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Letters to the Editor

3-(Difluoro-λ^3-iodanyl)-4-methylfurazan: the first representative of (difluoro-λ^3-iodanyl)azoles

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Reported organic compounds containing an IF_2 group are few, all of them being synthesized from aliphatic or aromatic iodo derivatives.[1] Many of these compounds are unstable and exist only in solution or at reduced temperature. However, they are highly reactive and thus can serve as efficient fluorinating reagents.[1] The possibility of synthesizing azoles containing an IF_2 group has not been documented.

The difluoro-λ^3-iodanyl group can be obtained in the following three ways.

$$\mathrm{RIO} \xrightarrow{SF_4} \mathrm{RIF_2} \tag{1}$$

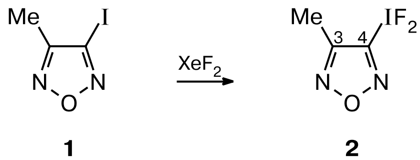
$$\mathrm{RICl_2} \xrightarrow{HF\ +\ HgO} \mathrm{RIF_2} \tag{2}$$

$$\mathrm{RI} \xrightarrow{XeF_2} \mathrm{RIF_2} \tag{3}$$

The first two approaches involve compounds of trivalent iodine, the preparation of which is an independent challenge. In the third method, accessible derivatives of monovalent iodine are used as starting reagents. Xenon difluoride is convenient for preparative purposes; however, the reaction of RI with XeF_2 sometimes gives no oxidation products, iodine being simply replaced by fluorine.[1,2]

We found that XeF_2 can also be efficient in the synthesis of (difluoro-λ^3-iodanyl)furazans. For instance, the oxidative fluorination of 3-iodo-4-methylfurazan (**1**)[3] (0.21 g, 1 mmol) with xenon difluoride (0.17 g, 1 mmol) in an atmosphere of dry argon at 20 °C in anhydrous MeCN (3 mL) yields the corresponding difluoroiodanyl azole **2** (Scheme 1). (*Caution*! The content of the latter in solution should not exceed 10% since its concentrated solution can explode!) However, a dilute solution does not decompose noticeably for a week when stored at 0—5 °C with protection against moisture and light. At room temperature or when exposed to light, the solution can spontaneously decompose (vigorous boiling up).

Scheme 1



1 **2**

Structure **2** was assigned to the fluorination product (NMR data). According to the literature data,[4] the IF_2 group exhibits electron-withdrawing properties and the

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signal for the IF_2-bound C atom in the phenyl ring is shifted upfield by 6 ppm ($SCS_i(IF_2) = -6$)[5] compared to the signal for unsubstituted benzene; the signals for the other phenyl C atoms are shifted less significantly ($SCS_o(IF_2) = 2.4$)*. Using known data[6] on the substituent effects on ^{13}C chemical shifts in methylfurazans, one can predict their values for compound **2**.

$$\delta_{C(4)} = 144.9 + 0.72 \cdot SCS_i(R)$$
$$\delta_{C(3)} = 151.0 + 0.42 \cdot SCS_o(R)$$

The calculated and experimental $\delta_{^{13}C}$ values for compound **2** agree well.

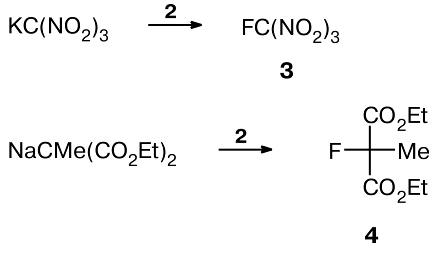
$\delta_{^{13}C}$	Calculated	Experimental
C(3)	152.0±4.4	154.5
C(4)	140.6±1.7	139.2

However, ^{19}F NMR spectra of RIF_2 are most indicative. The ^{19}F chemical shift for compound **2** is δ –173, which correlates with the δ values for the known compounds RIF_2 (δ –172 to –186).[5,7] ^{19}F NMR spectroscopy is convenient for monitoring of the fluorination process. For instance, an NMR monitoring of an equimolar mixture of compound **1** and XeF_2 in CD_3CN at 20 °C revealed a ~0.5-h induction period of the reaction, whereupon the starting reagents became 75% converted within 5 min. At 0 °C, the product in noticeable amounts was not detected even after 2 h.

Attempts at oxidative fluorination of 3-iodo-4-nitrofurazan, 3-azido-4-iodofurazan, and 4,4´-diiodoazofurazan under similar conditions were unsuccessful.

Like other RIF_2,[1,2] compound **2** is a more selective fluorinating reagent than XeF_2. For instance, fluoride **2** reacts with a potassium salt of nitroform (*cf.* the reaction with XeF_2)[8] in MeCN to give fluoro(trinitro)methane (**3**) in 87% yield (Scheme 2). A sodium derivative of diethyl methylmalonate (*cf.* the reaction with XeF_2)[9] under analogous conditions converts into diethyl fluoro(methyl)malonate (**4**) in 74% yield.

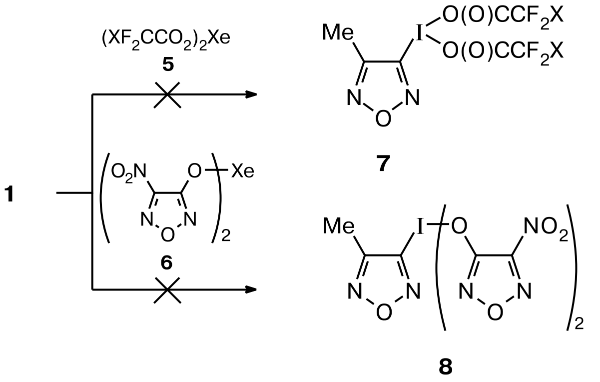
Scheme 2



A typical procedure for the fluorination is that a solution of difluoroiodanylfurazan **2** prepared from compound **1** (0.21 g, 1 mmol) and XeF_2 (0.17 g, 1 mmol) in 3 mL of anhydrous MeCN is added dropwise at 0 °C to a stirred suspension of a salt of the corresponding CH acid (1 mmol) in 5 mL of MeCN. The reaction mixture was kept for 0.5 h, diluted with CH_2Cl_2 (15 mL), and washed with water. The extract was dried with $MgSO_4$ and analyzed by GLC (Biokhrom-1 chromatograph, flame ionization detector, capillary column (0.2 mm × 20 m, phase SE-54), helium as a carrier gas) with reference to authentic samples of **3** [8] and **4** [9].

The reactivities of other derivatives of bivalent xenon, *e.g.*, reagents **5** (X = F or NO_2) and **6** (prepared *in situ*[10] from XeF_2 and the corresponding acid in the presence of a dehydrating agent) toward iodofurazan **1** were also investigated (Scheme 3). However, the expected products **7** and **8** were not detected even by the NMR method. Neither did the treatment of iodofurazan **1** with a trifluoroacetic anhydride—87% H_2O_2 mixture afford compound **7** (X = F).

Scheme 3



Thus, the present study showed that not all approaches used to obtain alkyl and aryl derivatives of trivalent iodine are suitable for the preparation of analogous furazan derivatives. Nevertheless, the iodine atom bound to such a strong electron-withdrawing fragment as 3-methylfurazan-4-yl can be oxidized into a derivative of trivalent iodine. Although the resulting 3-(difluoro-λ^3-iodanyl)-4-methylfurazan was not isolated in the individual state, its structure was unambiguously confirmed by spectroscopic data and the possibility of using it as a fluorinating reagent was demonstrated. The fact itself of the construction of an azole-bound difluoro-λ^3-iodanyl group gives promise that further advances will be made in this field.

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* $SCS(R)_i$ and $SCS(R)_o$ are the increments of the corresponding substituents in the *ipso*- and *ortho*-positions of monosubstituted benzenes.

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