Xenon difluoride–trimethylsilyl isocyanate–triflic acid as a new system for the amination of aromatic compounds

Namig Sh. Pirkuliev,[a,b] Valery K. Brel,*[a] Novruz G. Akhmedov,[b] Nikolai S. Zefirov[a,b] and Peter J. Stang[c]

[a] *Institute of Physiologically Active Compounds, Russian Academy of Sciences, Chernogolovka, 142432 Moscow region, Russian Federation. Fax: +7 095 913 2113; e-mail: brel@ipac.ac.ru*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation*
[c] *Department of Chemistry, Unversity of Utah, Salt Lake City, UT 84112, USA*

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In the title system, $OCNXeOSO_2CF_3$ is formed, which readily oxidises iodobenzene to [PhI^+–NCO $^-$OTf]. The direct amination of aromatic substrates is possible with the use of XeF_2–Me_3SiNCO–CF_3SO_3H.

Since the discovery of the first xenon compounds by Bartlett[1] in 1962, a large number of xenon derivatives with Xe–F, Xe–Cl, Xe–O, Xe–N, Xe–C and Xe–N bonds were prepared.[2] The methodology of Xe–element bond formation is based on the rupture of M–element bonds (where M = Bi, Sb or Si) with the aid of xenon fluorides. The Si–element fission bond is most promising and interesting for obtaining compounds with Xe–N bonds.[2(a),3] Thus, D. D. DesMarteau[3(c)] used this approach for the preparation of the relatively stable compound $FXe(NSO_2F)_2$. Recently, theoretical computations and product analysis of the reaction of XeF_2 with NaN_3 and NaOCN indicated the intermediate formation of $FXeN_3$ and FXeNCO.[4]

Previously, we found that the reaction of trimethylsilyl isocyanate with XeF_2 or $FXeOSO_2CF_3$ in the presence of olefins proceeds through the formation of FXeNCO and $OCNXeOSO_2CF_3$ intermediates, which are easily added at the double bond of an olefin. In a continuation of this work, we studied the interaction of trimethylsilyl isocyanate with XeF_2 or $FXeOSO_2CF_3$ in the presence of aromatic compounds. It is well known that, in this case, the reaction path strongly depends on the order in which the reactants were added. In particular, if finely dispersed XeF_2 in CH_2Cl_2 was transformed into FXeOTf[5] and the latter was treated with trimethylsilyl isocyanate and then with iodobenzene, mixed iodonium sulfonate **3**[6] was obtained.†

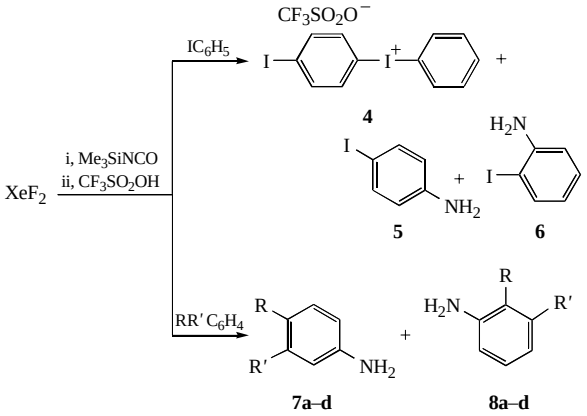
$$XeF_2 + HOTf \xrightarrow{CH_2Cl_2} \underset{\mathbf{1}}{FXeOTf} \xrightarrow[-\ TMSF]{Me_3SiNCO} \underset{\mathbf{2}}{[Xe(OTf)(NCO)]} \xrightarrow[-\ Xe]{PhI} \underset{\mathbf{3}}{TfO^-\ PhI^+–NCO}$$

Scheme 1

When trimethylsilyl isocyanate was added to a XeF_2 solution in CH_2Cl_2 and the resulting mixture was subsequently treated with triflic acid and iodobenzene, phenyl(*p*-iodophenyl)iodonium triflate **4** and iodoanilines **5**, **6** (as a mixture of *ortho* and *para* isomers) were isolated from the reaction mixture as a final products.‡ Note that in this case the formation of compound **3** was not detected.

Consequently, the XeF_2–Me_3SiNCO–CF_3SO_3H system acts as an aminating reagent for aromatic compounds.[7,8]

Moreover, we found that with the use of other aromatic compounds such as benzene, toluene, chlorobenzene and *o*-xylene instead of iodobenzene the formation of amines **7** and **8** takes place (Table 1).



a R = R′ = H
b R = Cl, R′ = H
c R = Me, R′ = H
d R = R′ = Me

Scheme 2

Table 1 Amination of aromatic compounds with XeF_2–Me_3SiNCO–CF_3SO_3H.

Substrate	Reaction time/h	Yield[a] (%)	*ortho*-isomer	*para*-isomer	Yield[a] of **4** (%)
C_6H_6	3	45	—		
MeC_6H_5	3	40	54	46	
IC_6H_5	4	38	50	44	44
ClC_6H_5	6	35	45	48	
o-Xylene	3	43	—	—	

[a]Isolated yields based on XeF_2 used.

† *Typical procedure for the preparation of [PhI^+NCO^-OTf].* 5.52 mmol of Me_3SiNCO was added to a stirred suspension of 4.72 mmol of CF_3SO_2OXeF[5] in 20 ml of CH_2Cl_2 at –78 °C under argon. The mixture was allowed to warm up to –40 °C and stirred until the formation of a yellow homogeneous solution. The solution was cooled to –78 °C; then, 4.72 mmol of iodobenzene was added using a syringe. The mixture was allowed to warm to –5 °C and stirred for ~2 h. The precipitate was filtered off under argon, washed with cold diethyl ether and dried *in vacuo* to yield the material of >98% purity. The analytically pure compound can be obtained by recrystallization from CH_2Cl_2–Et_2O.

[Isocyanato(trifyloxy)-λ³-iodo]benzene **3**. ^1H NMR (CD_3CN) δ: 8.3–7.5 (m). ^{13}C NMR (CD_3CN) δ: 172.5 (CO), 136.6, 135.0, 132.9, 122.7 (Ph), 120.8. ^{19}F NMR (CD_3CN) δ: –78.6 (CF_3). IR (CCl_4, ν/cm^{-1}): 2510, 1625 (NCO), 1258, 1178, 1023 (OTf).

‡ *Reaction of iodobenzene with XeF_2–Me_3SiNCO–HOTf.* XeF_2 (4.72 mmol) was dissolved in dry CH_2Cl_2 (15 ml)[10] under argon; then, Me_3SiNCO (5.1 mmol) was added. Triflic acid (10 mmol) was slowly added dropwise at –78 °C to the solution of FXeNCO in dry CH_2Cl_2 and then the mixture was stirred at –30 °C for ~1 h. Then, a large excess of PhI (12 mmol) was added to the suspension at –78 °C, and the mixture was stirred until no more gas (Xe) was evolved (see Table 1 for total reaction time). The solution was heated to room temperature and poured into a dilute solution of HCl with ice. An excess of iodobenzene and phenyl(*p*-iodophenyl)-iodonium triflate **4** were extracted with dichloromethane (3×15 ml). The volatile materials were then removed under reduced pressure to give an oily residue, which was dissolved in dry diethyl ether. The mixture was vigorously shaken for several minutes to precipitate slightly coloured crystals. Analytically pure samples were obtained by recrystallization from CH_2Cl_2–Et_2O. The aqueous layer was neutralised with a 30% sodium hydroxide solution to pH ~13. The mixture of *o*- and *p*-iodoanilines **5**, **6** was then extracted with dichloromethane and dried with $MgSO_4$. Products were isolated after evaporating the solvent. Isomeric mixtures were analysed by ^1H NMR.

*Phenyl(*p*-iodophenyl)iodonium triflate* **4**: yield 44%, mp 146–147 °C (lit.,[11] 144–148 °C). ^1H NMR ($CDCl_3$) δ: 7.48 (m, 2H, Ph), 7.64 (m, 1H, Ph), 7.80 (m, 4H, C_6H_4), 8.10 (m, 2H, Ph). ^{19}F NMR ($CDCl_3$) δ: –78.4 (CF_3SO_3).

These results indicate that the XeF_2–Me_3SiNCO–CF_3SO_3H system makes it possible to perform conveniently electrophilic one-step amination of aromatic compounds with the formation of anilines in moderate yields. Highly deactivated aromatics slowly react under these conditions to form anilines in low yields. Thus, with nitrobenzene, the yields of nitroanilines were lower than 5%. In this case, the deactivation of a benzene ring probably occurs not only owing to the nitro group but also due to the further deactivation of the ring by the protonation of the nitro group in a triflic acid medium.[9]

It is believed that the amination of aromatic compounds[§] involves the formation of the reactive triflate $[H_2N^+{=}C{=}O\ {}^-OTf]$ at the stage of the interaction of FXeNCO with triflic acid. This explanation was additionally supported by studies of the reactions with Me_3SiOTf in place of HOTf. In this case, the $[H_2N^+{=}C{=}O\ {}^-OTf]$ species was not formed, apparently, due to the absence of hydrogen ions. Most likely, the formation of $OCNXeOSO_2CF_3$ occurs, and hence the reaction with iodobenzene leads to the formation of only iodonium sulfonate **3** (Scheme 1).

Thus, we found that in the case of the XeF_2–CF_3SO_3H–Me_3SiNCO system the formation of $OCNXeOSO_2CF_3$ takes place, which readily oxidises iodobenzene to $[PhI^+$–$NCO\ {}^-OTf]$. The direct amination of aromatic substrates with reasonable yields is possible with the use of XeF_2–Me_3SiNCO–CF_3SO_3H.

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§ *General procedure for the amination of aromatic compounds.* The reactions with other aromatics were carried out as described above for the interaction of iodobenzene with XeF_2–Me_3SiNCO–HOTf system. Isomeric arylamines **7** and **8** were isolated in moderate yields (Table 1). Physico-chemical constants and spectral properties of **7** and **8** are in agreement with the published data.

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