Synthesis of an (Alkylperoxy)-λ³-iodane by the Reaction of 1-Hydroxy-1λ³,2-benziodoxol-3(1*H*)-one with 1,3-Bis(trimethylsilyl)-3-methylbut-1-yne

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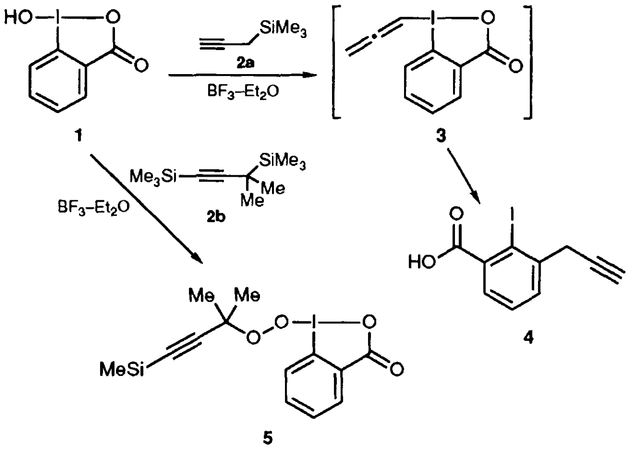
The BF_3-catalysed reaction of 1-hydroxy-1λ³,2-benziodoxol-3(1*H*)-one **1** with 1,3-bis(trimethylsilyl)-3-methylbut-1-yne **2b** in dichloromethane under nitrogen afforded the peroxy-λ³-iodane, 1-[1,1-dimethyl-3-(trimethylsilyl)-prop-2-ynyl]peroxy-1λ³,2-benziodoxol-3(1*H*)-one, **5** and its structure has been determined by single-crystal X-ray analysis.

Recently, we reported that the reaction of propynyl-silanes, -germanes, and -stannanes with aryl-λ³-iodanes in the presence of BF_3–Et_2O leads to a reductive iodonio-Claisen rearrangement under mild conditions, yielding *ortho*-propynyl-iodoarenes in good yields.[1] The reductive *ortho*-propynylation probably involves the intermediate formation of allenyl(aryl)-λ³-iodanes, which undergo [3,3] sigmatropic rearrangement. The lack of crossover products argues for the intramolecularity of the rearrangement. When both *ortho*-positions of the aryl-λ³-iodane are occupied with alkyl



Scheme 1

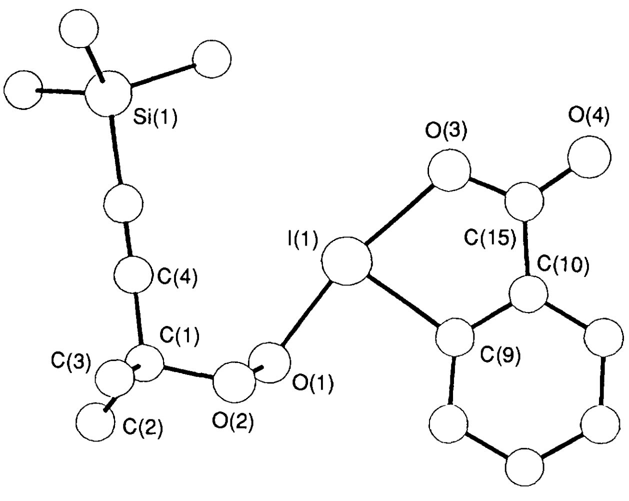


Fig. 1 The molecular structure of **5**. Selected bond lengths (Å) and angles (°) are as follows: I(1)–O(1) 2.032(6), I(1)–O(3) 2.153(7), I(1)–C(9) 2.099(8), O(1)–O(2) 1.48(1), O(3)–C(15) 1.28(1), O(4)–C(15) 1.24(2), O(1)–I(1)–O(3) 168.4(3), O(1)–I(1)–C(9) 91.1(3), O(3)–I(1)–C(9) 77.3(3), O(2)–C(1)–C(2) 110.1(8), O(2)–C(1)–C(3) 104.6(7), O(2)–C(1)–C(4) 109.0(7).

substituents, the reductive iodonio-Claisen rearrangement affords *meta*-substitution products. With (*p*-methoxy)aryl-λ^3-iodanes, an *ipso* iodonio-Claisen rearrangement is observed.[2]

To detect the intervention of allenyl(aryl)-λ^3-iodanes in the reductive propynylations of aryliodanes, we have carried out the reaction of 1-hydroxy-1λ^3,2-benziodoxol-3(1*H*)-one **1** with 1,3-bis(trimethylsilyl)-3-methylbut-1-yne **2b**. The reaction, however, led to the unexpected formation of an (alkylperoxy)-λ^3-iodane.

The BF_3-catalysed reaction of **1** with 1-(trimethylsilyl)prop-2-yne **2a** leads to reductive iodonio-Claisen rearrangement *via* the formation of the allenyl-λ^3-iodane **3**, yielding 2-iodo-3-prop-2-ynylbenzoic acid **4** in 46% yield.[1] However, when **1** was treated with bis(trimethylsilyl)butyne **2b**[3] at room temperature in the presence of BF_3–Et_2O in dichloromethane under nitrogen, formation of the corresponding *ortho*-propynyliodoarene *via* reductive iodonio-Claisen rearrangement was not observed. To our surprise, the reaction afforded the highly oxidized (alkylperoxy)-λ^3-iodane **5**, along with the reduced aryl iodide *ortho*-iodobenzoic acid. The peroxyiodane **5** was obtained in 59% yield from the reaction of **2b** with 3.5 equiv. of **1** following Florisil column chromatography and purified by recrystallization from dichloromethane–hexane as colourless prisms, m.p. 131–132 °C (decomp.). Recently, we prepared the first example of a stable crystalline (alkylperoxy)iodane, 1-(*tert*-butylperoxy)-1λ^3,2-benziodoxol-3(1*H*)-one, by BF_3-catalysed ligand exchange of **1** with *tert*-butyl hydroperoxide.[4] The peroxyiodane **5** is also stable in the solid state and can be stored at room temperature indefinitely.

^1H and ^{13}C NMR and IR spectra and elemental analysis support the structure of **5**,† which was confirmed by a single-crystal X-ray analysis.‡ The PLUTO drawing (Fig. 1) clearly illustrates the presence of the peroxy ligand, which occupies an apical position in a distorted trigonal-bipyramidal geometry around the iodine(III) as was observed in 1-(*tert*-butylperoxy)-1λ^3,2-benziodoxol-3(1*H*)-one.[4] In comparison with the short hypervalent exocyclic I(1)–O(1) bond to the peroxide oxygen, the endocyclic I(1)–O(3) bond to the ring oxygen shows considerable ionic character. The O(1)–O(2) bond length is similar to standard bond lengths of dialkyl peroxides.[6] The O(3)–C(15) and O(4)–C(15) bond distances show substantial delocalization of the π-bond of the carbonyl group of **5**. The C(3)–C(1)–O(2) bond angle is smaller than C(2)–C(1)–O(2) and C(4)–C(1)–O(2). The C(3)–C(1)–O(2)–O(1) torsional angle is 175.8(6)°, and the reduced C(3)–C(1)–O(2) bond angle may be attributed to the stabilizing orbital interaction between σ[C(3)–C(1)] and σ*[O(1)–O(2)].[7] A similar substantial reduction in the C–C–O bond angle of peroxides has been observed in 1-(*tert*-butylperoxy)-1λ^3,2-benziodoxol-3(1*H*)-one[4] and bis(triphenylmethyl) peroxide.[8,§]

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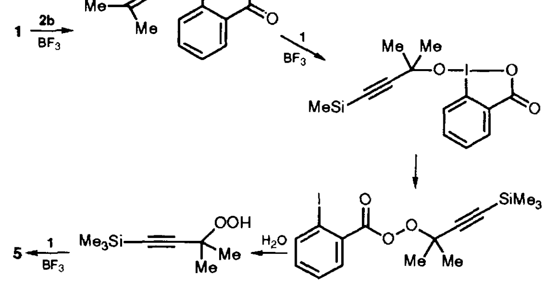
† *Selected spectroscopic data* for **5**: IR ν_{max}/cm^{-1} ($CHCl_3$) 2960, 2150, 1660, 1570, 1435, 1355, 1280, 1240–1180, 1125, 955 and 835; ^1H NMR (400 MHz; $CDCl_3$) δ 0.28 (9H, s), 1.52 (6H, s), 7.70 (1H, dt, *J* 1.0 and 7.8 Hz), 7.91 (1H, ddd, *J* 8.2, 7.8 and 1.5 Hz), 8.12 (1H, dd, *J* 8.2 and 1.0 Hz) and 8.26 (1H, dd, *J* 7.8 and 1.5 Hz); ^{13}C NMR (68 MHz; $CDCl_3$) δ −0.1, 26.5, 79.0, 91.4, 108.2, 120.2, 127.8, 129.7, 131.0, 132.7, 135.3 and 168.2; MS, *m/z* (relative abundance) 386 (1, M^+), 330 (17), 305 (18), 248 (47), 231 (51), 203 (26), 139 (36), 124 (49) and 97 (100).

‡ *Crystal data* for **5**: $C_{15}H_{19}O_4SiI$, M = 418.3, monoclinic, space group $P2_1/c$, a = 16.583(2), b = 6.477(1), c = 17.382(2) Å, β = 105.54(1)°, Z = 4, U = 1798.8(3) Å^3. D_c = 1.545 g cm^{-3}, Ni-filtered Cu-Kα radiation (λ = 1.54178 Å), μ = 149.87 cm^{-1}, crystal size 0.3 × 0.3 × 0.3 mm, 2671 unique reflections measured ($2\theta_{max}$ = 120°), 2221 reflections observed [$F_o > 3\sigma(F_o)$]. The structure was solved by the heavy-atom method, and refined by the block-diagonal least-squares technique to R = 0.073, R_w = 0.103, and S = 1.236 for 2213 reflections. All H atoms were located on a difference electron density map. The thermal parameter of each H atom was assumed to be isotropic and equal to B_{eq} of the bonded atom. Absorption corrections were applied after isotropic least-squares refinement by an empirical method based on the differences between the observed and calculated structure factors.[5] Weights were taken as $w = [\sigma^2(F_o) + 0.00484|F_o|^2]^{-1}$ for the reflections with $w^{\frac{1}{2}}|\Delta F_o| < 4$, and $w = 0$ otherwise. The relatively large R value may be due to the poor quality of the crystal. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ At the request of a referee, we outline below a current working hypothesis of the mechanism for the formation of **5**.



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