrafluoroborate* **1**, **2** *and* **3** *in [D_6]Acetone*

$ArN_2^+ BF_4^-$	ArF	ArOH
2,4,6-CH_3	36%	64%
2,6-CH_2CH_3[b])	33%	58%
2,6-$CH(CH_3)_2$	38%	62%

[a]) Calculated from the relative areas in GC, total aromatic products = 100%. [b]) In addition to the two products indicated, 5% of 4-[D_3]acetyl-2,6-diethylphenol were also found.

Because of the poor solubility of **3** in acetone below room temperature, the dediazoniation could not be followed by NMR. When the temperature was allowed to rise slowly to increase solubility, dediazoniation proceeded and was complete in *ca.* 5 min. 2-fluoro- 1,3-diisopropylbenzene (**13**) *(cf. Scheme 5)* and 2,6-diisopropylphenol were again found (GC/MS) *(Table 4).*

The fluoroarenes formed in the dediazoniations of compounds **1**, **2** and **3** are the expected *Schiemann* reaction products. On the other hand, the formation of phenols in these reactions must be due to the presence of a trace of water in [D_6]acetone. Considering the large excess of solvent compared to the diazonium

[3]) These products must have arisen from a reaction between [D_6]acetone and the acid formed on dediazoniation. They were identified on the basis of their mass spectra as: $CD_3COCD_2COCD_3$, CD_3COCD_2COF and $CD_3COCD_2COCD_2COCD_3$.

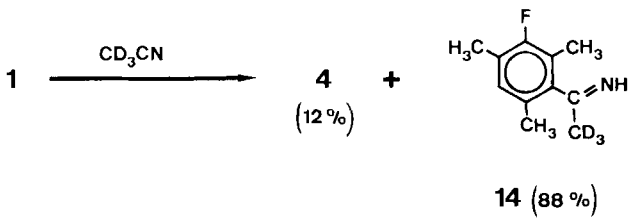
[4]) In view of the detection of a fluoro-substituted condensation product arising from [D_6]acetone during dediazoniation, it is probable that acetyl fluoride (formed *in situ*) is the acetylating agent. BF_3 is an efficient catalyst for acetylation of aromatic compounds and yields in reactions with phenols exclusively *p*-substituted products [17].

salt used and the obviously much higher reactivity of water relative to acetone, even a trace of water can result in a large amount of phenol. The fact that the phenolic protons are not seen by NMR suggests that the phenol is protonated by the acid formed by dediazoniation and that the proton must be exchanging under these conditions. It is surprising that the formation of the acetylated phenol was only observed in the reaction of the 2,6-diethyl compound **2** and not in the reactions of **3**. The *o*- and *p*-positions in **1** are occupied by CH_3-groups and therefore acetylation here is not expected. The same pertains to fluoroarenes, which are much less prone to electrophilic aromatic substitution than the phenols.

Dediazoniation of **1**, **2** *and* **3** *in* CD_3CN. The kinetics of dediazoniation of benzenediazonium salt in CD_3CN and other polar aprotic solvents is reported, and the reaction is thought to proceed by a heterolytic mechanism [16], but again, as far as we know, no product analysis in this solvent has been described.

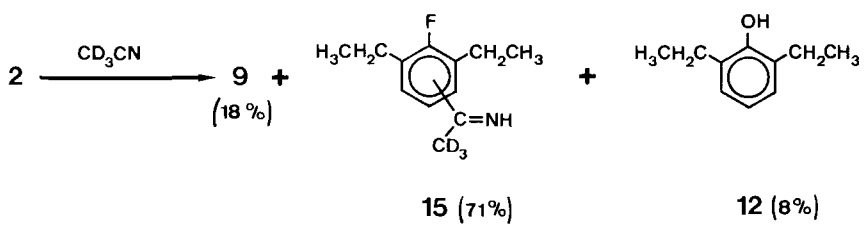
The reactions of **1**, **2** and **3** in CD_3CN were followed by ^{1}H-NMR. The NMR spectrum of **1** in CD_3CN after standing at room temperature for 3.5 h showed *ca.* 60% dediazoniation. After the reaction was complete, a GC/MS analysis showed the formation of fluoromesitylene (**4**) and the imine **14**, obviously resulting from a reaction with the solvent *(Scheme 3)*.

Scheme 3



The NMR spectrum of **2** in CD_3CN recorded at $-15°$ showed *ca.* 26% dediazoniation. A broad peak at 4.62 ppm due to the presence of water in CD_3CN is seen[5]). After complete dediazoniation, 1,3-diethyl-2-fluorobenzene (**9**), the imine **15** and 2,6-diethylphenol (**12**), obviously resulting from the reaction with water present in the solvent were identified (GC/MS) *(Scheme 4)*.

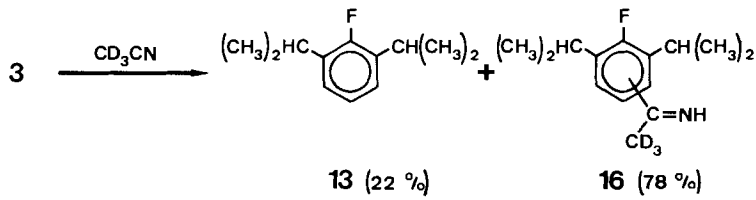
Scheme 4



[5]) A different batch of CD_3CN was used for the reaction of **2** than for those of **1** and **3**.

The NMR spectrum of **3** in CD_3CN recorded at $-15°$ showed already *ca.* 30% dediazoniation. 2-Fluoro-1,3-diisopropylbenzene (**13**) and the imine **16** were formed (GC/MS) *(Scheme 5)*.

Scheme 5

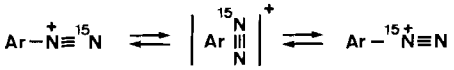


13 (22 %) **16** (78 %)

The fluoroarenes observed in the dediazoniation of **1**, **2** and **3** in CD_3CN are again the expected *Schiemann* reaction products. The formation of phenol **12** is also easily explained by the presence of water in the particular batch of CD_3CN used for the reaction of **2**. The imines **14**, **15** and **16** obviously resulting from a reaction with CD_3CN may be surprising products at first sight. However, the condensation of nitriles with reactive aromatic compounds under *Friedel-Crafts* conditions is well known (*Houben-Hoesch* synthesis) [18]. It has also been shown recently that nitrilium triflates formed by protonation of nitriles with trifluoromethane sulfonic acid react with phenols to give ketones as final products after the hydrolysis of the intermediate imines [19].

N_α-N_β Rearrangement Accompanying the Dediazoniation of **1**, **2** *and* **3**. The N_α-N_β rearrangement was studied in 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), two solvents in which the detailed dediazoniation mechanism of arenediazonium salts is known [6] [7] [20], as well as in magic acid. We were interested in the effects of the reaction medium and of the size of the *o*-substituents on the rearrangement *(Scheme 6)* relative to the dediazoniation reaction.

Scheme 6



Rearrangement studies require an exact knowledge of the degree of dediazoniation [5–7] to be able to relate an observed percentage of rearrangement to an exact percentage of dediazoniation (for convenience usually 70%). Because of the large difference in the reactivity of **1**, **2** and **3** as well as in the solvent properties, a series of experiments was carried out in which the progress of dediazoniation was monitored by ^{1}H-NMR until suitable temperatures and reaction times were found. Owing to experimental difficulties (high reactivity of **2** and **3**, high viscosity of magic acid, high freezing point of HFIP) the data obtained are not as complete as we would have wished, and the accuracy is lower than that in earlier work [5–7]. To determine the percentage of rearrangement, in addition to MS analysis of the anilines obtained after reduction of the corresponding azo dyes [5–7], we also used ^{15}N-NMR spectroscopy of the azo dyes.

Because of the high reactivity of diazonium salts **2** and **3**, control experiments were carried out to ensure that the rate of azo coupling (*i.e.* trapping of the remaining diazonium ion at a certain percentage of dediazoniation) to R-salt (disodium salt of 2-naphthol-3,6-disulfonic acid) and to 2-naphthol was fast compared to the rate of dediazoniation in water (the reaction medium in which coupling was performed). The longest wavelength maxima of the azo dyes obtained are shown in *Table 5*. The hypsochromic shift of the maxima in going from **1** to **2** to **3** is attributed to steric crowding which leads to some loss of coplanarity and conjugation. A similar phenomenon has recently been observed when a proton was substituted by chlorine in the position *ortho* to the azo group [21].

Table 5. *Longest Wavelength Maxima [nm] of Azo Dyes Obtained by Coupling Diazonium Salts* **1**, **2** *and* **3** *with R-Salt and with 2-Naphthol*

Diazonium salt	Coupling component	
	R-salt[a])	2-Naphthol[b])
1	492	480
2	483	476
3	465	469

[a]) In H_2O. [b]) In acetone.

The dediazoniation of the compound under study in each of the solvents was stopped by azo coupling with 2-naphthol after the time necessary for *ca.* 80% reaction. The arylazonaphthols were isolated, purified and their ^{15}N-NMR spectra were recorded. The same dye samples were then reduced and the resulting anilinium hydrochlorides were analyzed for ^{15}N by MS. The data obtained are shown in *Table 6*. The observed variations in the ^{15}N chemical shifts for the same compound are a result of several factors, *e.g.* the effect of concentration, temperature *etc.* ^{15}N-NMR chemical shifts can be highly sensitive to different effects [22].

Table 6. *^{15}N-NMR Chemical Shifts (ppm) for N_α.N_β-^{15}N-Labelled Arylazonaphthols Obtained by Coupling Diazonium Salts* **1**, **2** *and* **3** *after 65–80% Dediazoniation with 2-Naphthol, and the % Rearrangement Determined by NMR and by MS*

Diazonium salt	Solvent[a])	%-Dediazoniation	N_α	N_β	% N_α-N_β Rearrangement	
					^{15}N-NMR[b])	MS
1	TFE	70				20.9[c])
	HFIP	70	270.0	419.6	25–28	37[c])
	FSO_3H/SbF_5	70–80	259.4	446.7	–	43[d])
2	TFE	74	240.2	411.3	18–25	
	HFIP	69	254.7	417.9	*ca.* 20	39
3[e])	–	0		409.6		

[a]) TFE = 2,2,2-trifluoroethanol, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

[b]) Estimated from the relative hights of the ^{15}N-signals for the α- and β-N-atoms. As the comparison with MS results demonstrates, the delay time of 20 s was not long enough for complete relaxation of both N-atoms.

[c]) From [7].

[d]) Very approximate value due to the impurity of the sample.

[e]) Owing to experimental problems no rearrangement data could be obtained.

The percentages of rearrangement determined by ^{15}N-NMR are only very crude estimates. A more accurate determination would require not only knowledge of the relaxation times of the two N-atoms, but also more concentrated solutions to obtain appropriate signal to noise ratios.

The data obtained by MS analysis are, except for the two values for salt **1** [7], unfortunately not accurate enough to allow any interpretation which would be other than speculative. Therefore, owing to experimental difficulties, no trends for the rearrangement depending on the solvent or diazonium salt structure can be determined.

Conclusion. – All the data obtained indicate that diazonium salts **1**, **2** and **3** react by a heterolytic dediazoniation mechanism in all the media investigated. The aryl cations as key intermediates of our postulated mechanism [20] are also steady-state intermediates in superacid media. Therefore, they could not be characterized by any method of instrumental analysis (NMR, IR or UV).

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Experimental Part

General. 2,6-Diethylaniline and 2,6-diisopropylaniline (both from *Fluka*) were distilled under reduced pressure prior to use. Magic acid and SbF_5 (both from *Aldrich*) were kept in a dry-box and used without further purification. 2,4,6-Trimethylbenzenediazonium tetrafluoroborate (**1**) was prepared as previously described [6]. β-^{15}N labelled diazonium salts were prepared in the same manner as the unlabelled compounds.

GC was carried out on a *Hewlett-Packard* series *588A* instrument equipped with a capillary column *(SE 30)* and an on-line automatic integrator. GC/MS was performed on a *Carlo Erba 2150* gas chromatograph (with the same column as above) and on a *Finnigan MAT 112* mass spectrometer equipped with an INCOS Data System. ^1H-NMR spectra were recorded on a *Bruker HXE-90* instrument equipped with a variable temperature probe, precalibrated with a thermocouple. *Wilmad* external capillary tubes containing TMS/[D_6]acetone were used as reference and for internal field frequency locking. ^{15}N-NMR spectra were recorded on a wide-bore *Bruker WM-400* with a spectrum frequency of 40.55 MHz at a probe temperature of 297 K and a delay time of 20 s. NH_3 was used as external reference and the spectrometer was adjusted so that the ^{15}N-signal of $HCO^{15}NH_2$ was at 112.4 ppm. $CDCl_3$ was used as solvent and for internal field frequency locking. To overcome the nuclear *Overhauser* effect arising from proton-decoupling, the spectra were recorded in inverse-gated mode, *i.e.* the decoupler was switched on only during the acquisition time. The INEPT [23][6]) technique was used to increase the signal-to-noise ratio when necessary.

2,6-Diethylbenzenediazonium Tetrafluoroborate (**2**). To 2,6-diethylaniline (5.37 g, 0.036 mol) 50% HBF_4 (31 ml) was added slowly at 0°. Water[7]) was added to the suspension until a cloudy solution was obtained. A cold solution of $NaNO_2$ (1.2 g, 0.016 mol)[8]) in *ca.* 5 ml H_2O was then added dropwise with efficient stirring. An orange colour developed and persisted throughout the addition. The mixture was stirred for 5 more min at 0° before filtration. The diazonium salt was washed three times with

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6) We assumed a coupling constant $J_{N,H}$ of 50 Hz.

7) The amount of water seems to be crucial, since with both dilute and very concentrated solutions we failed to isolate the diazonium salt or obtained it only in very poor yields.

8) If a quantity of $NaNO_2$ closer to the equimolar amount was added, the solution became even stronger coloured, and very low yields of **2** were obtained.

Et_2O, reprecipitated from cold CH_3CN/Et_2O and again washed with Et_2O. It was cooled to $-30°$ and the residual ether removed *in vacuo*. The IR spectrum recorded in cold Nujol immediately on preparation showed $\nu_{NN} = 2235\ cm^{-1}$.

2,6-Diisopropylbenzenediazonium tetrafluoroborate (**3**) was prepared by the method described for **2**. The high reactivity of **3** did not allow precipitation from acetonitrile owing to competitive dediazoniation in that solvent. The IR spectrum recorded immediately in cold Nujol showed $\nu_{NN} = 2230\ cm^{-1}$.

Preparation of the Acid Solutions. a) Solutions of diazonium salts in magic acid were prepared by slow addition of magic acid (1 ml) dissolved in SO_2 (*ca.* 1 ml) to a solution of the diazonium salt (10-15 mg) in SO_2 (*ca.* 1 ml), at $-75°$ with efficient mixing. *b)* To the diazonium salt (10 mg) dissolved in 1 ml of SO_2ClF was added a cold solution of SbF_5 (0.5 g, 0.0023 mol) in *ca.* 1 ml SO_2ClF with efficient mixing at $-75°$. In both *a* and *b* aliquots were directly transferred into 5-mm NMR tubes precooled to $-75°$ and a cold *Wilmad* capillary containing TMS/[D_6]acetone was inserted into the NMR tube.

Dediazoniation of **1**, **2** *and* **3** *in Neat Magic Acid. Ca.* 20 mg of the salt were allowed to dediazoniate in *ca.* 0.5 ml of magic acid at 0° (at r.t. for **1**). After completion of the evolution of N_2, a pale brown solution resulted. The mixture was carefully quenched in ice/$NaHCO_3$, extracted with Et_2O, dried ($MgSO_4$) and Et_2O was removed slowly on a rotary evaporator to give a pale yellow residue. This was diluted with acetone and analyzed by GC/MS.

Dediazoniation of **1**, **2** *and* **3** *in [D_6]Acetone and CD_3CN.* The solutions were prepared by addition of the solvent (*ca.* 0.25 ml) to the diazonium salt (20-30 mg) placed in a 5-mm NMR tube cooled to $-30°$, with efficient mixing. Usually NMR spectra were recorded starting at $-15°$ up to r.t. When the reaction was completed, the sample was poured onto solid $NaHCO_3$ to neutralize the acid, filtered and analyzed by GC/MS.

Monitoring of the Progress of the Dediazoniation by ^1H-NMR. The salt (10-15 mg) was placed in a precooled NMR tube, which was then placed in a cold bath at *ca.* $-30°$ and the desired solvent was added. For HFIP, owing to its high freezing point, the temperature had to be raised slowly until it melted and mixing became possible. It was recooled to $-30°$ until entering the probe. We determined the freezing points of TFE and HFIP by direct measurement in the NMR probe showing the upper limit of the sample remaining liquid to be $-54°$ for the former and $-7°$ for the latter. The progress of dediazoniation was followed at different time intervals or temperatures by monitoring the signals of the reaction products, which are all to the high field of those of the corresponding diazonium salts.

Rearrangement of **1** *in Magic Acid.* Compound **1** (103 mg) was placed in a ^{13}C-NMR tube cooled to $-30°$ and magic acid (5 ml) was added slowly. The sample was allowed to warm slowly to r.t. with efficient mixing. Teflon coated caps were placed on the tubes and the sample was kept at r.t. in the hood for 4.5 h. The % dediazoniation based on UV measurement was 70–80.

Rearrangement of **2** *and* **3** *in TFE and HFIP.* The appropriate solvent (4 ml) was added to *ca.* 100 mg of the salt (β-^{15}N labelled) placed in a ^{13}C-NMR tube cooled to $-30°$ with efficient mixing until homogeneous. The capped NMR tubes were placed in a thermostatic bath and allowed to dediazoniate for the necessary time. The remaining diazonium salt was coupled with 2-naphthol and the dyes were purified by recrystallization from EtOH.

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