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IODOSOBENZENE TETRAFLUOROBORATE: FIRST EXAMPLE OF A STABLE ELECTROPHILIC HYPERVALENT IODINE REAGENT WITHOUT NUCLEOPHILIC LIGANDS

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ABSTRACT: Iodosobenzene tetrafluoroborate 1 has been prepared by the reaction of $PhI(OAc)_2$ and aqueous HBF_4, and its reactions with alkenes, silyl enol ethers, and acetylenes have been studied.

A considerable number of hypervalent iodine reagents have been developed in the last century, and many of these have found wide synthetic applications [1a]. Most of these reagents are derivatives of carboxylic or strong inorganic acids [1], anions of which can participate in reactions as nucleophiles. Until now only two examples of electrophilic iodine reagents without nucleophilic anionic ligands were known: complexes of PhIO with BF_3 [2a] and $Et_3O^+BF_4^-$ [2b], which are unstable even at 0°C.

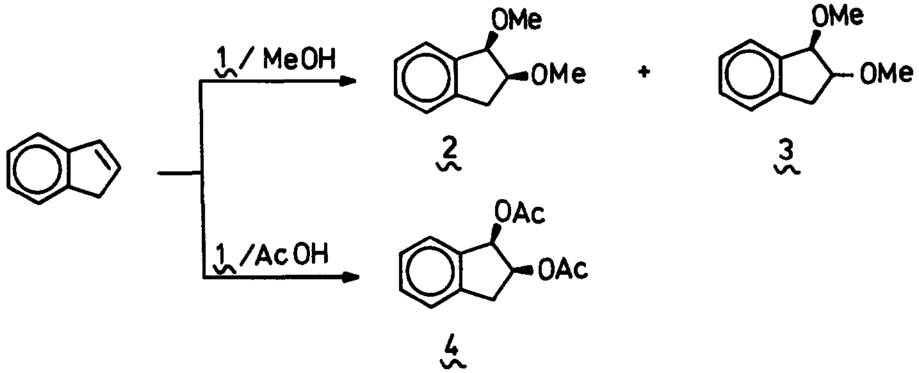
In this article we report the synthesis of the first stable hypervalent iodine reagent without a nucleophilic ligand - iodosobenzene tetrafluoroborate 1. Compound 1 is easily prepared by the reaction of commercially available iodosobenzene diacetate and aqueous HBF_4, yielding a yellow, crystalline product with mp 160°C [3].

$$2\,PhI(OAc)_2 + 2\,HBF_4 + H_2O \longrightarrow \underset{BF_4^-}{Ph\overset{+}{I}}\diagup^{O}\diagdown\underset{BF_4^-}{\overset{+}{I}Ph} + 4\,AcOH$$

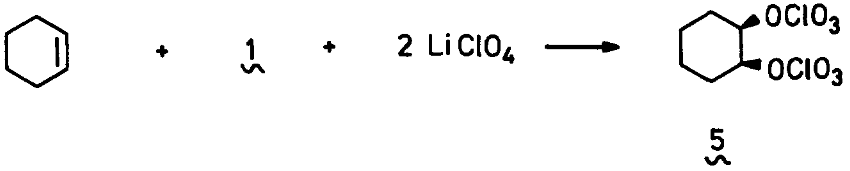
1

The structure of reagent 1 was supported by NMR, IR, and microanalysis. It's yellow color is consistent with the proposed μ-oxo-bridged structure [4]. Compound 1 is quite stable at room temperature, has good solubility in methanol and acetic acid, but is only slightly soluble in water, chloroform, ethyl acetate, and methylene chloride.

Reagent 1 exhibits high electrophilic properties and reacts with alkenes, silyl enol ethers, and acetylenes under mild conditions. Reactions with alkenes in nucleophilic solvents (such as methanol or acetic acid) or in the presence of anionic nucleophiles lead exclusively to products of vicinal disubstitution (according to ^1H NMR data). For example, the reaction of indene in methanol yields a mixture of cis-(2) and trans-(3) dimethoxy derivatives in the ratio 1:2 [5a]. The same reaction in AcOH lead to cis-diacetate 4 [5b].



Reaction of cyclohexene with 1 in ethylacetate in the presence of lithium perchlorate produced a product identical in all respects to the known [6a] cis-1,2-diperchlorate 5.



Reagent 1 readily reacts at room temperature with silyl enol ethers in CH_2Cl_2 giving 1,4-butanediones as the sole product, for example 6 [6b] and 7 [6c]:

$$PhC(OSiMe_3)=CH_2 \xrightarrow{1} PhC(=O)-CH_2CH_2-C(=O)Ph$$

6

7

It is worth emphasizing that the previously reported attempt at coupling the silyl enol ether of cyclohexanone with the electrophilic complex PhIO-BF_3 was unsuccessful [6b].

Compound 1 reacts at room temperature with acetylenes yielding unstable iodonium salts 8 [7], identified by NMR spectra.

8: a, R = C_3H_7

b, R = Ph

In conclusion we should emphasize that reagent 1 could find synthetic applications for the preparation of different kinds of reactive iodonium salts and as a mild oxidizing agent which does not contaminate the reaction media with external nucleophiles.

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3. Solution of 3.22 g $PhI(OAc)_2$ in 10 mL $CHCl_3$ was mixed with 3 mL aqueous HBF_4 (40%). Reaction mixture was rotavaped 30 min. at 50°C, then poured into 5 mL of water and crystallized for 2 hrs. Crystals of 1 were filtered, washed with 50 mL of water, and 50 mL of ether, dried for 24 hrs. in vacuo. Yield 2.24 g (75%), m.p. 160°C (dec.), IR (nujol): 460, 530, 2900 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.44 (dd, 2H, J = 7.8 Hz), 7.58 (dd, 1H, J = 7.1 Hz), 7.88 (d, 2H, J = 7.8 Hz); ^{13}C NMR (DMSO-d_6): δ 131, 132, 133.

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5. (a) 2; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.80 (dd, 1H, J = 16.0, and 5.4 Hz), 3.32 (dd, 1H, J = 16.0, and 6.9 Hz), 3.47 (s, 3H), 3.57 (s, 3H), 4.10 (m, 1H), 4.74 (d, 1H, J = 4.2 Hz), 7.30 (m, 4H); MS: m/z = 178 (M^+). 3; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.90 (dd, 2H, J = 7.2, and 2.8 Hz), 3.42 (s, 3H), 3.51 (s, 3H), 4.08 (td, 1H, J = 7.2, and 4.9 Hz), 4.61 (d, 1H, J = 4.9 Hz), 7.38 (m, 4H); MS: m/z = 178 (M^+). Configurational assignment of methoxy groups was done on the basis of chemical shifts of protons in CH_2 group. Thus in the cis isomer 2 there is a large $\Delta\delta$ between these protons whereas in the trans isomer 3 they are very close in chemical shift. (b) 4; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.08 (s, 3H), 2.10 (s, 3H), 2.90 (dd, 1H, J = 16.7, and 4.5 Hz), 3.53 (dd, 1H, J = 16.7, and 7.1 Hz), 5.49 (ddd, 1H, J = 7.1, 4.5, and 3.5 Hz), 6.26 (d, 1H, J = 3.6 Hz), 7.30 (m, 4H); MS: m/z = 174 (M^+ - CH_3COOH).

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7. (a) Typical procedure: Mixture of 0.3 g 1, 0.2 mL 1-pentyne, and 3 mL CH_2Cl_2 was stirred for 3 hrs at 25°C until full disappearance of the reagent. Solution was dried with Na_2SO_4, and rotavaped. Elution with CCl_4 gave 0.15 g (42%) of 8a as unstable oil, ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.94 (t, 3H, J = 7.3 Hz), 1.59 (m, 2H), 2.58 (t, 2H, J = 7.1 Hz), 7.61 (m, 3H), 8.01 (m, 2H). (b) Ochiai, M.; Kunishima, M.; Sumi, K.; Nagao, Y.; Fujita, E. Tetrahedron Letters 1985, 26, 4501.

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