

SYNTHESIS AND STRUCTURE OF 1-(DIACETOXYIODO)-2,4,6-TRI-*TERT*- BUTYLBENZENE AND ITS ANALOGUES

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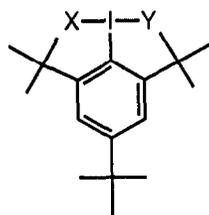
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Summary: The title hypervalent aryl iodine (1), which has sterically demanding *tert*-butyl groups at both ortho sites of the aromatic ring, was synthesized. The X-ray structure analysis of 1 revealed some degree of deformation from the normal geometries.

While a variety of hetero ligands of hypervalent organoiodine(III) reagents (ArIL₂) such as acyloxy, alkoxy, sulfonyloxy, and phosphoryloxy groups have been developed,¹ modifications of the aromatic carbon ligands are very limited, and aryl iodines with sterically demanding groups at the ortho sites of the aromatic ligands have not been synthesized. Ortho alkyl groups of aromatic ligands have been shown to play an essential role in determining the reaction course on the ligand coupling of diaryliodonium halides. For example, thermolysis of mesityl(phenyl)iodonium bromide afforded preferentially bromomesitylene in high yield.² We now report the first synthesis of a sterically crowded organoiodine, 1-(diacetoxyiodo)-2,4,6-tri-*tert*-butylbenzene (1), and its X-ray structure analysis.

Oxidation of 1-iodo-2,4,6-tri-*tert*-butylbenzene, prepared from 1,3,5-tri-*tert*-butylbenzene by the reported method,³ with chlorine in hexane gave the unstable dichloroiodine (2) (55% yield), which, on the attempted ligand exchange using mercuric oxide and acetic acid, gave a complex mixture of products. McKillop oxidation⁴ of 1-iodo-2,4,6-tri-*tert*-butylbenzene with excess amounts of sodium perborate in acetic acid at 40 °C for 17 h afforded quantitatively the desired diacetate (1), m.p. 126-130 °C. The iodine (1) is highly stable, presumably due to steric protection with the bulky *tert*-butyl groups, and standing at room temperature for more than six months showed no decomposition. The tosyloxy (3) and phosphoryloxyiodine (4) were also synthesized. Treatment of 1 with *p*-toluenesulfonic acid in acetonitrile gave 3, m.p. 84-86 °C, in 58% yield. The phosphoryloxyiodine (4) was prepared by the reaction of 1 with diphenyl phosphate in acetonitrile spiked with water. Attempted synthesis of the corresponding bis(trifluoroacetoxy)iodine by the reaction with trifluoroacetic acid led to the reductive iodination affording 1,2-diiodo-3,5-di-*tert*-butylbenzene in 95% yield.

Interestingly, single-crystal X-ray diffraction analysis of 1 revealed the presence of three crystallographically independent molecules, which are referred to as molecules 1a, 1b, and 1c, in an asymmetric unit (Figure 1). All of the molecules adopt T-shaped structures, in which the plane of the phenyl ring and the plane of I(1)-O(1)-C(1) or I(1)-O(3)-C(1) are almost perpendicular with dihedral angles of 87.3(5)°-89.8(5)°. The selected bond lengths and bond angles are summarized in Table 1. The deviation of torsion angles of C(1)-I(1)-O(1)-C(19) and C(1)-I(1)-O(3)-C(21) from 180° in 1c is much larger than those in 1a and 1b. The expected severe non-bonded repulsion between the



- 1** X = Y = OAc
2 X = Y = Cl
3 X = OH, Y = OTs
4 X = OH, Y = OPO(OPh)₂

Table 1 A) Selected interatomic distances (Å) and B) bond angles (degrees)^a of **1** and PhI(OAc)₂

	1a	1b	1c	PhI(OAc) ₂
A)				
I(1)-C(1)	2.11(2)	2.15(1)	2.11(1)	2.090(6)
I(1)-O(2)	2.88(2)	2.90(2)	2.84(2)	2.817(6)
I(1)-O(4)	2.88(2)	2.89(2)	2.98(2)	2.850(5)
B)				
O(1)-I(1)-C(1)	85.1(5)	80.7(5)	85.4(5)	81.4(2)
O(3)-I(1)-C(1)	82.5(5)	84.0(5)	82.2(5)	82.6(3)
C(1)-C(2)-C(7)	126(1)	130(2)	130(1)	-
C(1)-C(6)-C(15)	128(1)	129(2)	127(1)	-
C(1)-I(1)-O(1)-C(19) ^b	179(1)	180(1)	165(1)	-
C(1)-I(1)-O(3)-C(21) ^b	172(1)	177(1)	158(1)	-

a) Numbers in parentheses are e.s.d. values. b) Torsion angles.

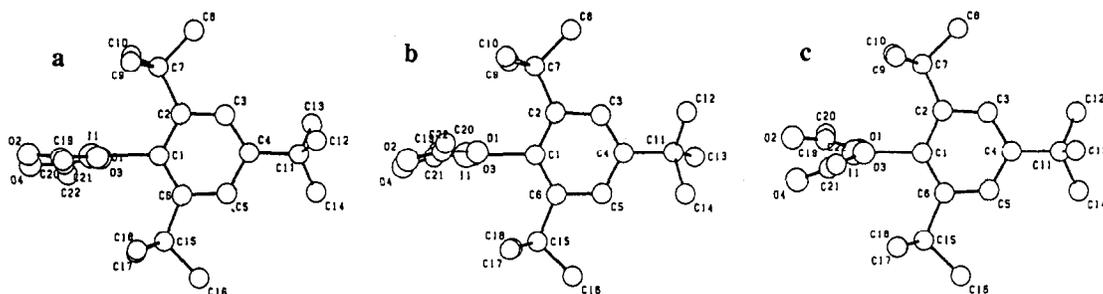


Figure 1. Perspective view of the diacetoxyiodinane (**1**): a, **1a**; b, **1b**; c, **1c**.

diacetoxyiodine(III) group and the bulky two *tert*-butyl groups at the ortho sites results in the some deviation of bond distances of **1b** and of bond angles of **1a** and **1c** from the normal values of the uncrowded PhI(OAc)₂.⁵ The I(1)-C(1) bond distance of **1b** is much longer than that of PhI(OAc)₂, while in **1a** and **1c** the O(1)-I(1)-C(1) and O(3)-I(1)-C(1) bond angles are larger than those of PhI(OAc)₂. The C(1)-C(2)-C(7) and C(1)-C(6)-C(15) bond angles of **1** are opened to 126°-130°.

Application of these new sterically crowded aryl iodinanes to organic synthesis is under way.

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