Catalytic Oxidation

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Versatile Hypervalent-Iodine(III)-Catalyzed Oxidations with *m*-Chloroperbenzoic Acid as a Cooxidant**

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As oxidants, hypervalent iodine(III) reagents are widely recognized as alternatives to highly toxic heavy-metal oxi-

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dizers such as lead, mercury, and thallium reagents (Figure 1).[1] They are generally used as stoichiometric oxidants, though it may be possible to carry out oxidations under catalytic conditions. Indeed, oxidative fluorination reactions with a catalytic amount of iodobenzene difluoride or 4-iodotoluene difluoride were reported in which the reoxidation of the iodine groups of iodoarenes was carried out electronically.[2,3] However, to our knowledge, a catalytic system for the formation of other bond types has not yet been reported. This is probably due to the lack of efficient procedures for the reoxidation of organoiodine(I) to hypervalent iodine(III) species[4–8] in the reaction system. Although new preparative methods that use sodium periodate ($NaIO_4$),[6] chromium trioxide (CrO_3),[7] and dimethyldioxirane[8] have been reported, they remain unsatisfactory in terms of product yield, ease of operation, and other aspects.

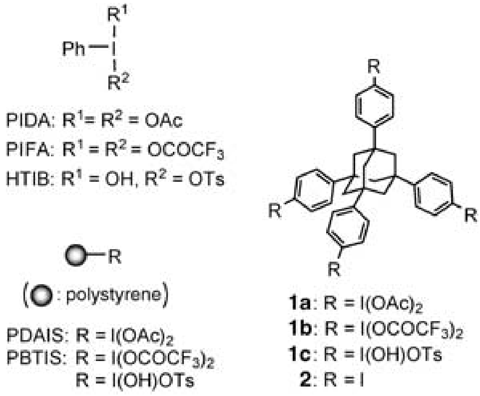
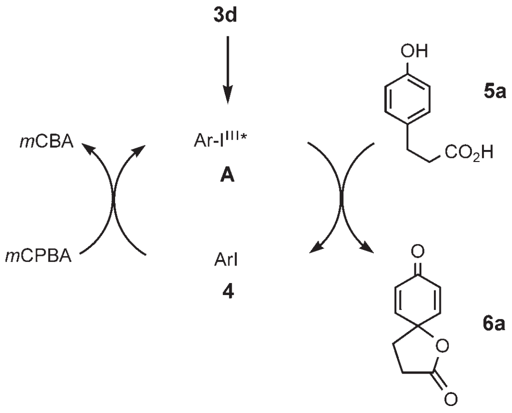


Figure 1. Hypervalent iodine(III) reagents. PIDA = phenyliodine diacetate; PIFA = phenyliodine bis(trifluoroacetate); HTIB = (hydroxy-(tosyloxy)iodo)benzene; PDAIS = poly(diacetoxyiodo)styrene; PBTIS = poly(bis(trifluoroacetoxy)iodo)styrene.

We have recently developed environmentally friendly, recyclable hypervalent iodine(III) reagents **1a–c** with high reactivities.[9] In its synthesis, we realized the need to prepare **1a** with nearly quantitative yield to make it a practical recyclable reagent; we also found that only an oxidation system using *meta*-chloroperbenzoic acid (*m*CPBA)[10] in dilute acetic acid/dichloromethane was suitable for this purpose. This interesting aspect prompted us to explore the possibility of these adamantane-based recyclable reagents as catalysts by combination with *m*CPBA as a stoichiometric chemical oxidant.

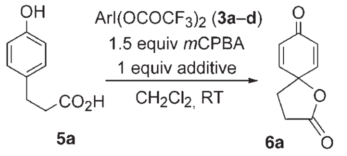
Herein, we demonstrate oxidative transformations with catalytic amounts of hypervalent iodine(III) reagents, which enable versatile C–O and even C–C bond formations. Relying on the previous conditions to synthesize **1a**, we first examined the oxidative spirocyclization reaction of the phenol **5a**[11] with 0.1 equivalent of phenyliodine diacetate (PIDA), which gave disappointing results (Table 1, entry 1). Therefore, the reaction conditions were optimized. With **3a** instead of PIDA, a catalytic reaction was observed (entry 2). As the amount of trifluoroacetic acid (CF_3CO_2H) increased, the catalytic efficiency increased (entries 2 and 3). In the absence of **3a**, no reaction was observed. Interestingly, the rapid conversion of **5a** was observed in these cases. The nature of the acids and the presence of water were also influential (entries 4–7). The hypervalent iodine(III) reagent **3d** gave the best results of those examined (entries 10 and 11). It was possible to decrease the amount of **3d** to as low as 0.01 equivalent without a significant loss in catalytic efficiency (entry 11). The spirocyclization of **5a** using **3d** with other cooxidants such as peracetic acid,[4] sodium perborate,[5] $NaIO_4$,[6] and CrO_3[7] were not successful.

A proposed catalytic cycle is depicted in Scheme 1. First, **3d** forms the hypervalent iodine(III) active species **A** (which occurs under the stated reaction conditions, although a certain



Scheme 1. A possible catalytic cycle for oxidation by hypervalent iodine(III) species. Ar = 4-MeC_6H_4; *m*CBA = *meta*-chlorobenzoic acid.

Table 1: Optimization of the hypervalent-iodine(III)-catalyzed spirocyclization reaction of **5a**.



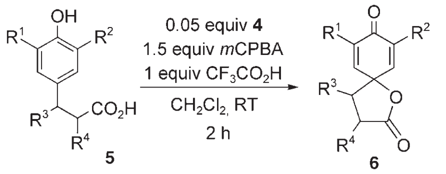
Entry	Ar	Equiv	Additive	t [h]	Yield [%]
1[a]	–	0.1	none	4	15
2	C_6H_5 (**3a**)	0.1	none	3	56
3	C_6H_5 (**3a**)	0.1	CF_3CO_2H	2	66
4	C_6H_5 (**3a**)	0.1	AcOH	3	49
5	C_6H_5 (**3a**)	0.1	$BF_3\cdot Et_2O$	2	73
6	C_6H_5 (**3a**)	0.1	TMSOTf	2	16
7	C_6H_5 (**3a**)	0.1	4 Å MS[b]	3	35
8	2,4-F_2-C_6H_3 (**3b**)[c]	–	CF_3CO_2H	17	60
9	4-MeO-C_6H_4 (**3c**)[d]	–	CF_3CO_2H	2	21
10	4-Me-C_6H_4 (**3d**)	0.05	CF_3CO_2H	2.5	67
11	4-Me-C_6H_4 (**3d**)	0.01	CF_3CO_2H[e]	2	71

[a] 0.1 equiv PIDA was used. [b] 1 g mmol^{-1} **5a**. [c] Prepared from 0.1 equiv 2,4-difluoroiodobenzene in situ. [d] Prepared from 0.1 equiv 4-iodoanisole in situ. [e] 50 equiv CF_3CO_2H was used.

degree of **3d** formation was observed in the absence of these phenol derivatives). The intermediate **A** transforms phenol **5a** into **6a** with concomitant formation of 4-iodotoluene (**4**), which then regenerates **A** by the action of *m*CPBA. The effect of the methyl group in the aryl substituent of **3d** might be to accelerate the conversion of **4** into **A**. With 0.05 equivalent of **4** instead of **3d**, the spirocyclization of **5a** also occurred with nearly the same efficiency (2 h, 72 % yield). This result strongly supports the formation of **4** during the catalytic cycle.

The results of the oxidation of a series of phenol derivatives with a catalytic quantity of **4** are shown in Table 2. This procedure imparts more versatility to the catalytic reaction, as the initial preparation of hypervalent iodine(III) reagents could be avoided. Thus, the oxidative transformations of various phenol derivatives proceeded smoothly in good yields with short reaction times. The recyclable reagent **1b** was also usable in this catalytic reaction (entry 2). After reaction completion, **2** was recovered nearly quantitatively in this case by taking advantage of its insolubility in methanol. Although further exploration is required, this catalytic approach was extended to other oxidative bond-formation reactions such as those of C–C bond formation[12] (Scheme 2).

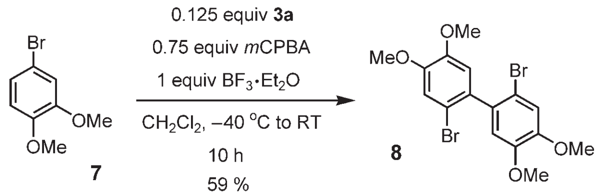
Table 2: Spirocyclization reaction of various phenol derivatives with a catalytic amount of **4**.



5 **6**

Entry	Substrate	R¹	R²	R³	R⁴	Product	Yield [%]
1	**5a**	H	H	H	H	**6a**	72
2[a,b]	**5a**	H	H	H	H	**6a**	74
3	**5b**	Br	H	H	H	**6b**	77
4	**5c**	Me	H	H	H	**6c**	66
5	**5d**	H	H	Me	H	**6d**	76
6	**5e**	H	H	H	Me	**6e**	73
7	**5f**	Br	Br	Me	H	**6f**	91
8	**5g**	Br	Me	Me	H	**6g**	80
9	**5h**	H	H	=CH–CH=CH–CH=		**6h**	79

[a] 0.05 equiv **1b** was used instead of **4**. [b] 1.05 equiv *m*CPBA was used.



Scheme 2. Intermolecular C–C bond-formation reaction catalyzed by **3a**.

In summary, we have established the efficient catalytic reactions of hypervalent iodine(III) reagents at room temperature by using *m*CPBA as an effective chemical cooxidant. These catalytic approaches have the following characteristics: rapid conversion (short reaction time), high catalytic efficiency, and no need for the preparation of hypervalent iodine(III) reagents. As **2** was also usable in the catalytic reaction, it has the advantage of the net recycling capacity of **1b**, considering the loss in the preparation of **1b** from **2**. The catalytic use of hypervalent iodine(III) reagents is our highly desirable goal. The application of other effective cooxidants with these hypervalent iodine(III)-catalyzed reactions is now in progress.

Experimental Section

Typical experimental procedure with **1b**: Compound **1b** (92.4 mg, 0.05 mmol) was added to a stirred solution of 3-(4-hydroxyphenyl)-propionic acid (**5a**; 166 mg, 1.0 mmol), trifluoroacetic acid (114 mg, 1.0 mmol), and *meta*-chloroperbenzoic acid ($\approx$69 % purity, 224 mg, $\approx$1.05 mmol), in CH_2Cl_2 (3 mL) at ambient temperature under a nitrogen atmosphere. The mixture was stirred for 2 h under the same reaction conditions while the reaction was monitored by TLC. The aqueous work-up was successive with saturated $NaHCO_3$ (20 mL), sodium thiosulfate (15 mL), and then the organic phase was evaporated to dryness. MeOH (10 mL) was added to the residue, and the resulting suspension was filtered to separate **2** from the product. The recovery of **2** was nearly quantitative. The filtrate was evaporated and subject to column chromatography (SiO_2/*n*-hexane/AcOEt) to give 1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (**6a**)[11c] as a white powder (121 mg, 74 %).

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