Mendeleev Commun., 2001, 11(5), 171–172

Interaction of trimethylsilyl isocyanate with xenon difluoride and fluoroxenonium triflate in the presence of alkenes

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10.1070/MC2001v011n05ABEH001492

The title reactions lead to the corresponding β-fluoroisocyanates and β-isocyanatotriflates with the formation of the intermediates FXeNCO and $OCNXeOSO_2CF_3$.

Xenon difluoride and its derivatives have been used in organic synthesis for fluorination,[1] oxidative decarboxylation,[2] fluorodeiodination,[3] generation of nitrenes,[4] mono-[2] and biradicals[5] and intermolecular rearrangements,[6] as well as for the oxidation of organoelement compounds. The last direction is of great interest since it opens up possibilities for the synthesis of novel xenon compounds. In particular, the cleavage reactions of the Si–C, Si–Cl and Si–N bonds with XeF_2 were studied in detail.[1(a),7] These reactions are assumed to occur through the formation of intermediates with Xe–N and Xe–C bonds.[7]

We studied the interaction of trimethylsilyl isocyanate with XeF_2 and $FXeOSO_2CF_3$ in the presence of unsaturated compounds. The initial fluoroxenonium triflate as a solution in CH_2Cl_2 was obtained from xenon difluoride and triflic acid (or trimethylsilyl triflate) in accordance with a well-known procedure.[8] The subsequent addition of trimethylsilyl isocyanate to the resulting solution afforded a solution of $OCNXeOSO_2CF_3$ **1**. If at the first step XeF_2 was treated with trimethylsilyl isocyanate, highly reactive intermediate FXeNCO **2** was generated.

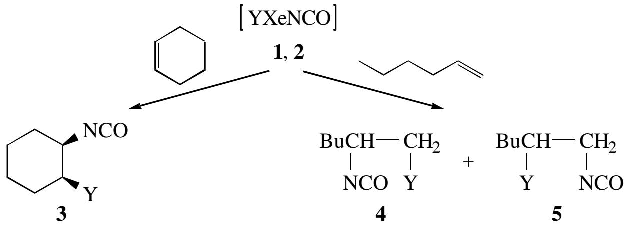
$$\underset{\mathbf{1}}{[FXeNCO]} \xleftarrow{Me_3SiNCO} XeF_2 \xrightarrow[\text{ii, } Me_3SiNCO]{\text{i, } CF_3SO_2OH \text{ or } CF_3SO_2OSiMe_3} \underset{\mathbf{2}}{[CF_3SO_2OXeNCO]}$$

Intermediates **1** and **2** were obtained at –40 to –30 °C as clear solutions in CH_2Cl_2. Our attempts to isolate intermediates **1** and **2** resulted in their fast decomposition at –20 °C with the formation of, presumably, Xe, CO and N_2. The formation of a homogeneous solution during a metathetical reaction at –30 °C indicated the end of the reaction, and the resulting solution of compounds **1** and **2** can be used for further transformation *in situ*. The conclusions concerning the structure of **1** and **2** were made on the basis of published data[1(a),9] and the results of the subsequent chemical transformations, particularly, the reactions with alkenes.

The reactions of compounds **1** and **2** with cyclohexene and hex-1-ene were investigated.[†] The addition of an alkene to a solution of fluoroxenonium isocyanate **2** in CH_2Cl_2 at –78 °C resulted in rapid darkening of the reaction mixture. However, xenon evolution and concomitant reactions were observed only upon warming the reaction mixture to –30 °C. The products were isolated by column chromatography on silica gel. The ratio of the regioisomers in the reaction mixture and their structure were determined by NMR spectroscopy. In general, β-fluoroisocyanate **3b**–**5b** and β-isocyanotriflate **3a**–**5a** were relatively unstable and slowly decomposed in storage at room temperature.

The reactions of isocyanatoxenonium triflate **1** and fluoroxenonium isocyanate **2** with cyclohexene lead to only product **3**. The *cis* configuration of **3** was established by the vicinal H–H and H–F couplings in the ^{1}H NMR spectra. The sum of J_{HH} for H^1 and H^2 is 13–14 Hz, which is typical of *cis* substituted cyclohexanes.[10]

The reactions of xenonium compounds **1** and **2** with hex-1-ene resulted in the mixture of products **4** and **5** with domination of regioisomers **4**. Each of the regioisomers was isolated and identified by ^{1}H and ^{19}F NMR. The ^{19}F NMR spectrum of regioisomer **4b** has the F signal as a doublet of triplets (δ 220.7 ppm) with a geminal proton coupling of 47 Hz and a vicinal coupling of J_{HF} = 23 Hz, while regioisomer **5b** exhibited an analogous signal as multiplets with a chemical shift of 183 ppm.



a $Y = OSO_2CF_3$
b $Y = F$

[†] *General procedure for the interaction of* $OCNXeOSO_2CF_3$ **1** *with alkenes*: TMSNCO (5.52 mmol) was added to a suspension of FXeOTf[8] (4.72 mmol) in methylene chloride (20 ml) at –78 °C with stirring. The reaction mixture was then stirred at –40 °C for 1 h until formation of a colourless solution. The solution was cooled down to –78 °C, and a solution of an appropriate alkene (8 mmol) in methylene chloride (5 ml) was added. The reaction mixture was heated to 10 °C, washed with 30 ml of ice water, extracted with CH_2Cl_2, dried with Na_2SO_4, and concentrated in a vacuum at 10 °C. Products **3a**–**5a** were separated by column chromatography on silica gel with 2:1 petroleum ether–diethyl ether as an eluent.

cis-*1-Trifyloxy-2-isocyanatocyclohexane* **3a**: oil, yield 53%. ^{1}H NMR ($CDCl_3$) δ: 1.2–2.3 (m, 8H, $4CH_2$), 4.4–4.7 [m, 2H, CH(OTf)CHNCO]. ^{19}F NMR ($CDCl_3$) δ: –74.9 (CF_3SO_3).

1-Trifyloxy-2-isocyanatohexane **4a**: unstable oil, yield 45%. ^{1}H NMR ($CDCl_3$) δ: 0.9–1.8 (m, 9H, Bu), 4.1–4.7 [m, 3H, CH(NCO)CH_2OTf]. ^{19}F NMR ($CDCl_3$) δ: –73.9 (CF_3SO_3).

1-Isocyanato-2-trifyloxyhexane **5a**: unstable oil, yield 11%. ^{1}H NMR ($CDCl_3$) δ: 0.9–1.9 (m, 9H, Bu), 4.2–4.9 [m, 3H, CH(OTf)CH_2NCO]. ^{19}F NMR ($CDCl_3$) δ: –74.7 (CF_3SO_3).

General procedure for reactions of FXeNCO **2** *with alkenes*: TMSNCO (5.52 mmol) was added to a suspension of XeF_2 (4.72 mmol) in dichloromethane (20 ml) at –78 °C with stirring. The reaction mixture was then stirred at –40 °C for 1 h. The resulting solution was cooled down to –78 °C, and a solution of an appropriate alkene (8 mmol) in CH_2Cl_2 (5 ml) was added. The mixture was allowed to warm to 10 °C with stirring. When the evolution of xenon gas ceased (0.5–1 h), the mixture was poured into solution of ice water, then extracted three times with CH_2Cl_2, dried ($MgSO_4$), and concentrated in a vacuum at 10 °C. Products **3b**–**5b** were isolated by column chromatography on silica gel with 2:1 petroleum ether–diethyl ether as an eluent.

cis-*1-Fluoro-2-isocyanatocyclohexane* **3b**: oil, yield 47%. ^{1}H NMR ($CDCl_3$) δ: 1.4–2.1 (m, 8H, $4CH_2$), 4.54 (m, 1H, CHNCO), 4.82 (dddd, 1H, CHF, $^1J_{HF}$ 48 Hz, $^2J_{HH}$ 8, 2.5 and 2.5 Hz). ^{19}F NMR ($CDCl_3$) δ: –74.6 (CF_3SO_3), –193.4 (CHF).

1-Fluoro-2-isocyanatohexane **4b**: unstable oil, yield 51%. ^{1}H NMR ($CDCl_3$) δ: 1.2–2.1 (m, 9H, Bu), 4.2–4.8 [m, 3H, CH(NCO)CH_2F]. ^{19}F NMR ($CDCl_3$) δ: –74.8 (CF_3SO_3), –220.7 (dt, CH_2F, $^1J_{HF}$ 47 Hz, $^2J_{HF}$ 47 Hz, $^2J_{HF}$ 23 Hz).

1-Isocyanato-2-fluorohexane **5b**: unstable oil, yield 15%. ^{1}H NMR ($CDCl_3$) δ: 1.0–2.1 (m, 9H, Bu), 4.2–4.8 (m, 3H, $CHFCH_2NCO$). ^{19}F NMR ($CDCl_3$) δ: –73.5 (CF_3SO_3), –183 (CHF).

In the light of these observations, we can suggest a mechanism[1(*a*)] that involves the initial electrophilic addition of the xenonium ion to the double bond leading to an organoxenonium intermediate. At the second step, nucleophilic substitution of Xe with the neighbouring fluorine or triflate anion occurs. This is an S_N2 type process, which is analogous to the reactions of iodine(III) with olefins.[11]

Thus, we found that the reactions of xenon difluoride and fluoroxenonium triflate with trimethylsilylisocyanate in the presence of alkenes lead to the corresponding β-fluoroisocyanates and β-isocyanatotriflates. This fact indirectly confirms the formation of the intermediates FXeNCO and $OCNXeOSO_2CF_3$.

We are grateful to NIH, FIRCA (2R03 TW00437) for financial support.

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Received: 3rd July 2001; Com. 01/1818