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Oxidative Properties of Xenon (II) Compounds. A New, Convenient Synthesis of [bis(trifluoroacetoxy)iodo]arenes, [bis(trifluoroacetoxy)iodo]perfluoroalkanes and μ-Oxo-bridged Aryliodoso-Derivatives.

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Abstract: The oxidative properties of xenon bis(trifluoroacetate) relative to aryl- and perfluoroalkyliodide were studied. The interesting feature of the reaction is the formation of the iodosoesters of trifluoroacetate or their μ-oxo-derivatives. Copyright © 1996 Elsevier Science Ltd

There is great current interest in the chemistry of aryliodine(III) dicarboxylates (AID).[1] They are widely used in organic synthesis as efficient oxidants,[1, 2] acetoxylating[3] and aryliodinating reagents.[4] Considerable effort has been devoted to the search for new methods of synthesis and structure investigation of AIDs.[1, 5] To date the great majority of AID preparations are based on the reaction of aryliodine(III) dichlorides and other iodosoarenes with Ag^{-} and Pb^{2+} carboxylates and carboxylic acids or their anhydrides.[2a] However, incomplete esterification of iodosoderivatives result in μ-oxo-bis[dicarboxylato(aryl)]iodine compounds. Also AID can exchange their acyloxy-groups with strong acids and so can be transformed into new AIDs.[6] The reaction of tris(trifluoroacetoxy)iodine [$I(OC(O)CF_3)_3$] with arenes is the most widespread method to synthesize [bis(trifluoroacetoxy)iodo]arenes.[7] However, this reaction does not work in the case of nitrobenzene due to its lack of reactivity. The direct oxidation of iodoarenes with peracids in the presence of corresponding carboxylic acid is another popular procedure for the preparation of AIDs,[8] for example aryliodine(III) bis(trifluoroacetates) are prepared using $(CF_3CO)_2O$ and HNO_3.[9] In this reaction CF_3CO_3H was formed *in situ*.[3] Iodobenzene can be oxidized electrolytically in the presence of the carboxylic acid to afford phenyliodine(III) dicarboxylates (PID).[10] Aliphatic iodocompounds do not normally form dicarboxylates with the exception of perfluoro and polyfluoroalkyl iodides, which on oxidation with trifluoroperacetic acid gave [bis(trifluoroacetoxy)iodo]perfluoroalkanes.[11] This reaction requires 60-80% H_2O_2 for the preparation of CF_3CO_3H, and large amounts of the expensive anhydride.[11]

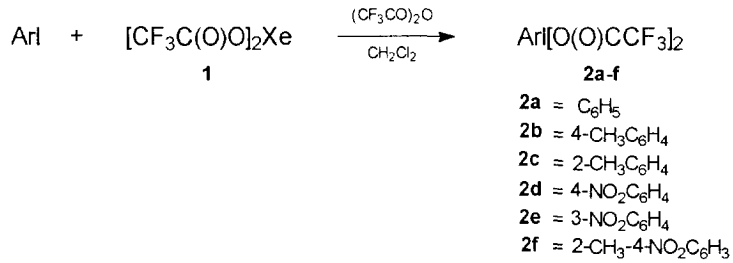
In the search for new, more efficient oxidizing reagents we turned our attention to the highly reactive xenon(II) derivatives.[12] The metathesis reaction of XeF_2 with the appropriate quantity of strong acids allows

the formation of mono- , and disubstituted xenon oxyesters; FXeOR, $Xe(OR)_2$.[13] Recently new interesting studies of the interaction of xenon oxyesters with alkenes were conducted. Like trivalent iodine reagents, xenon oxyesters interact with alkenes to yield the esters of the corresponding acids.[14] There is little information about the oxidant properties of xenon (II) esters in the literature.

In the present paper we are reporting the results of our studies of the oxidation of aryl- and perfluoroalkyliodides with xenon bis(trifluoroacetate) 1 formed *in situ* from a 1:2 molar ratio of XeF_2 and CF_3CO_2H.[13c]

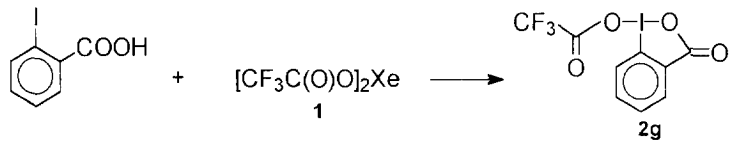
We found that xenon bis(trifluoroacetate), **1**, reacts with aryliodides in the presence of trifluoroacetic anhydride (commonly used to create an anhydrous reaction medium) in dichloromethane under mild condition yielding [bis(trifluoroacetoxy)iodo]arenes **2a-f**, the iodosoesters of trifluoroacetic acid (Scheme 1) in 79-93% isolated yields.

Scheme 1



Oxidation of ortho-iodobenzoic acid under these conditions proceeds with the formation of 1,3-dihydro-1-trifluoroacetoxy-3-oxo-1,2-phenyliodoxol **2g** (62%) (Scheme 2).

Scheme 2



Iodosoesters **2** were characterised by ^1H, ^{19}F, ^{13}C NMR and IR-spectroscopy. For example, the IR-spectra of **2g** show bands at 1660 and 1615 cm^{-1} due to the carbonyl group of the heterocycle and an absorption at 1720 cm^{-1} due to the trifluoroacetyl carbonyl group.[15] Spectral and physical-chemical data of iodosoesters **2a,b,d,e** correspond to the known literature data.[7, 9b] In addition to the spectral data the compositions of **2c**, **2f** and **2g** were established by elemental analysis.

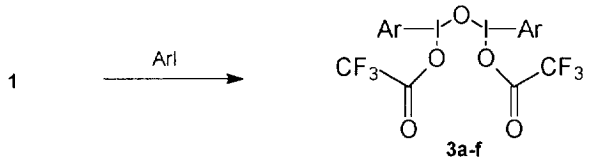
The oxidation of iodoarene by concentrated nitric acid also affords the [bis(trifluoroacetoxy)iodo]arenes. However this method appears appropriate only for deactivated substrates.[9b] In contrast, use of $Xe(OCOCF_3)_2$ allows the formation of iodosoesters with both electron-withdrawing and electron-donating substituents in the aromatic ring.

It was shown that hydrolysis of aromatic iodosoesters affords meso-oxo-derivatives.[16] The ease of hydrolysis depends on the nature of the corresponding acid and the substituent on the aromatic ring. The

stronger the acid and the more electron-withdrawing the substituent on the aromatic ring, the easier the hydrolysis of the iodosoester. For example, iodosoesters of sulfuric, trifluoromethanesulfonic, nitric and chromic acids readily hydrolyse to yield μ-oxo-bridged compounds.[16] However in the case of tetrafluoroboric and $HClO_4$ only μ-oxo-derivatives are obtained.[17] Hydrolysis of [bis(trifluoroacetoxy)iodo]-1,1-dihydroperfluoroalkanes also results in similar products.[18] As far as we know, there is no information in the literature concerning the hydrolysis of [bis(trifluoroacetoxy)iodo]arenes. A very interesting fact is that the hydrolysis of [bis(trifluoroacetoxy)iodo]arenes in boiling water results in formation of iodylarenes $ArIO_2$ presumably by disproportionation.of the initialy formed iodosylarene.[9b]

Thus we studied the reactions of iodoarenes with $Xe(OCOCF_3)_2$ in the absence initally of trifluoroacetic anhydride. As expected, the main products under these conditions were μ-oxo[bis(trifluoroacetatoxy)aryliodine],[3] with 62-96 % yield (Scheme 3):

Scheme 3



3a-f

3a: Ar = C_6H_5
3b: Ar = 4-$CH_3C_6H_4$
3c: Ar = 2-$CH_3C_6H_4$
3d: Ar = 4-$C_6H_5C_6H_4$
3e: Ar = 4-$[CH_3C(O)O]C_6H_4$
3f: Ar = 4-$NO_2C_6H_4$

The μ-oxo-bridged-derivatives are yellow crystals, soluble in dichloromethane and chloroform, partially soluble in ether, and insoluble in hexane. They slowly decompose in solution and upon exposure to the atmosphere at room temperature. However, they are stable if stored at lower temperatures (<-15^{O}C).

The structures of **3a - 3f** were elucidated by analysis of ^{1}H, ^{19}F, ^{13}C NMR and IR-spectroscopic data. In addition the composition of products **3b - 3f** are supported by elemental analysis. Finally the structure of **3b** was established by X-ray data.[19] Spectral data of **3a** corresponds to that previously reported.[5b]

It is possible to differentiate between compounds **2** and the corresponding μ-oxo-bridged aryliodoso-derivatives **3** by analysis of their NMR spectra, in particular the chemical shifts of the aromatic protons are characteristic. The signals due to the aromatic protons of μ-oxo-derivatives are located in the range of 7.0-7.9 ppm while the corresponding signals for $PhI(OCOCF_3)_2$ and other iodosoesters are found at a lower field, between 7.3 and 8.6 ppm.[5b] Even though the ^{19}F chemical shift can vary with solvent by a small degree, it is commonly observed that the fluorine atoms of [bis(trifluoroacetoxy)iodo]arenes **2** are shifted by 0.9 - 1.8 ppm relative to the corresponding μ-oxo-derivatives **3**.

To find other possible applications of the oxidation with $Xe[OC(O)CF_3]_2$, we studied its reactions with perfluoroalkyliodides in the presence of trifluoroacetic anhydride. We found that the reaction of xenon bis(trifluoroacetate), **1**, with perfluoroalkyliodides gives the corresponding [bis[trifluoroacetoxy)iodo]

perfluoroalkanes **4a,b** in high yield, and the [bis(trifluoroacetoxy)iodo]perfluoroalkanes **4a,b** have melting points and spectra similar to the previously reported data.[20]

Scheme 4

$$R_f\text{—}I + [CF_3C(O)O]_2Xe \longrightarrow R_fI(OOCCF_3)_2$$

$R_f = C_3F_7, C_4F_9$ **4a,b**

The formation of μ-oxo-derivatives in the oxidation reactions of iodoarenes with xenon bis(trifluoroacetate) may be explained by the suggestion that the primary products of oxidation are the corresponding iodosoesters.

We have shown that in the reaction of aryliodids with $Xe(OCOCF_3)_2$ varying the reaction conditions allows one to obtain either [bis(trifluoroacetoxy)iodo]arenes[2] or their μ-oxo-derivatives[3]. Oxidation of perfluoroalkyliodide in the presence of trifluoroacetatic anhydride yields [bis(trifluoroacetoxy)iodo]perfluoroalkanes. Also it was shown that the interaction of xenon bis(trifluoroacetate) with orthoiodinebenzoic acid results in a stable iodosobenzoate **2g**.

Experimental

NMR Spectra were obtained on a Varian VXR - 400 spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 187.2 MHz (^{19}F NMR). ^{1}H, ^{13}C and ^{19}F NMR chemical shifts are reported in ppm. ^{1}H chemical shifts are referenced to the residual protons in the deuteriated NMR solvents. ^{13}C chemical shifts were measured relative to signals of these solvents. ^{19}F chemical shifts are given relative to external $CFCl_3$. IR spectra were recorded on a Perkin - Elmer spectrometer. Microanalysis were performed an a Carlo Erba instrument.

Xenon bis(trifluoroacetate), **1**, was prepared according to known procedure[13c] by reaction of commercially available xenon difluoride with trifluoroacetic acid. CH_2Cl_2 was distilled from P_2O_5 immediately prior for use.

General Procedure for synthesis of bis(trifluoroacetoxy)iodoarenes (2a-f). To a stirred solution of $Xe(OCOCF_3)_2$ (prepared from XeF_2 (0.26 g, 1.53 mmol) and trifluoroacetic acid (0.24 ml, 3.06 mmol)) in dichloromethane (10 ml) was added trifluoroacetic anhydride (5 ml) followed by iodoarene (1.53 mmol) at -50°C under argon. The resulting mixture was stirred for 30 min at -20° - 0°C and then for 1h at room temperature. Evaporation and drying gave **2a-f** in 75-87%.

Bis(trifluoroacetoxy)iodobenzene (2a), yield 84%, m.p. 120-122°C. Lit.[7] m.p. 120-121° C.

Bis(trifluoroacetoxy)p-iodotoluene (2b), yield 90%, m.p. 115-116°C. Lit.[7] m.p. 114-116°C.

Bis(trifluoroacetoxy)-o-iodotoluene (2c), yield 87 %, m.p. 88-90°C. IR (n, cm^{-1}): 1670 (CO), 560 (I-O), 430 (I-C). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.25 m (H^6, Ar), 7.58 m (H^3, H^5, Ar), 7.32 m (H^4, Ar), 2.77 s (3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 161.14 q (CO, J_{CCF} = 40.7 Hz), 141.18 (C^2, Ar), 137.51 (C^6, Ar), 134.53 (C^3, Ar), 131.66 (C^4, Ar), 129.29 (C^5, Ar), 128.56 (C^1, Ar), 112.91 q (CF_3, J_{CF}= 286.7), 25.34 (CH_3); ^{19}F NMR (187.2 MHz, $CDCl_3$, δ ppm): -76.06 (CF_3). Elemental analysis: found (%): C, 30.02; H, 1.24. Calc. for $C_{11}H_7F_6IO_4$: C, 29.75; H, 1.59.

Bis(trifluoroacetoxy)-p-nitro-iodobenzene (2d), yield 79%, m.p. 160-161°C. Lit.[9d] m.p. 160°C.

Bis(trifluoroacetoxy)-m-nitro-iodobenzene (2e), yield 79%, m.p. 141-142°C. Lit.[7] m.p. 143°C.

Bis(trifluoroacetoxy)-2-methyl-5-nitro-iodobenzene (2f), yield 93 %, m.p. 159-161°C. IR (n, cm^{-1}): 1710 (CO), 580 (I-O), 475 (I-C). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.64 m (H^6, Ar), 7.89 m (H^4, Ar), 7.27 m (H^3, Ar), 2.52 s (3H, CH_3). ^{19}F NMR (187.2 MHz, $CDCl_3$, δ, ppm): -77.51 (CF_3). Elemental analysis: found (%): C, 27.36; H, 1.42, N, 3.02. Calc. for $C_{11}H_6F_6INO_6$: C, 27.01; H, 1.24; N, 2.86.

1-Trifluoroacetoxy-1,2-benziodoxol-3(1H)-one (2g), yield 69 %, m.p. 210-212°C. IR (n, cm $^{-1}$): 1720, 1660, 1615 (CO), 665 (I-O), 480 (I-C). ^{1}H NMR (400 MHz, CD_3OD, δ, ppm): 8.18 m (H^6, Ar), 7.90 m (H^3, Ar), 7.79 m (H^5, Ar), 7.68 m (H^4, Ar). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 168.40 (CO), 158.73 q (CO, J_{CCF} = 38.8 Hz), 134.70 (C^5, Ar), 132.18 (C^6, Ar), 130.48 (C^4, Ar), 130.40 (C^2, Ar), 125.67 (C^3, Ar), 118.83 (C^1, Ar), 112.89 q (CF_3, J_{CF}= 286.7 Hz); ^{19}F NMR (187.2 MHz, CD_3OD, δ, ppm): -77.51 (CF_3). Mass spectrum (m/z): 360 (M+). Elemental analysis: found (%): C, 29.92; H, 1.21. Calc. for $C_9H_4F_3IO_4$: C, 30.02; H, 1.12.

General Procedure for synthesis of m-oxo-bridged aryliodoso compounds (3a-f). A solution of iodoarene (1.65 mmol) in CH_2Cl_2 (5 ml) was added dropwise at -78°C to the solution of [$Xe(O(O)CCF_3)_2$] (prepared from XeF_2 (0.28 g, 1.65 mmol) and trifluoroacetic acid (0.25 ml, 3.3 mmol)) in dichloromethane (15 ml). The mixture was warmed to room temperature and stirred for 6h. After filtration the solvent was evaporated. The residual material was crystallized from ether and hexane then the crystals were filtered, washed with hexane and ether and dried in vacuum. Further purification for microanalysis was carried out by recrystallisation from chloroform and hexane.

m-Oxo-bis[tifluoroacetato(phenyl)iodine] (3a), yield 70%, m.p. 161-162°C. Lit.[5b] m.p. 161°C.

m-Oxo-bis[tifluoroacetato(p-methylphenyl)iodine] (3b), yield 62%, m.p.84 - 86 °C , IR (n, cm $^{-1}$): 1666 (CO), 560 (I-O), 450 (I-C). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.77 m (H^2, H^6, Ar), 7.21 m (H^3, H^5, Ar), 2.44 s (3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 161.07 q (CO, J_{CCF} = 39.5 Hz), 143.66 (C^4, Ar), 133.83 (C^2, Ar), 132.08 (C^3, Ar), 120.76 (C^1, Ar), 112.87 q (CF_3, J_{CF}= 286.8), 21.55 (CH_3); ^{19}F NMR (187.2 MHz, $CDCl_3$, δ, ppm): -77.63 (CF_3). Elemental analysis: found (%): C, 32.31; H, 2.24; Calc. for $C_{18}H_{14}F_6I_2O_5$: C, 31.88, H, 2.08.

m-Oxo-bis[tifluoroacetato(o-methylphenyl)iodine] (3c), yield 68%, m.p.115-116°C. IR (n, cm^{-1}):1670 (CO), 560 (I-O), 430 (I-C). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.78 m (H^6, Ar), 7.37 m (H^5, Ar), 7.25 m (H^3, Ar), 7.04 m (H^3, Ar), 2.44 s (3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 160.42 q (CO, J_{CCF} = 40.7 Hz), 140.35 (C^2, Ar), 136.43 (C^6, Ar), 133.73 (C^3, Ar), 131.42 (C^4, Ar), 128.90 (C^1, Ar), 128.85 (C^5, Ar), 114.12 q (CF_3, J_{CF}= 286.7 Hz), 24.83 (CH_3); ^{19}F NMR (187.2 MHz, $CDCl_3$, δ, ppm): -77.70 (CF_3). Elemental analysis: found (%): C, 31.74; H, 2.02; Calc. for $C_{18}H_{14}F_6I_2O_5$: C, 31.88; H 2.08.

m-Oxo-bis[trifluoroacetato(p-diphenyl)iodine] (3d), yield 72%, m.p. 107-109°C. IR (n, cm^{-1}): 1675(C-O), 555(I-O), 450(I-C). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.73 m (2H, Ar), 7.51 m (2H, Ar), 7.39 - 7.29 m (5H, Ar); ^{19}F NMR (187.2 MHz, $CDCl_3$, δ, ppm): -77.56 (CF_3); Elemental analysis: found (%): C, 42.25; H, 2.34; Calc. for $C_{28}H_{18}F_6I_2O_5$: C, 41.92, H, 2.26.

m-Oxo-bis[tifluoroacetato(p-acetoxyphenyl)iodine] (3e), yield 96 %, m.p. 105-106°C. IR (n, cm^{-1}): 1660 (CO), 562 (I-O), 446 (I-C). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.78 m (H^2, H^6, Ar), 7.22 m (H^3, H^5, Ar), 2.45 s (3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 162.07 q (CO, J_{CCF} = 38.5 Hz), 143.96 (C^4, Ar), 133.77 (C^2, Ar), 132.05 (C^3, Ar), 120.91 (C^1, Ar), 113.74 q (CF_3, J_{CF} = 289.8), 21.60 (CH_3); ^{19}F NMR (187.2 MHz, $CDCl_3$, δ, ppm): -77.38 (CF_3). Elemental analysis: found (%): C, 32.28; H, 1.96; Calc. for $C_{20}H_{14}F_6I_2O_5$ C 32.02, H, 1.88.

m-Oxo-bis[tifluoroacetato(p-nitrophenyl)iodine] (3f), yield 93 %, m.p. 157-158°C. IR (n, cm^{-1}): 1670 (CO), 565 (I-O), 450 (I-C); ^{1}H NMR (400 MHz, $CDCl_3$/DMSO (d_6), δ, ppm): 7.89 m (H^2, H^6, Ar), 7.85 m (H^3, H^5, Ar); ^{19}F NMR (187.2 MHz, $CDCl_3$/DMSO (d_6), δ, ppm): -78.48 (CF_3). Elemental analysis: found (%): C, 25.61; H, 1.17; N, 4.06; Calc. for $C_{16}H_8F_6I_2N_2O_9$: C, 25.97, H, 1.09, N, 3.79.

General Procedure for synthesis of [bis(trifluoroacetoxy)iodo]perfluoroalkanes (4a, b). Perfluoroalkyliodide (1.27 mmol) was added at -50°C to a stirred solution of [$Xe(O(O)CCF_3)_2$] (prepared from XeF_2 (0.22 g, 1.27 mmol) and

trifluoroacetic acid (0.20 ml, 2.54 mmol)) and trifluoroacetic anhydride (1.5 ml) in dichloromethane (15 ml) under argon. The resulting mixture was warmed to room temperature and stirred for 4h. Evaporation and drying gave **4** in 90-93%.

[Bis(trfluoroacetoxy)iodo]perfluoropropane (4a), yield 90%, m.p. 100°C. Lit.[20] m.p. 100°C.

[Bis(trfluoroacetoxy)iodo]perfluorobutane (4b), yield 93%, m.p. 97-98°C. ^{19}F NMR (187.2 MHz, CD_3CN, δ, ppm): -75.8 m (CF_3), -76.6 s (CF_3), -79.7 m (CF_2), -115.2 m (CF_2), -124.5 m (I-CF_2). Elemental analysis: found (%): C, 16.95; F, 49.51; I, 22.02; Calc. for $C_8F_{15}IO_4$: C, 16.78; F, 49.83; I, 22.19.[20]

Acknowledgement

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