

## Synthesis of diols using the hypervalent iodine(III) reagent, phenyliodine(III) bis(trifluoroacetate)

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Received 6 February 2006; revised 10 March 2006; accepted 22 March 2006

Available online 12 April 2006

**Abstract**—1,2- and 1,3-Bis(trifluoroacetoxy) alcohols are easily obtained from the one-pot reaction of alkenes with phenyliodine(III) bis(trifluoroacetate) (PIFA) in the absence of any additive or catalyst. The products were converted into the corresponding diols by ammonolysis. The use of bicyclic alkenes has shown that rearranged 1,3-diacetoxy alcohols are mostly formed as the major products.

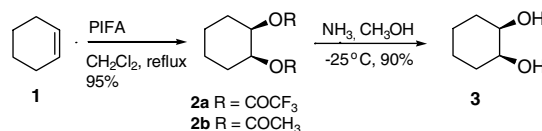
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Alkene oxidation is a subject of general interest, which profoundly influences the development of synthetic organic chemistry.<sup>1</sup> For example, *cis*-dihydroxylation<sup>2</sup> of alkenes by OsO<sub>4</sub> provides an efficient synthetic route to *cis*-diols, which are important precursors for a variety of synthetic applications<sup>3</sup> where this functionality is found in various pharmaceuticals. Due to the high cost and toxicity of OsO<sub>4</sub>, there is a need to search for alternative metal catalysts for alkene *cis*-dihydroxylations.<sup>4</sup> 1,3-Diols have attracted considerable attention in recent years due to the ubiquitous presence of this moiety in macrolide antibiotics.<sup>5,6</sup> Therefore, the development of methodologies for the preparation of 1,2- and 1,3-diols are of considerable interest. We report herein a new procedure for the synthesis of these diols based on the reaction of olefins with the hypervalent iodine compound, phenyliodine(III) bis(trifluoroacetate) (PIFA).<sup>7</sup>

Hypervalent iodine(III) reagents have recently received much attention due to their low toxicity, easy handling, and reactivities, which are similar to those of heavy metal reagents. We focused our studies on the hydroxylation of various alkenes using PIFA.

To a solution of cyclohexene dissolved in methylene chloride, PIFA was added portionwise to give the product **2**. Ammonolysis of *cis*-1,2-trifluorobisacetoxy-cyclohexane **2a** with ammonia afforded *cis*-1,2-cyclohexanediol **3**<sup>8</sup> in 95% yield (Scheme 1, Table 1, entry 1), which was transformed into diacetate **2b**. The *cis*-geometry in **3** was confirmed by comparison of the <sup>1</sup>H NMR spectrum with those of authentic *cis*- and *trans*-1,2-cyclohexanediol. Koser et al.<sup>9</sup> and Zefirov et al.<sup>10</sup> have reported the formation of *cis*-1,2-bis(tosyloxy)cyclohexane and *cis*-1,2-(perchloryloxy)cyclohexane upon treatment of cyclohexene with appropriate hypervalent iodine compounds.

The oxidation of 1,4-cyclohexadiene **4** (entry 2) took place in 20 h to give bis(trifluoroacetate) **5** as the major product (59%), which was hydrolyzed to the corresponding *cis*-diol.<sup>11</sup> The tetraacetate **6**<sup>12</sup> was formed as a minor product in 11% yield. The presence of a cyclopropane ring in **5** was established by measuring the coupling constants <sup>1</sup>J<sub>CH</sub> = 161.7 and 162.2 Hz for the cyclopropyl carbons with attached protons. The lack



Scheme 1.

**Keywords:** Phenyliodine(III) bis(trifluoroacetate); PIFA; Oxidation; Rearrangement; 1,2-Diols; 1,3-Diols.

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**Table 1.** Bis(trifluoromethylacetoxy)hydrocarbons from the reaction of alkenes with PIFA

Entry	Alkene	Product <sup>a</sup>	Yield	Conditions	Ref. <sup>b</sup>
1			95%	CH <sub>2</sub> Cl <sub>2</sub> , reflux 36 h	8
2			70% (5:1)	CH <sub>2</sub> Cl <sub>2</sub> , reflux 20 h	11 12
3			98% (55:45)	CH <sub>2</sub> Cl <sub>2</sub> , reflux 12 h	13
4			Quantitative	CH <sub>2</sub> Cl <sub>2</sub> , reflux 18 h	
5			90%	CH <sub>2</sub> Cl <sub>2</sub> , reflux 36 h	
6			95% (97:3) <b>22:23</b>	CH <sub>2</sub> Cl <sub>2</sub> , reflux 11 d	14
7			92% (95:5) <b>23.22</b>	CH <sub>2</sub> Cl <sub>2</sub> , reflux 11 d	14
8			90% (6:3:1)	CH <sub>2</sub> Cl <sub>2</sub> , reflux 36 h	15
9			95%	CH <sub>2</sub> Cl <sub>2</sub> , reflux 12 h	16 18
10			94% (3:7)	CH <sub>2</sub> Cl <sub>2</sub> , reflux 24 h	18
11			90% (68:22:7:3) <b>35:36:37:38</b>	CH <sub>2</sub> Cl <sub>2</sub> , reflux 36 h	

<sup>a</sup> R = COCF<sub>3</sub>. The formed trifluoroacetates were transformed into the diols.<sup>b</sup> The references are for the corresponding diols and acetates.

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