165. Attempts at Solvolytic Generation of Phenyl Cations[1])

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Summary

New substrates and reaction conditions which may be expected to yield phenyl cation intermediates have been investigated. The approaches used were: (*a*) solvolysis of PhX in fluorinated alcohols, where X = $-N(O)=NOTs$ (tosyloxyazoxy), $-N(O)=NONf$ ($Nf = C_4F_9SO_2^-$) and $-OSO_2\overset{+}{N}(CH_3)_3\bar{O}Tf$ ($Tf = CF_3SO_2^-$); (*b*) solvolysis of ArBr, PhOTf and $PhOSO_2\overset{+}{N}(CH_3)_3\bar{O}Tf$ (phenyl 'betylate triflate') in superacid solvents ($FSO_3H \cdot SbF_5$, SbF_5, $AgSbF_6$). Analysis of the product mixtures provided no evidence for the intermediacy of phenyl cations as a major pathway in any of the reactions. This result is remarkable, since the 'betylate', for example, is a better leaving group by a factor of at least 10^5 than the 'super' leaving group triflate in the solvolysis of alkyl sulfonates. These results are a further indication of the extremely low stability of phenyl cations, as well as of the very special properties of the nitrogen leaving group in arenediazonium ions.

Introduction. – The solvolytic formation of aryl cations as intermediates in the heterolytic dediazoniation of arenediazonium ions is well documented [1–6]. On the other hand, all attempts at producing phenyl cations by solvolyzing arenesulfonates with 'super' leaving groups, for example trifluoromethanesulfonates (triflates) and nonafluorobutanesulfonates (nonaflates) in polar non-nucleophilic solvents have failed up to now [7] [8].

Some of the few examples where the intermediacy of aryl cations was demonstrated in the gas phase or in solution are listed below. Ion-assisted dehalogenation reactions of halobenzenes are a convenient source of phenyl cations in the gas phase [9] [10]. Also, aryl cations were reported in the photosolvolysis of 3,4-dichloroaniline in water [11]. [p-^{3}H]Phenyl cations can be generated in the gas phase and in solution by spontaneous decay of 1,4-ditritiated benzene [12]. Evidence for the intermediacy of phenyl cations was also found in the solvolysis of dienynyl triflates [13] [14] *(Scheme 1)*.

Compared to the few reactions where aryl cation intermediates have been demonstrated experimentally, this species has been dealt with in many theoretical studies and various semiempirical [2] [15–19] and *ab initio* [20–22] molecular orbital calculations of its structure and energy have been performed.

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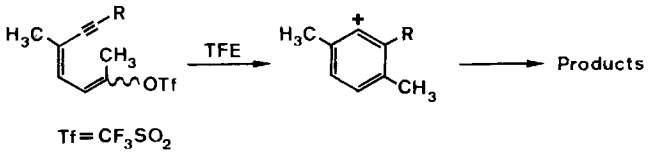
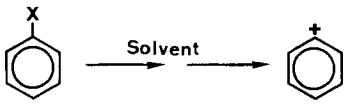
Scheme 1



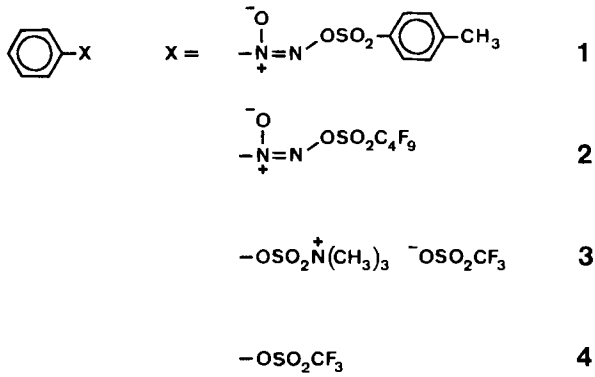
Tf = CF_3SO_2

Scheme 2



The purpose of this work was to search for new substrates and reaction conditions, which may be expected to yield phenyl cation intermediates *(Scheme 2)*.

Two approaches were used: (*a*) the investigation of relatively little explored leaving groups by solvolyzing PhX (X = tosyloxyazoxy **1**, X = nonafluorobutylsulfonyloxyazoxy ('azoxynonaflate') **2**, and 'betylate triflate'[3]) **3**) in alcohols and in water; (*b*) the solvolysis of bromomesitylene (**5**) *(cf. Scheme 11)* and of PhX (X = 'triflate' **4**, as well as 'betylate triflate'[3]) **3**) in superacid solvents.

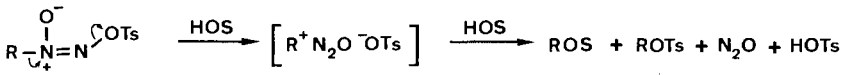


Tosyloxyazoxy-alkanes and -arenes[4]) are known [23]. The solvolysis of tosyloxyazoxy-alkanes has been investigated [24–26] and a mechanism involving unimolecular fragmentation and carbenium ion intermediates was proposed [25] [26] *(Scheme 3)*. The reactions of tosyloxyazoxybenzene were studied in non-polar

[3]) The name 'betylate' was proposed by the original authors [30] for reasons of simplicity for compounds which in current Chem. Abstr. usage would be called aryloxy- (or alkoxy-)sulfonyl-*N*,*N*,*N*-trialkyl-1-alkanaminium salts and *N*-aryloxy- (or alkoxy-)sulfonyl-*N*,*N*-dimethylmethanaminium salts.

[4]) Alternative names: nitrosohydroxylamine *p*-toluenesulfonates, *N'*-tosyloxydiimide-*N*-oxides, *N'*-tosyloxydiazene-*N*-oxides.

Scheme 3



solvents with [23] and without [27] added nucleophiles, as well as in the solid state [28] [29]. Nucleophiles reacted either at N- or at S-atom [23]. For reactions without added nucleophiles a radical decomposition was proposed [27] [28].

Since the decomposition of azoxytosylates yields an inert molecule (N_2O) between the carbenium ion and the anion *(Scheme 3)*, this reaction could constitute a link between deaminations and solvolyses of halides and sulfonates. In view of the easy generation of aryl cations from arenediazonium ions [1–6] and the unsuccessful attempts to do so from arenesulfonates [7] [8], we studied the reactions of compounds **1** and **2** in polar solvents of low nucleophilicity.

'Phenyl betylate'[3]) (**3**) has recently been synthesized [30]; nucleophiles reacted with it either by attack at the S- or at the methyl-C-atoms [30]. Alkyl betylates, on the other hand, could not be isolated, but the reaction products indicated that they decompose yielding carbenium ions [31]. A comparison of the extremely short lifetime of alkyl betylates with that of alkyl trifluoromethanesulfonates (triflates) has led to the conclusion that the betylate is a better leaving group than triflate by a factor of more than 10^5 [31], and thus with the exception of the diazonio group probably the best leaving group known. This prompted us to investigate the solvolyses of 'phenyl betylate' (**3**) in polar solvents of low nucleophilicity.

Bromomesitylene (**5**) has been studied by NMR in HF-SbF_5 and the spectrum of the resulting 2-bromomesitylenium ion reported [32]. Also, the products of the reaction with SbF_5 at room temperature are known [33]. In this work we attempted to ionize **5** with $AgSbF_6$ and with SbF_5.

Finally, the behaviour of 'phenyl triflate' (**4**) in magic acid (FSO_3H/SbF_5 1:1) was investigated in the hope that this super-acid medium would be more likely to generate phenyl cations than the standard solvolytic solvents used earlier [7] [8].

Results and Discussion. – *Reactions of Phenylazoxysulfonates.* Tosyloxyazoxybenzene (**1**) [23] was heated under reflux in 2,2,2-trifluoroethanol (TFE) and in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), and the reaction mixture checked at certain time intervals for the presence of products (phenyl fluoroalkyl ether, phenyl *p*-toluenesulfonate), which would be expected if the reaction proceeded via a phenyl cation (see *Scheme 3*). No such products were found at any stage of the solvolysis. Moreover, the TFE as well as the HFIP solution turned brown (after 15 min and 2 h, respectively) and the major product seemed to be polymeric. This indicates that phenyl radicals, rather than phenyl cations, are most likely involved, and that thermolysis in the polar solvents of low nucleophilicity TFE and HFIP does not differ much from that in non-polar solvents [27] or in the solid phase [28].

An extrapolation of the relative rate constants calculated for 2-adamantyl derivatives [25] leads to the conclusion that the tosyloxyazoxy group is a faster leaving group than tosyloxy by about two orders of magnitude. Consequently, if 'phenylazoxynonaflate' (nonafluorobutylsulfonyloxyazoxybenzene, **2**) or 'phenyl-

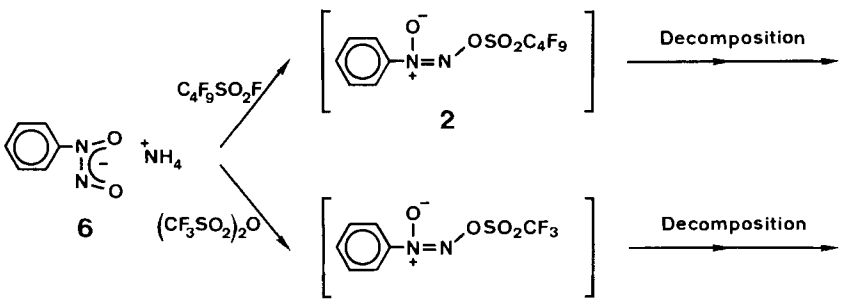
azoxytriflate' (trifluoromethylsulfonyloxyazoxybenzene) could be prepared, they should be better leaving groups than nonafluorobutanesulfonate or trifluoromethanesulfonate groups. An additional advantage of these starting materials for the generation of phenyl cations would be that no radical cleavage of a fluoroalkanesulfonate leaving group is yet known. Therefore, various attempts[5]) were made to synthesize these compounds starting from cupferron (**6**) and the corresponding sulfonic acid fluoride or anhydride in a manner similar to that described for the synthesis of **1** [23]. However, the desired azoxyfluoroalkanesulfonates were unstable and only their decomposition products were obtained *(Scheme 4)*.

If compound **2**, for example, decomposed by a mechanism similar to that shown in *Scheme 3*, the resulting phenyl cation could be captured by nucleophiles (F^-, $C_4F_9SO_3^-$, solvent) to give fluorobenzene, phenylnonaflate *etc.* After the decomposition of **2** in aqueous $NaHCO_3$ and MeOH no phenyl cation-derived products could be detected by GC/MS (in the MeOH-reaction anisole was detected in 0.2% overall yield based on **6**) and, among the products identified, benzene, biphenyl, azobenzene, diphenylamine and nitrobenzene corresponded to those found earlier in the homolytic decomposition of arenediazonium ions [34], again indicating radical intermediates.

Reactions of 'Phenyl Betylate Triflate'[3]) (**3**). Compound **3** was prepared by the method described for 'phenyl betylate fluorosulfate' [30]. As opposed to its relatively high reactivity towards nucleophiles [30] (EtOH, secondary and tertiary amines), **3** proved to be quite stable in TFE, HFIP, water and magic acid. To obtain a reasonable conversion in water, for example, **3** was heated at reflux for 11 days. The major solvolysis products in EtOH, TFE and water, as determined by GC/MS are shown in *Scheme 5*[6]).

'Phenyl betylate' (**3**) exhibits ambident reactivity towards nucleophiles. The possible pathways and the corresponding products are shown in *Scheme 6*. Nucleophilic attack at S-atom (pathway 1) leads to two products, depending on whether phenolate ion or trimethylamine is the leaving group. Nucleophilic attack at the C-atom of the CH_3-group (pathway 2) yields phenyl *N*,*N*-dimethylsulfamate (**10**).

Scheme 4



[5]) The reaction media used were aqueous $NaHCO_3$ (according to [23]), water with pyridine, MeOH and two-phase systems with phase transfer catalysis by quaternary ammonium salts or crown ethers, all at different low temperatures as well as at room temperature.

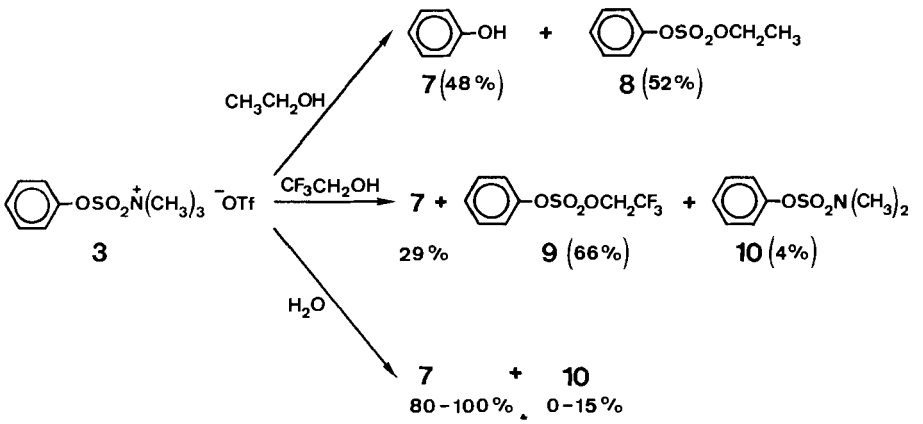
[6]) The product composition is given in area % of the volatile products.

The third pathway indicated is *via* the phenyl cation. Comparison of *Schemes 5* and *6* leads to the conclusion that nucleophilic attack on the CH_3-group C-atom takes place in TFE and water (product **10**), while that on S-atom certainly takes place in EtOH and in TFE[7]) (products **7**, **8** and **9**), and possibly also in water (product **7**).

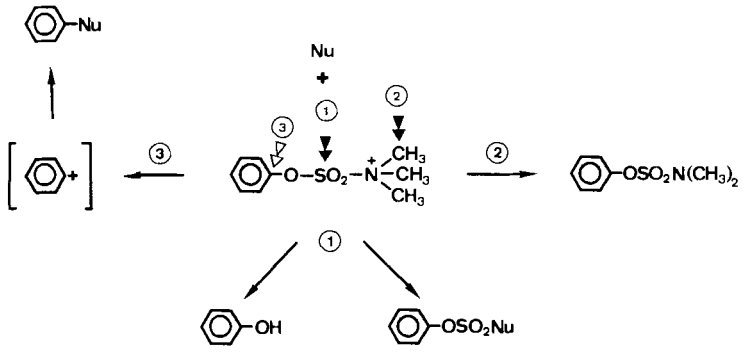
Phenol (**7**), however, the major product in water, could also have been formed by pathway 3, *i.e.* by reaction of a water molecule with the phenyl cation intermediate. Whether **7** is formed in aqueous solution by pathways 1 or 3 can easily be differentiated by using O-labelled water. An experiment was therefore run in $H_2{}^{18}O$, but no O-labelling was observed in the phenol isolated, meaning that there is no indication for the involvement of phenyl cations in this reaction.

The ^{1}H-NMR of **3** dissolved in magic acid in SO_2ClF at $-75°$ (CH_3: 4.04, *s;* Ph: 7.97, *m*)[8]) compared with that of **3** in SO_2 at $-75°$ (CH_3: 3.74, *s;* Ph: 7.58, *m*)

Scheme 5



Scheme 6



[7]) The reaction in HFIP proceeded in a similar way yielding phenol and hexafluoroisopropyl-phenyl sulfate as the major products.

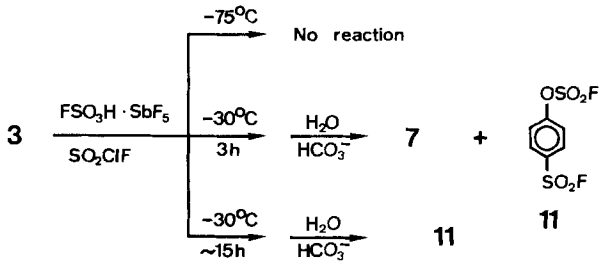
[8]) δ-values, relative to external TMS capillary.

indicates that no protonation of the phenolic oxygen by magic acid occurs. The magic acid solution of **3** at $-75°$ is stable, and a reaction takes place only after longer standing at $-30°$. The major products (GC/MS), after quenching the solution and extraction, are shown in *Scheme 7*. Comparison of the product composition after 3 h with that after 15 h leads to the conclusion that again, even in this extremely polar and non-nucleophilic medium, the main reaction is the cleavage of the phenolic O,S-bond following nucleophilic attack on the S-atom. The primary product, phenol (**7**), is eventually esterified and sulfonated to give (4-fluorosulfonyl)phenylfluorosulfate (**11**).

Reactions of 'Phenyl Triflate' (**4**). The ^{1}H-NMR of **4** dissolved in magic acid in SO_2ClF shows a somewhat broad aromatic absorption centred at 8.09 ppm. As the temperature was raised, additional signals corresponding to several *AB*-systems appeared. The products[6])[9]) (GC/MS), after quenching the solution and extraction for the three experiments are shown in *Scheme 8*, and the reaction mechanism which we feel accounts for their formation is shown in *Scheme 9*.

The formation of the triflate fluorosulfate **12** can be explained by ring protonation[10]) followed by the trapping of the σ-complex **16** by fluorosulfonic acid. Fluorosulfonylphenyl triflate (**15**) may be formed by sulfonation of **4** with FSO_3H. HF_n which is probably present in small amounts in the mixture, is an efficient catalyst for sulfonations [35]. 4,4'-Biphenyl ditriflate (**14**) could be formed *via* a *Scholl*-type condensation [36]. Finally, the formation of 4-chlorophenyl triflate (**13**) suggests that the solvent, SO_2ClF, has chlorinating properties[11]). Although SO_2ClF has been used extensively as a solvent for protonation studies, there is little information available on its chemistry [37]. Recently fluorinating and chlorinating properties of SO_2ClF towards organophosphorus compounds have been observed [38] [39]. The structure of products **13** and **14** was also confirmed by comparison with authentic samples synthesized independently from the corresponding phenols and triflic anhydride [8].

Scheme 7

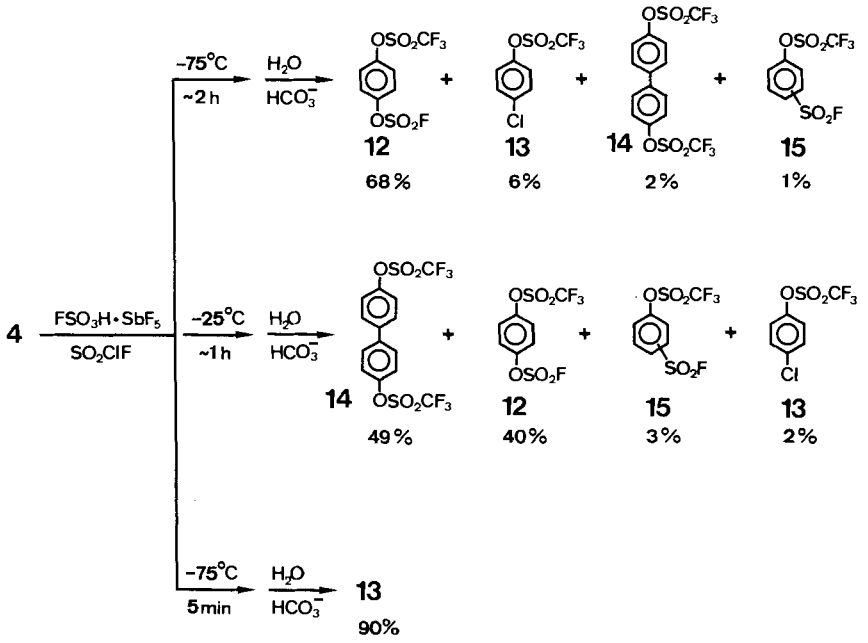


[9]) In addition to the products shown in *Scheme 8*, 5%, 6% and 10%, respectively, of unreacted phenyl triflate (**4**) were found by GC/MS in the reaction mixtures from the three experiments.

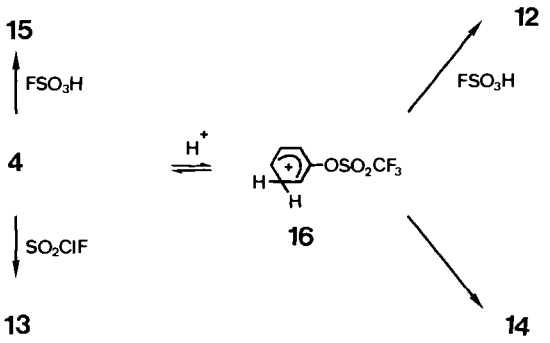
[10]) Although there is no direct NMR evidence for ring protonation at low temperature, in a kinetic sense it cannot be excluded.

[11]) Inspection of the product composition in the three experiments performed under different conditions indicates that **13** must be formed from unreacted phenyl triflate (**4**) during quenching, since the amount of **13** produced depends upon the amount of unreacted **5** in the reaction mixture.

Scheme 8



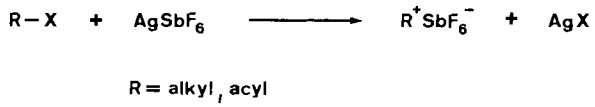
Scheme 9



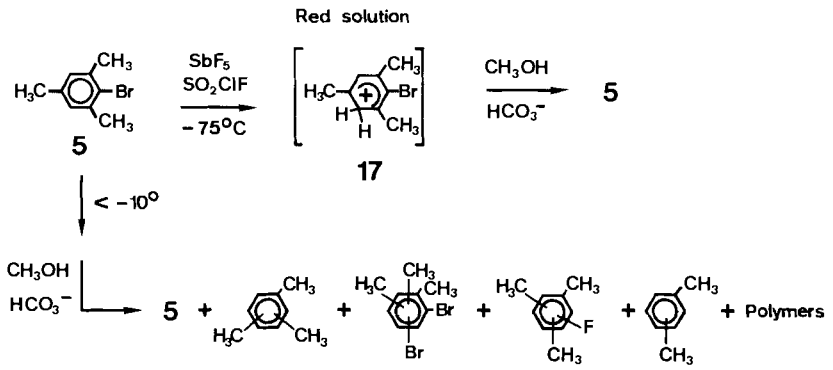
It is interesting to compare the reactivity of phenyl triflate (**4**) in magic acid with that of 'phenyl betylate' (**3**). The triflate **4** seems to be considerably more reactive in magic acid than the betylate **3** (*cf. Schemes 7* and *8*), which is contrary to the observation made for alkyl derivatives [31], the 'betylate' being more than 5 orders of magnitude more reactive than the triflate. Obviously, the relative reactivities of different leaving groups depend very much on the substrate and reaction conditions.

In conclusion, none of the reactions observed for phenyl triflate (**4**) indicates the intermediacy of phenyl cations.

Scheme 10



Scheme 11



Reactions of Bromomesitylene (**5**). Although $AgSbF_6$ has been used successfully to generate alkyl- and acylcarbenium ions [40] [41] *(Scheme 10)*, no AgBr formed in its reaction with **5** in SO_2. After quenching the reaction mixture with MeOH/$NaHCO_3$ a white crystalline complex was isolated which decomposed in water to give **5**. The structure of the crystalline material was not investigated, but it is probably a donor/acceptor complex between **5** and $AgSbF_6$.

When **5** was mixed with SbF_5 in SO_2ClF at $-75°$, a red solution was obtained, the ^{1}H-NMR spectrum of which was consistent with that of the 2-bromomesitylium ion[12]) (**17**), previously reported by *Brouwer* [32]. The starting material **5** was recovered by quenching the cation **17** in MeOH/$NaHCO_3$. When the temperature of the red solution was allowed to rise to *ca.* $-10°$ prior to quenching, transalkylation, transbromination and fluorination reactions occurred (GC/MS) *(Scheme 11)*. Similar mixtures were also observed when **5** reacted with SbF_5 in Freon (CCl_3CF_3) at $-30°$ to $-10°$. Such processes occur with alkylhalobenzenes over acidic catalysts such as SbF_5 [33], Nafion-H [42] [43] and SbF_5 intercalated graphite [44]. The results of all the reactions of **5** show that no ionisation to aryl cations takes place.

Conclusion. – No evidence was found for the intermediacy of phenyl cations in any of the reactions studied. Even under conditions which normally easily yield carbenium ions, the aryl substrates under investigation react by a variety of

[12]) Protonation of 70–75% of **5** to give **17** was estimated by integration of the NMR spectrum. The presence of small amounts of protic acid impurities in the SbF_5/SO_2ClF solvent is apparently sufficient for the protonation of **5**.

alternative pathways. These results are a further indication of the high energy content of aryl cations as well as of the very special properties of the nitrogen leaving group in arenediazonium ions.

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Experimental Part

General. GC Analyses were performed on a *Helwett-Packard*, Series *5880A* instrument with a capillary column *(SE 30)*.

GC/MS was performed on a *Carlo Erba 2150* gas chromatograph and a *Finnigan MAT 112* equipped with INCOS Data System.

Materials. SbF_5 *(Aldrich)* and $AgSbF_6$ *(Alfa)* were kept in a dry box and were used without further purification. $AgSbF_6$ was thoroughly protected from light. Magic acid, SO_2ClF, Freon, bromomesitylene (**5**) (all from *Aldrich*), cupferron (**6**), triflic anhydride, methyl triflate (all from *Fluka*), nonafluorobutane sulfonyl fluoride *(Bayer)* and $H_2{}^{18}O$ (60% ^{18}O *Stohler Isotope Chemicals*) were used as received. Phenylazoxy *p*-toluenesulfonate (**1**) [23], phenyl triflate (**4**) [8], 4-chlorophenyl triflate (**13**) [8], 4,4′-biphenyl ditriflate (**14**) [8] and phenyl *N,N*-dimethylsulfamate (**10**) [30] were prepared by known methods.

Phenyl Betylate Triflate[3]) (**3**) was synthesized by methylation of phenyl *N,N*-dimethylsulfamate (**10**) with methyl triflate according to *King & Lee* [30]. Yield 53%, m.p. 102–103°.

Solvolysis of Phenylazoxy p-*Toluenesulfonate* (**1**). Compound **1** (292 mg, 0.001 mol) were refluxed in 20 ml TFE or HFIP. Samples were taken at certain time intervals and compared with authentic expected products by TLC.

Reaction of Cupferron (**6**) *with* $C_4F_9SO_2F$ *in MeOH.* A solution containing 3.35 g (0.0216 mol) of **6** and 7.02 g (0.0232 mol) of $C_4F_9SO_2F$ in 80 ml of MeOH was stirred for 4 h at r.t. After evaporation of methanol and addition of CH_2Cl_2 a white solid was obtained which was identified by IR and ^{19}F-NMR spectroscopy as $C_4F_9SO_3^-NH_4^+$. The remaining solution was analyzed by GC and compared with authentic samples of expected products. A capillary column (50 m × 0.31 mm) of methyl silicone *(HP 19091-61050)* was used at 35° (5 min), then programmed at 20°/min, 200° (10 min).

Reactions of 'Phenyl Betylate Triflate[3]) (**3**). A solution of 50 mg (0.00014 mol) of **3** in 5 ml TFE or HFIP was stirred under N_2, at r.t. for seven days. The reaction was poured into 5 ml ice/water and extracted with $CHCl_3$. The $CHCl_3$-solution was dried ($MgSO_4$), filtered and analyzed by GC/MS on the same above column at 50° (2 min), then programmed at 10°/min, 150° (10 min). The reaction in *EtOH* was carried out similarly, reaction time 1 h at r.t. Reaction in *water:* a solution of 100 mg (0.00028 mol) of **3** in 1.5 ml $H_2{}^{18}O$ was kept in an ampoule at 100° for 11 days, poured onto 15 g of ice and extracted with CH_2Cl_2. The residue after evaporation of CH_2Cl_2 was purified by thick layer chromatography and analyzed by MS for incorporation of ^{18}O, which was not found. Reaction in *magic acid:* **3** is poorly soluble in SO_2ClF. The acid solution was prepared by slow addition of magic acid (1 ml) dissolved in SO_2ClF (1 ml) to a suspension of **3** (30 mg, 0.00011 mol) in SO_2ClF (1 ml) at −75° with efficient mixing. An aliquot was directly transferred into a 5-mm NMR tube for low temperature studies, and the stock solution was allowed to stand at −75° or −30° until quenching. The acid solutions were quenched by carefully pouring onto ice containing $NaHCO_3$. The aq. solution was extracted with Et_2O, dried ($MgSO_4$), filtered and evaporated slowly on a rotary evaporator. The residue was taken up in $CDCl_3$ for NMR studies and for GC/MS. The ^1H-NMR spectra were recorded using external *Wilmad* tubes containing TMS and [D_6]acetone.

The Reaction of Phenyl Triflate (**4**) in magic acid was performed in the same way as that of **3**.

Reactions of Bromomesitylene (**5**). a) *With* $AgSbF_6$ *in* SO_2*:* 3 ml of SO_2 were added to 900 mg (0.0026 mol) of $AgSbF_6$ and the mixture was shaken until a cloudy solution resulted. Allowing the temperature to rise, a homogeneous solution was obtained at −10°. 300 mg (0.0015 mol) of **5** dissolved

in 1 ml of SO_2 was added with efficient mixing while the temperature was kept around $-40°$. There was no indication of AgBr precipitating. The sample was allowed to warm slowly until SO_2 started to boil and then quenched in MeOH/$NaHCO_3$. The solution was filtered and most of the MeOH was distilled off slowly leaving a white solid, which reacted with added water. A GC of the ethereal extract showed only **5**. b) *With SbF_5 in SO_2ClF:* to a solution of **5** (500 mg, 0.0025 mol) in 1 ml of SO_2ClF was added a solution of 1 g (0.0046 mol) of SbF_5 in 1 ml of SO_2ClF, at $-75°$ with efficient mixing. A deep red solution resulted. A portion of this solution was poured into cold MeOH/$NaHCO_3$ and the colour immediately disappeared. After filtration, evaporation of MeOH, and extraction with Et_2O a GC analysis showed only **5**. The other portion of the red solution was allowed to warm slowly until SO_2ClF started to boil and was then quenched with ice/$NaHCO_3$, extracted with Et_2O, dried ($MgSO_4$) and analyzed by GC/MS. c) *With SbF_5 in Freon:* a solution (1 g 0.005 mol) of **5** in 2 ml of Freon was added to 2.1 g (0.01 mol) of SbF_5 in 2 ml of Freon at *ca.* $-30°$. After an exothermic reaction the colourless solution turned brown. The mixture was poured into 10 ml of cold MeOH with efficient mixing. Two layers, a pale brown upper liquid layer and a dark green solid were formed. The solution was filtered, neutralized and analyzed by GC/MS.

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