Synthesis of bis(difluoronitroacetoxy)iodoarenes

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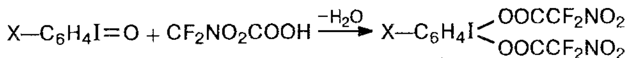
Two methods for synthesizing bis(difluoronitroacetoxy)iodoarenes, new compounds of tervalent iodine, have been proposed.

Key words: iodosylbenzene; difluoronitroacetic acid; xenon difluoride.

Compounds of tervalent iodine are of interest as reagents for the functionalization of olefins, ketones, amines, and other organic substrates.[1] Therefore, the development of new convenient methods of synthesizing polyvalent iodine derivatives of aromatic compounds is an important task of organic chemistry. In the present work we report a method for preparing bis(difluoronitroacetoxy)iodoarenes (**1—4**) by the interaction of iodosylbenzene with difluoronitroacetic acid (Scheme 1).

Scheme 1



$$\text{X—C}_6\text{H}_4\text{I=O} + \text{CF}_2\text{NO}_2\text{COOH} \xrightarrow{-\text{H}_2\text{O}} \text{X—C}_6\text{H}_4\text{I}<^{\text{OOCCF}_2\text{NO}_2}_{\text{OOCCF}_2\text{NO}_2}$$

1—4

X = H (**1**), 4-Me (**2**), 4-F (**3**), 4-MeO (**4**)

During the reaction, which is carried out in CH_2Cl_2, the products formed pass into solution, and then can be easily isolated with yields of 65—72 %. Difluoronitroacetates **1—4** are crystalline compounds soluble in dichloromethane, chloroform, and benzene. Their structures were estabilished by NMR and IR spectroscopy.

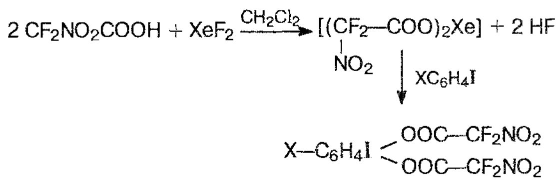
In an analogous reaction of chlorofluoronitroacetic acid with iodosylbenzene, *p*-iodonitrobenzene and *p*-chloroiodobenzene were obtained with low yields (~15 %); their physicochemical constants coincid completely with those reported in the literature.[2] Attempts to isolate and characterize the other reaction products were unsuccessful. Apparently, the process proceeds analogously to that represented in Scheme 1, but the corresponding nitroacetate is unstable and decomposes.

The formation of chloroiodo- and iodonitrobenzene can be explained as resulting from the interaction of intermediate $Cl^{\cdot}$ and $NO_2^{\cdot}$ radicals with iodobenzene.

The synthesis of bis(difluoronitroacetoxy)iodoarenes, which contain strong electron acceptor groups in the benzene ring, according to Scheme 1 is difficult because of the inaccessibility and instability of the corresponding iodosylarenes.

Another approach offered by us, based on the oxidation of iodoarenes by derivatives of bivalent xenon (in particular, $Xe(OCOCF_2NO_2)_2$, which is formed in CH_2Cl_2 at low temperatures from xenon difluoride and difluoronitroacetic acid), is possibly more general, since it can be used to synthesize bis(difluoronitroacetoxy)iodoarenes with different functional groups in the aromatic ring (Scheme 2).

Scheme 2



$$2\,\text{CF}_2\text{NO}_2\text{COOH} + \text{XeF}_2 \xrightarrow{\text{CH}_2\text{Cl}_2} [(\underset{\text{NO}_2}{\text{CF}_2}\text{—COO})_2\text{Xe}] + 2\,\text{HF} \xrightarrow{\text{XC}_6\text{H}_4\text{I}} \text{X—C}_6\text{H}_4\text{I}<^{\text{OOC—CF}_2\text{NO}_2}_{\text{OOC—CF}_2\text{NO}_2}$$

1—7

X = H (**1**), 4-Me (**2**), 4-F (**3**), 4-MeO (**4**), 3-CF_3 (**5**),
4-NO_2 (**6**), 4-Cl (**7**)

The structures of compounds **1—7** were confirmed by NMR and IR spectroscopy. Compounds of tervalent iodine **1—7** are stable at room temperature and can be used for the functionalization of olefins.

Experimental

^{1}H and ^{19}F NMR spectra were measured with a Bruker CXP-200 spectrometer, and IR spectra were measured on a Specord IR-75 spectrometer in thin layers between KBr plates.

Bis(difluoronitroacetoxy)-*p*-iodofluorobenzene (3). *A.* Difluoronitroacetic acid (564 mg, 4 mmol) was added dropwise to a suspension of *p*-fluoroiodosylbenzene (470 mg, 2 mmol) in 10 mL of dry CH_2Cl_2 at 20 °C with stirring (during this process fluoroiodosylbenzene completely dissolved). The mix-

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Table 1. Characteristics of bis(difluoronitroacetoxy)iodoarenes **1—7**

Compound	Method of preparation	Yield (%)	M.p. /°C	Found / Calculated (%)			Molecular formula	^{19}F NMR, δ	IR, ν/cm^{-1}	
				C	F	I			C=O	$NO_2(\nu_{as})$
1	***A*** ***B***	65 78	76—77 (hexane—$CHCl_3$)	25.03 24.79	16.34 15.70	27.00 26.23	$C_{10}H_5F_4IN_2O_8$	−12.8 (s)*	1700	1580
2	***A*** ***B***	68 75	70—72 (hexane—$CHCl_3$)	26.25 26.50	15.18 15.26	25.78 25.50	$C_{11}H_7F_4IN_2O_8$	−12.5 (s)	1705	1580
3	***A*** ***B***	72 80	78—79 (hexane)	24.37 23.90	18.34 18.34	25.48 25.29	$C_{10}H_4F_5IN_2O_8$	−12.75 (s); −21.25 (m, 1 F, C_6H_4F)	1700	1580
4	***A*** ***B***	72 80	71—73 (hexane)	26.13 25.68	15.44 14.78	24.91 24.70	$C_{11}H_7IN_2O_9$	−12.7 (s)	1700	1580
5	***B***	75	63—64 (ether—hexane)	23.60 23.91	24.12 24.09	23.78 23.00	$C_{11}H_4F_7IN_2O_8$	−12.0 (s); 15.1 (s, 3 F, CF_3)	1720	1585
6	***B***	80	110—112 (CCl_4)	22.18 22.68	14.84 14.36	24.50 24.00	$C_{10}H_4F_7IN_3O_{10}$	−12.6 (s)	1740	1590
7	***B***	78	94—95 (CCl_4)	23.48 23.16	14.55 14.67	24.00 24.51	$C_{10}H_4F_4ClIN_2O_8$	−12.3 (s)	1715	1580

* ^{1}H NMR ($CDCl_3$), δ: 7.0—8.0 (m, 4 H, C_6H_4).

ture was stirred for 1 h, filtered, and concentrated *in vacuo* to afford 0.73 g of white crystalline difluoronitroacetate **3**. Compounds **1**, **2**, and **4** were synthesized analogously.

B. XeF_2 (1.69 g, 0.01 mol) was added portionwise to a solution of difluoronitroacetic acid (2.82 g, 0.02 mol) in 10 mL of CH_2Cl_2 at −30 °C, and stirred for 1 h at the same temperature, then *p*-iodofluorobenzene (2.24 g, 0.01 mol) was added, and the mixture was stirred for 0.5 h at −10° C. The reaction mixture was warmed to 20 °C, the solvent was evaporated, and the residue was recrystallized from hexane to give 4.09 g of difluoronitroacetate **3**.

Compounds **1, 2, 4—7** were synthesized analogously.

The yields, melting points, data of elemental analysis, and parameters of ^{19}F NMR and IR spectra are listed in Table 1.

Mixing compounds **1—4** prepared by both methods did not result in depression of their melting points.

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