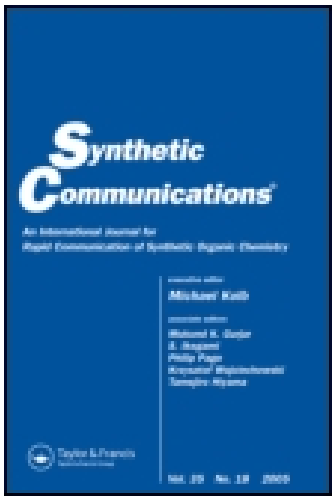

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HYPERVALENT IODINE IN SYNTHESIS. 61. REGENERATION OF CARBONYL FUNCTION FROM CARBONYL DERIVATIVES USING POLYMER-SUPPORTED PHENYLIODINE BIS(TRIFLUOROACETATE)

Da-Jun Chen [a] , Dong-Ping Cheng [a] & Zhen-Chu Chen [b]
[a] Department of Chemistry , Zhejiang University at Xixi Campus , Hangzhou, 310 028, P. R. China
[b] Department of Chemistry , Zhejiang University at Xixi Campus , Hangzhou, 310 028, P. R. China
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HYPERVALENT IODINE IN SYNTHESIS. 61. REGENERATION OF CARBONYL FUNCTION FROM CARBONYL DERIVATIVES USING POLYMER-SUPPORTED PHENYLIODINE *BIS*(TRIFLUOROACETATE)

Da-Jun Chen, Dong-Ping Cheng, and Zhen-Chu Chen*

Department of Chemistry, Zhejiang University at Xixi Campus, Hangzhou, 310028, P. R. China

ABSTRACT

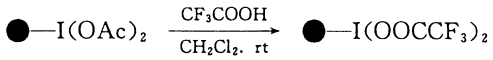
Polymer-supported phenyliodine *bis*(trifluoroacetate) was prepared and used in the regeneration of carbonyl function from carbonyl derivatives.

In this communication, we wish to report our results concerning the preparation and synthetic application of polymer-supported phenyliodine *bis*(trifluoroacetate) (PPIB).[1]

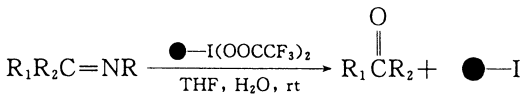
Phenyliodine *bis*(trifluoroacetate) (PIB), which is more reactive than phenyliodine diacetate (PID), has found wide synthetic utility as effective oxidizer. For the preparation of PIB, a practical method involves the ligand – exchange reaction of PID with trifluoroacetic acid.[2] Thus, an access

*Corresponding author.

to PPIB might be provided by translation of this conversion into a polymeric version. We first prepared PPID by our previously reported method[3] and subsequently treated it with trifluoroacetic acid. The resulting resin was characterised by IR to observe the desired functional conversion. As a result, the shift of carbonyl adsorption peaks from 1645 cm^{-1} to 1680 cm^{-1}, which corresponds exactly to the same spectroscopic feature of PID and PIB respectively, clearly indicated the successful preparation of the expected PPIB. Meanwhile, the resin was assayed by iodometry and offered a 2.10 mmol/g capacity of functional group.



To exploit the useful oxidative property of the prepared resin, it was employed to effect the transformation of ketonic carbonyl derivatives to their parent ketones. Recent advances in hypervalent iodine chemistry have revealed that phenyliodine dicarboxylates serve as efficient tools for this conversion under mild and non acidic condition.[4]



In fact, stirring a mixture of PPIB and carbonyl derivatives of ketones in aqueous THF at room temperature readily achieved the oxidative regeneration of carbonyl function in substrate molecules. The reaction offered mild condition, simple manipulation, high yield and general applicability to phenylhydrazones, oximes, semicarbazones and tosylhydrazones of aromatic or aliphatic ketones.

After the reaction, the resulting iodinated polystyrene was recovered by filtration and retreated with peracetic acid and trifluoroacetic acid. The regenerated PPIB possessed the same reactivity as the original one, since the oxidation reaction could be repeated without significant negative effect.

EXPERIMENTAL SECTION

All carbonyl derivatives were prepared by literature procedure[5] and identified by mp.

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Table 1. Regeneration of Ketones with PPIB

Entry	R_1	R_2	R	Time (min)	Yield[a,b] (%)
1	Ph	CH_3	PhNH	40	83
2	Ph	CH_3	PhNH	40	79[c]
3	*p*-Cl-Ph	CH_3	PhNH	45	86
4	*p*-Br-Ph	CH_3	PhNH	45	85
5	*p*-CH_3-Ph	CH_3	PhNH	45	91
6	*p*-CH_3O-Ph	CH_3	PhNH	45	90
7	Ph	Ph	PhNH	45	93
8	-$(CH_2)_5$-	/	PhNH	45	81
9	Ph	CH_3	OH	50	73
10	-$(CH_2)_5$-	/	OH	50	64
11	Ph	CH_3	$NHC(O)NH_2$	50	82
12	Ph	Ph	$NHC(O)NH_2$	40	76
13	-$(CH_2)_5$-	/	$NHC(O)NH_2$	50	71
14	Ph	CH_3	NHTs	25	88
15	-$(CH_2)_5$-	/	NHTs	25	85

[a]All compounds were confirmed by IR, ^{1}H-NMR in comparison with authentic samples. [b]Isolated yields. [c]Regenerated PPIB was employed in this case.

Preparation of PPIB: To a mixture of 5 g PPID in 40 mL CH_2Cl_2, 5 g trifluoroacetic acid were added with stirring. The mixture gradually became a dark reddish solution, and stirring was continued overnight. Ether was then introduced to precipitate the polymer species. The resulting resin was separated by filtration, washed with ether and dried to give 5.3 g PPIB. IR (KBr): 2920, 1680, 1485, 1410, 1180, 1005, 820 cm^{-1} functional capacity: 2.10 mmol/g.

General Oxidation Procedure: 1 g PPIB was dissolved in 10 mL THF, then 0.3 mL H_2O and 1 mmol carbonyl derivative were added. The mixture was stirred until no starting material was detected by TLC. H_2O (15 mL) was added to precipitate the spent polymer. After removal of the polymer specie by filtration, the filtrate was extracted with CH_2Cl_2 (10 mL × 3), then washed with 5% aq. Na_2CO_3 (10 mL × 2) and H_2O (10 mL × 2) respectively. The organic layer was dried with $MgSO_4$ and evaporated *in vacuo* to yield the desired ketones. Further purification would be achieved by plate chromatography if necessary.

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