# A New Route to Polykis(dialkylamino)benzenes and -naphthalenes Based on Protodefluorination of Electron-Rich Fluoroaromatics: Anion Radicals of Arenes as a Simple and Effective Alternative to 'Classical' LAH-Based Systems

Vladimir Igorevich Sorokin,*[a] Valery Anatolievich Ozeryanskii,[a] Gennady Sergeevich Borodkin[b]

[a] Department of Organic Chemistry, Rostov State University, Zorge street 7, 344090 Rostov-on-Don, Russia
Fax +7(863)2974156; E-mail: vsorokin@aaanet.ru

[b] Institute of Physical and Organic Chemistry, Stachki ave. 194/2, 344090 Rostov-on-Don, Russia

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Dedicated to Prof. Alexander F. Pozharskii on the occasion of his birthday

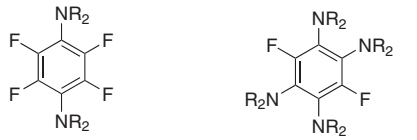
**Abstract:** A simple and effective procedure for protodefluorination of electron-rich fluoroaromatic compounds has been developed. It operates with aromatic anion radicals as reducing agents and shows superior results over 'classical' lithium aluminum hydride based systems.

**Key words:** fluorinated amino arenes, aromatic anion radicals, protodefluorination, lithium aluminum hydride, electron transfer

The carbon–fluorine bond is known as one of the strongest among all organoelement bonds. The dissociation energy is 116 kcal/mol in contrast to 85 kcal/mol for C–C, 99 kcal/mol for C–H and 79 kcal/mol for C–Cl bonds.[1] This is the main reason why only a limited range of reagents is available for its hydrogenolysis. The most effective and widely used reagents are systems based on lithium aluminum hydride (LAH).[2] As an alternative for C–F bond cleavage, Ni(0)/*N*-heterocyclic carbene complexes, recently suggested by Fort et al., should also be mentioned.[3]

Earlier, we developed an effective approach to a wide variety of 1,4-bis(dialkylamino)tetrafluoro- (**1**–**4**) and 1,2,4,5-tetrakis(dialkylamino)difluorobenzenes (**5**–**8**) (Figure 1)[4] as well as 2,3,6,7-tetrakis(dialkylamino)tetrafluoronaphthalenes (**9**–**11**) (Figure 2),[5] via nucleophilic substitution of fluorines in hexafluorobenzene and octafluoronaphthalene. Continuing our investigations in the field of amino-substituted perfluoroaromatics, we noticed that their defluorinated analogues, due to their easily oxidizable nature, find application, for example, in the preparation of different magnetic and conductive materials,[6] or as mediators of glucose oxidase in glucose amperometric detection.[7]

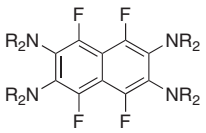
One of the main synthetic approaches to such compounds is still a step-by-step functionalization, (e.g., arene nitration–reduction–alkylation technique).[8] Cross-coupling methodology, becoming more and more popular for its high effectiveness and selectivity, is limited by the introduction of primary and cyclic secondary amino groups into aromatic compounds.[9]



**1** $NR_2 = NMe_2$
**2** $NR_2$ = Piperidin-1-yl
**3** $NR_2$ = Pyrrolidin-1-yl
**4** $NR_2 = NBu_2$

**5** $NR_2 = NMe_2$
**6** $NR_2$ = Piperidin-1-yl
**7** $NR_2$ = Pyrrolidin-1-yl
**8** $NR_2 = NBu_2$

**Figure 1**

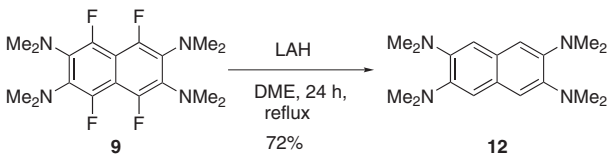


**9** $NR_2 = NMe_2$
**10** $NR_2$ = Piperidin-1-yl
**11** $NR_2$ = Pyrrolidin-1-yl

**Figure 2**

Hence, we have developed an effective protodefluorination procedure should result in a good two-step (nucleophilic substitution–hydrogenolysis) alternative to synthesize polykis(dialkylamino)arenes, easily accessible from hexafluorobenzene and octafluoronaphthalene compounds **1**–**11**.

We started our efforts using LAH alone, by refluxing amines **1**–**11** for 24 hours with ten equivalents of LAH per fluorine atom in DME (smaller amounts of LAH led to incomplete defluorination). These condition turned out to be effective only in the case of dimethylamino naphthalene **9** (Equation 1).




**9** → **12**

**Equation 1**

The nature of the solvent had a similar effect on this transformation as that observed in other LAH reductions.[10] Thus, in dioxane, the reduction **9** → **12** did not occur, and in diethyl ether, only traces of product **12** formed after 24 hours, whereas in THF, amine **12** was almost the sole product, and was the only product when DME was used.

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Benzene derivatives, as well as tetraaminonaphthalenes **10** and **11**, remained unchanged under the conditions shown in Equation 1.

Interestingly, tetraamine **12** was earlier synthesized in a four-step procedure starting from 2,7-dihydroxynaphthalene in a total yield of about 10%.[11] Taking into account that compound **9** is prepared from octafluoronaphthalene in 80% yield, our methodology is at least six times more effective.

Semi-empirical AM1 calculations[12] helped to gain deeper insight into this phenomenon (Table 1). As can be seen, tetraamine **9**, among others, has the highest sum of total charges on the aromatic carbons (as the measure of electron deficiency in the aromatic ring) and the lowest LUMO energy (as the measure of electron acceptor ability of the molecule). As a result, derivative **9** should be the most reactive towards reducing species.

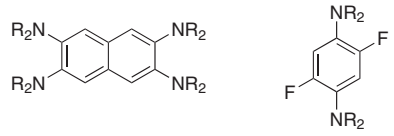
It is well-known that the combination of LAH with some transition-metal salts can significantly increase the reducing power of such systems.[10] The most active additives toward protodefluorination are known to be cerium(III) chloride[13] and, as suggested recently, niobium pentachloride.[14] Nevertheless, up to now, these salts were not tested in the defluorination of strongly electron-enriched arenes, nor was their hydrogenolysis strength compared.

In the present work, the protodefluorination with cerium trichloride as additive has been conducted according to a literature procedure,[13] using 1.5 equivalents of the salt, 10 equivalents of LAH per fluorine atom, and DME as the solvent. The results obtained after 24 hours of refluxing are presented in Table 2. Evidently, the addition of the cerium compound significantly increases the reducing activity of LAH and allows the inclusion of benzenes **1**–**5** (but not **6**–**8**) in the transformation.

**Table 1** Selected AM1-Calculated Parameters of Arenes **1**–**11**

| Compound | Average twisting of the $NR_2$ groups relative to the aromatic ring plane (°) | Sum of total charges on aromatic carbons | LUMO energy (eV) |
|---|---|---|---|
| **1** | 47 | 0.44 | –0.63 |
| **2** | 47 | 0.38 | –0.53 |
| **3** | 39 | 0.38 | –0.51 |
| **4** | 49 | 0.40 | –0.53 |
| **5** | 77 | 0.56 | –0.23 |
| **6** | 79 | 0.34 | –0.17 |
| **7** | 77 | 0.51 | –0.15 |
| **8** | 79 | 0.38 | –0.06 |
| **9** | 93 | 0.94 | –1.10 |
| **10** | 78 | 0.74 | –0.86 |
| **11** | 65 | 0.68 | –0.73 |

Unfortunately, we were unable to isolate any products from the reaction with polyaminonaphthalenes **10** and **11**, despite the 100% conversion of the starting compounds. Extraction of the reaction mixture with diethyl ether, even using standard precautions and argon atmosphere, led to complete tarring of the extract. Such behavior arises possibly from a high electron density in the naphthalene ring of the defluorinated products **23** and **24** (Figure 3). This results in a much better conjugation of the piperidino and pyrrolidino groups with the aromatic system [if compared to **12** (Table 1)], along with lengthy π–systems which favor the oxidation of amines **23** and **24**.




**23** $NR_2$ = Piperidin-1-yl
**24** $NR_2$ = Pyrrolidin-1-yl

**25**

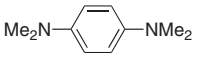
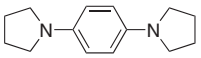
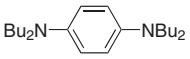
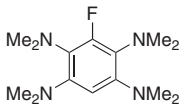
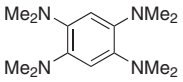
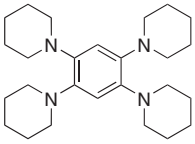
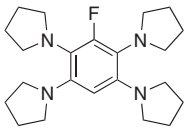
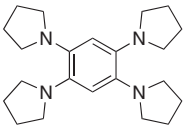
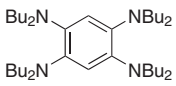
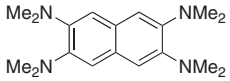
**Figure 3**

In the case of diaminobenzenes **1**–**4**, completion of the reaction after 12 hours of heating allowed the detection of *p*-difluoro-substituted derivatives of type **25** along with other products, as evidenced by NMR techniques. In particular, both $^1H$ and $^{19}F$ spectra of **25** ($NR_2$ = piperidin-1-yl) exhibit a doublet of doublets near $\delta = 6.6$ ($^1H$) and $\delta = -150.4$ ($^{19}F$) with coupling constants of 9.1 Hz and 15.2 Hz, characteristic for $^3J_{HF}$ and $^5J_{FF}$, respectively.[15] These observations helped to shed light on the defluorination sequence of fluorobenzenes **1**–**4**. Spectral data of the reaction mixture of naphthalenes **9**–**11** were too complex and did not allow the determination of the defluorination order.

Tetrakis(dimethylamino)benzene **5** gave a mixture of **17** and **18** (Table 2). Compound **17** shows doublets in the $^1H$ as well as the $^{19}F$ NMR spectra with the characteristic coupling constant of $^5J_{HF} = 1.9$ Hz.[15] The relative distribution of the products in the reaction mixture did not change significantly even after 48 hours of heating, possibly due to some loss of LAH in side reactions.

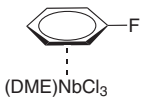
Protodefluorination with niobium pentachloride as an additive was performed in a manner similar to the literature procedure[14] using 0.1 equivalent of the niobium(V) chloride together with 10 equivalents of LAH per fluorine atom (Table 2). In general, this system has a reducing power similar to that of the cerium-based composition. Again, tetraamines **6**–**8** remained unchanged. It should be stressed, however, that the reaction rate increased significantly, which can be seen especially well by comparing the results on protodefluorination of compound **5** (Table 2). As before, we were unable to isolate any defluorinated products in the case of naphthalenes **10** and **11**, observing only strong tarring. It should also be mentioned that, as observed for the cerium-based system, the partially reduced derivatives of type **25** were also detected here.

**Table 2** Protodefluorination of Polyamines **1**–**11** under Various Conditions

| Substrate | Product(s) | Yields (%)[a] | | |
|---|---|---|---|---|
| | | $CeCl_3$/LAH/DME | $NbCl_5$/LAH/DME | $Na^+Ar^-$/DME |
| **1** |  **13** | 100 (59) | 100 (61) | 100 (65)[b] |
| **2** |  **14** | 100 (59) | 100 (59) | 100 (63)[b] |
| **3** |  **15** | 100 (57) | 100 (59) | 100 (60)[b] |
| **4** |  **16** | 100 (56) | 100 (61) | 100 (62)[b] |
| **5** |  **17** | 95 | 78[c] | 0[b] |
| |  **18** | 5 | 22[c] | 100 (68)[b] |
| **6** |  **19** | 0[d] | 0[d] | 100 (77)[e] |
| **7** |  **20** | 0[d] | 0[d] | 100 (56)[e] |
| **7** |  **21** | 0[d] | 0[d] | 100 (63)[f] |
| **8** |  **22** | 0[d] | 0[d] | 100 (60)[e] |
| **9** |  **12** | 100 (61) | 100 (63) | 100 (65)[b] |

[a] Isolated yields are given in parentheses.
[b] Ar = Naphthalene.
[c] 3 Equiv of $NbCl_5$ were used to compare with $CeCl_3$ experiments.
[d] Starting compound was recovered.
[e] Ar = Biphenyl.
[f] Ar = 4-Methylbiphenyl.

Interestingly, despite the similarity of the two mentioned additives, completely different mechanisms of action were suggested in the literature. For cerium trichloride, the single-electron transfer (SET) process with low-valent cerium as the actual reducing agent was proposed.[13] In the case of niobium pentachloride, a nucleophilic substitution in the $\eta^6$-arene complexes of type **26** was postulated to occur.[14]




**26**

**Figure 4**

If the SET mechanism takes place in the defluorination with cerium(III) chloride, utilization of certain radicals can lead to the same or even better results, since this will shorten the electron-transfer pathway from an electron donor to a fluoroaromatic compound.

We decided to use sodium naphthalenide as electron source. This compound can be easily prepared by action of sodium metal on a naphthalene solution in THF at room temperature.[16] We suggested the general procedure consisting of two simple steps to follow: generation of naphthalenide (or other arene anion radicals, see below) (3 equiv per fluorine) and its interaction with selected fluoroaromatic compounds (r.t., 12 h).

Indeed, amines **1**–**5** and **9**–**11** undergo C–F bond hydrogenolysis in the above system; for example, tetraamine **5** gave a mixture of **17** and **18** in 33% and 67%, respectively, indicating the system to be more powerful than LAH-based mixtures (compare with data from Table 2). We have also found that DME is superior over THF as a solvent, leading to compound **18** exclusively under similar conditions (Table 2). Interestingly, the use of sodium alone in DME did not cause defluorination. However, derivatives **6**–**8** are still inert to sodium naphthalenide. To involve them in the protodefluorination sequence, much stronger electron donors like the anion radical of biphenyl,[17] are required. With this anion radical, tetraamines **6** and **8** gave the corresponding di(defluorinated) derivatives **19** and **22**. Compound **7** undergoes only monodefluorination leading to **20**.

4-Methylbiphenyl, with an ionization potential lower than that of biphenyl,[17] makes it possible to overcome this obstacle. It is necessary to note that compound **21** shows the same oxidizable nature as do naphthalenes **23** and **24**. In solution, compound **21** readily becomes green and then turns to a dark-brown color. As a result, we did not manage to collect its NMR data, but in contrast to compounds **23** and **24** the structural information was in part derived from mass spectra and elemental analysis data of the solid.

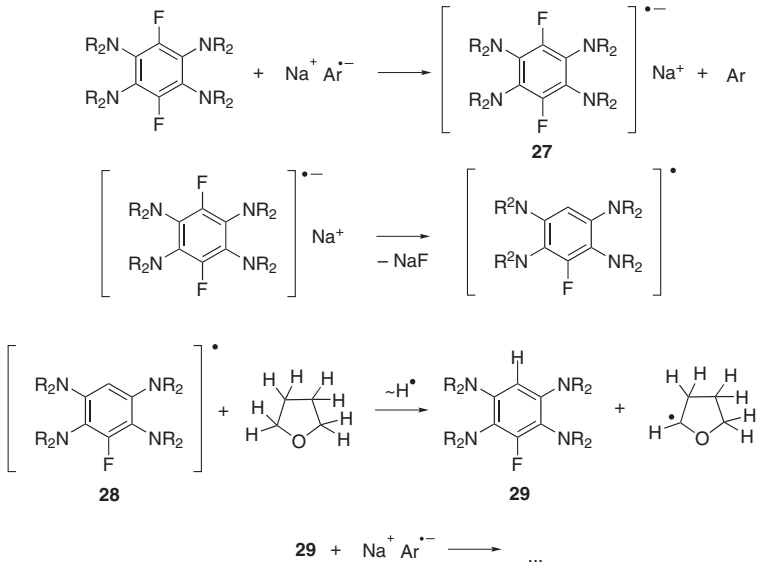
As demonstrated, the nature of the arene plays a key role determining the overall strength of the protodefluorinated system. The influence of solvent in this transformation can be explained based on data from Arnett and co-workers.[18] They showed that the sodium cation is much stronger when solvated by DME than by THF, with solvation energies of –0.45 kcal/mol and –0.08 kcal/mol, respectively. Hence, the ion pair between $Na^+$ and the arene anion radical in DME is much more separated, leading to more reactive reducing species. This also explains why in dioxane (solvation energy is still lower, –0.06 kcal/mol) the starting compounds remain in solution even after 24 hours. We suggested the following reaction mechanism, presented in Scheme 1, using the example of 1,2,4,5-tetrakis(dialkylamino)benzenes and THF.

The mechanistic pathway begins with the electron transfer from the arene anion radical to the polyamine leading to the anion radical of **27**. Its subsequent transformation to radical **28**, which abstracts a hydrogen atom from the solvent and turns into product **29**, terminates the reaction.

Studied polyamines can be arranged according to their protodefluorination potential in the following order: **7** < **8** < **6** < **5** < **3** < **2** ~ **4** < (**11**, **10**) < **9**. In general, this row fits with the sequence predicted on the basis of AM1 calculations (Table 1), with the exception of tetraamines **5**–**8**. This deviation compared to the data observed experimentally arises possibly from the lack of a strict geometry prediction for such complexes and, probably more important, strained systems.

In conclusion, the proposed protodefluorination technique is a good alternative both to classical and cross-coupling methodologies. For example, for 1,4-bis(piperidin-1-yl)benzene (**14**), which can be obtained by alkylation of *p*-phenylenediamine with 1,5-dibromopentane in 70% yield,[8] or by cross-coupling approach from 1,4-dibromobenzene and piperidine using $Pd(dba)_2/P(o\text{-tolyl})_3$ as catalyst in 63% yield,[19] our method (starting from hexafluorobenzene) gave 50% yield. The difference becomes already more important in the case of 1,4-bis(pyrrolidin-1-yl)benzene (**15**) and 1,2,4,5-tetrakis(dimethylamino)benzene (**18**). Compound **15** was obtained from *p*-phenylenediamine in only 29% yield,[8] compared to 47% if prepared by our method; compound **18**, synthesized from 1,2,4,5-tetraaminobenzene in 27% yield,[11] shows comparable results yielding 59% by employing hexafluorobenzene. A remarkable feature of the suggested system, along with high effectiveness, is its customizability. Choosing an appropriated arene allows to remove but one among several fluorine substituents from a molecule, as for instance, it was the case in the protodefluorination of tetraamine **7** (Table 2).

LAH and niobium(V) chloride were purchased from Aldrich. Cerium(III) chloride heptahydrate was purchased from Lancaster and made anhydrous according to a literature procedure.[20] NMR spectroscopy was performed on a Varian Unity-300 spectrometer. Melting points were obtained on a PTP-1 melting point apparatus. Mass spectrometry was carried out on a VG AutoSpec instrument. Elemental analyses were obtained from the elemental analysis laboratory of Institute of Physical and Organic Chemistry (Rostov-on-Don). Compounds **1**–**11** were synthesized in conformity with the literature,[4,5] their properties are identical with those described. The




**Scheme 1** Proposed mechanism for aromatic anion radical mediated defluorination

correctness of the structures assigned for **12**–**16** and **18** was proven by comparison with authentic samples prepared as described in the literature for **13**–**15**[8] and for **16**,[21] and using the Staab method for compounds **12** and **18**.[11]

**1,2,4,5-Tetrakis(dibutylamino)difluorobenzene (8)**
Colorless crystals; mp 55–56 °C (from MeOH).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.0 Hz, 24 H, $CH_3$), 1.20 (m, 16 H, $CH_2CH_2$), 3.03 [t, *J* = 7.5 Hz, 16 H, $N(CH_2)_2$].

$^{19}$F NMR (282 MHz, $CDCl_3$): δ = –133.57 (s).

MS (EI, 70 eV): *m*/*z* (%) = 623 (25) [M$^+$], 622 (76), 579 (30), 566 (100), 479 (31), 465 (38), 365 (17), 57 (22), 43 (42).

Anal. Calcd for $C_{38}H_{72}F_2N_4$: C, 73.26; H, 11.65; N, 8.99. Found: C, 73.28; H, 11.61; N, 8.89.

**Hydrogenolysis of Fluorinated Amines under the Action of Aromatic Anion Radicals in DME; General Procedure**
Finely crashed sodium (3 equiv per fluorine atom) was added to a solution of the corresponding arene (3 equiv per fluorine atom) in DME (8 mL) under argon atmosphere. After 2 h of stirring at r.t., the solid fluorinated amine (0.1 mmol) was added to the deep green solution and stirring was continued for additional 12 h. The reaction solution was then poured on 20% aq HCl (15 mL, **Caution, violent heating!**). Some more aq HCl was added to adjust the acidity to pH 2. The precipitated arene was separated by filtration and then, to remove arene traces, the mixture was extracted with hexanes (2 × 10 mL). The resulting clear solution was made basic (pH 10–11) using ammonia and the resulting amines were taken up into $Et_2O$ (5 × 4 mL). The ethereal solution was dried ($Na_2SO_4$) and quickly evaporated to prevent oxidation of the resulting products.

**1,2,4,5-Tetrakis(piperidin-1-yl)benzene (19)**
Colorless powder; mp 256–257 °C (from MeOH).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 1.64 (m, 24 H, $CH_2CH_2CH_2$), 3.02 [m, 16 H, $N(CH_2)_2$], 6.50 (s, 2 H, H-3,6).

MS (EI, 70 eV): *m*/*z* (%) = 410 (100) [M$^+$], 205 (14), 84 (17), 55 (17).

Anal. Calcd for $C_{26}H_{42}N_4$: C, 76.05; H, 10.31; N, 13.64. Found: C, 76.25; H, 10.01; N, 13.82.

**1,2,4,5-Tetrakis(pyrrolidin-1-yl)-3-fluorobenzene (20)**
Colorless crystals; mp 139–140 °C (from MeOH).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 1.86 (m, 16 H, $CH_2CH_2$), 3.08 [m, 8 H, $N(CH_2)_2$], 3.36 [m, 8 H, $N(CH_2)_2$], 5.72 (d, *J* = 1.5 Hz, 1 H, H-6).

$^{19}$F NMR (282 MHz, $CDCl_3$): δ = –129.8 (d, *J* = 1.6 Hz, F-3).

MS (EI, 70 eV): *m*/*z* (%) = 372 (100) [M$^+$], 344 (14), 302 (19), 149 (23), 70 (17), 57 (20), 43 (31).

Anal. Calcd for $C_{22}H_{33}FN_4$: C, 70.93; H, 8.93; N, 15.04. Found: C, 71.20; H, 8.94; N, 15.36.

**1,2,4,5-Tetrakis(pyrrolidin-1-yl)benzene (21)**
Due to the fast oxidation on air and in solution, physical data for the crude product are given. Light-yellow powder; mp 193–195 °C.

MS (EI, 70 eV): *m*/*z* (%) = 354 (100) [M$^+$], 326 (15), 297 (13), 284 (20), 255 (13), 70 (12), 58 (13), 55 (15), 43 (35).

Anal. Calcd for $C_{22}H_{34}N_4$: C, 74.53; H, 9.67; N, 15.80. Found: C, 74.40; H, 9.70; N, 15.89.

**1,2,4,5-Tetrakis(dibutylamino)benzene (22)**
Colorless oil.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 8.3 Hz, 24 H, $CH_3$), 1.23 (m, 16 H, $CH_2$), 1.36 (m, 16 H, $CH_2$), 3.02 [t, *J* = 8.7 Hz, 16 H, $N(CH_2)_2$], 6.49 (s, 2 H, H-3,6).

Anal. Calcd for $C_{38}H_{74}N_4$: C, 77.75; H, 12.71; N, 9.54. Found: C, 77.71; H, 12.53; N, 9.55.

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