Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 493–498

TETRAHEDRON

Polymer-supported tertiary amine in organic synthesis: a useful reagent in the conversion of alkenes to carbonyl compounds via the corresponding ozonides

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Received 20 August 2002; revised 4 November 2002; accepted 28 November 2002

Dedicated to Professor Chun-Chen Liao of National Hsing Hua University on the occasion of his 60th birthday

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Abstract—Polymer-supported tertiary amine **6** is useful to workup the ozonolytic reaction of alkenes. The corresponding carbonyl products can be isolated in excellent yields by simple filtration. For some substituted alkenes, carboxylic acids were formed as the major products and can be isolated from the polymeric resin by washing with 1 M HCl followed by extraction with organic solvent. In all cases, simply washing with aqueous NaOH can regenerate the polymeric amine **6**. The reactivity of the regenerated polymeric amine is as effective as that of the freshly prepared one. © 2003 Elsevier Science Ltd. All rights reserved.

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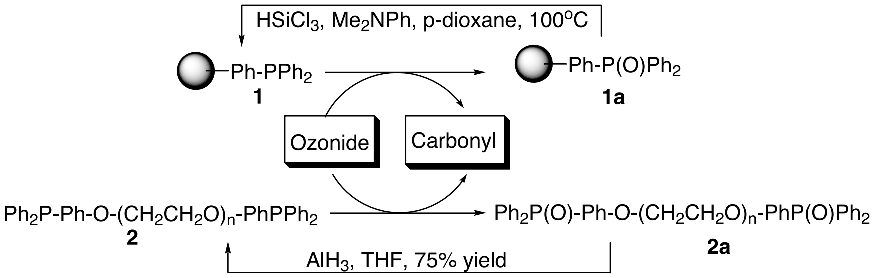
1. Introduction

A variety of reduction methods, such as palladium catalyzed hydrogenation, zinc in acetic acid, Ph_3P and Me_2S, are employed to workup the ozonolysis of alkenes.[1] Among them, Ph_3P is one of the most widely used reducing reagents for this purpose. However, one often faces problems in the purification of the carbonyl product from the unreacted Ph_3P, especially if the polarities of the carbonyl product and Ph_3PO are very similar. In order to overcome this problem, polystyryldiphenylphosphine resin **1** has been used for the reduction of ozonides to the corresponding carbonyl compounds.[2] The advantages of such supported reagents include the simplicity in the workup procedure and in the purification process. The oxidized polymer reagent (i.e. phosphine oxide **1a**) can be regenerated using polymethylhydrosiloxane (PMHS)[3a] or trichlorosilane[3b–e] under high temperature reaction conditions (Scheme 1). Recently, soluble matrixes such as poly(ethyleneglycol) (PEG) are receiving increasing attention both for combinatorial synthesis and as reagent supports.[4] The PEG–triarylphosphine derivative **2** has been applied to the liquid-phase organic synthesis (LPOS) for a redox reaction involving ozonide decomposition.[5] The liquid-phase reagent **2** gave a better yield than the Merrifield resin-bound triarylphosphine derivative **1** in the ozonide reduction.[5] However, the regeneration of the polymer-supported phosphine **2** from phosphine oxide **2a** was achieved with freshly prepared alane (AlH_3)[6] in THF in only 75% yield (Scheme 1). The incomplete polymer recovery is attributed to problems



Scheme 1.

Keywords: polystyryldiphenylphosphine; polymer-bound piperidine; poly(ethyleneglycol); ozonide; ozonolysis.

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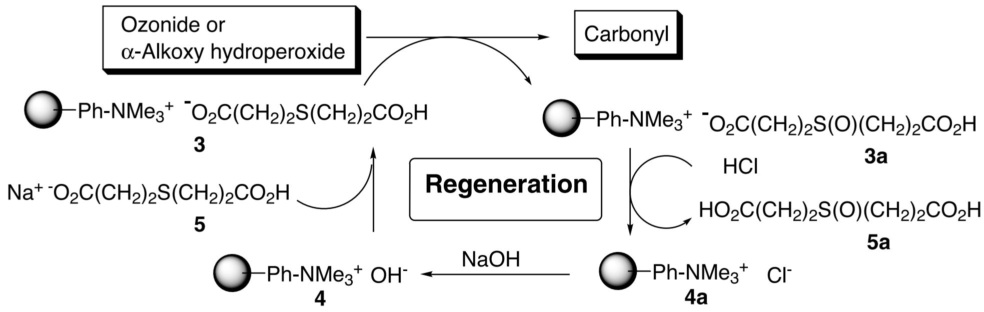
PII: S0040-4020(02)01558-2



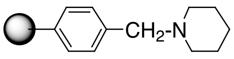
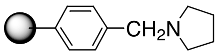
Scheme 2.

associated with the byproduct aluminum salts that prevent precipitation or polymer-backbone hydrolysis during the reduction process.

Polymer-bound 3,3′-thiodipropionic acid (**3**), made by treating DOWEX SBR resin (in hydroxide form, **4**) with an excess of 3,3′-thiodipropionate (**5**) in methanol, was shown to be quite effective in the reductive quenching of the ozonolysis reactions.[7] The oxidation product **5a** could be washed out of the resin **3a** with acid. The resin **4a** was first treated with base and then with fresh 3,3′-thiodipropionic acid to give polymer-bound 3,3′-thiodipropionic acid (**3**) (Scheme 2).

We have demonstrated that the E1cb mechanism is the major process in the reaction of tertiary amines and ozonides.[8] Based on this chemical knowledge, several useful synthetic methodologies have been developed.[9] The use of polymer-bound amines as scavenger reagent in the purification step of solution-phase reactions has recently gained much attention.[10] To the best of our knowledge, the polymer-bound amines have not been utilized to workup the ozonolytic reactions. In this report, an extremely useful methodology using the polymer-bound amines as bases to quench the ozonides via E1cb mechanism is described.

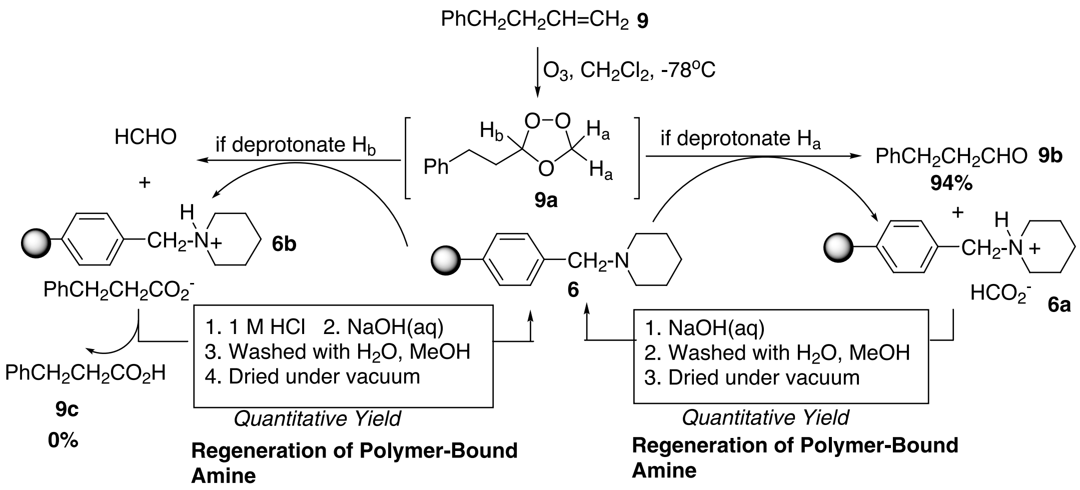
Table 1. Reaction of the ozonide **9a** with polymer reagents

Entry	Polymer reagent (2 mol equiv amine)	Time (h)	**9b** (%)	**9c** (%)
1		8	94	0
2		8	71	20
3	Amberlite (IRA-400 (OH) **8**	9	80	13

2. Results and discussions

Polystyrene-derived resin **6** was prepared from chloromethyl polystyrene (2% cross-linked Merrifield peptide resin; chloromethylated styrene/divinylbenzene copolymer; 200–400 mesh, contained 2.0–2.5 mmol Cl/g) by treatment with piperidine (4.2 mol equiv.) in refluxing benzene for 11 h in excellent yield.[11] Each gram of resin **6** contains approximately 2.0 mmol of nitrogen as estimated from elemental analysis. Resin **7** was prepared by treatment with pyrrolidine in excellent yield under similar conditions. It also contains approximately 2.0 mmol of nitrogen per gram.

Since the ozonide formation from terminal olefins is excellent, it is feasible to carry out the ozonolysis followed by reaction with polymer-bound amine in the same flask. The ozonide **9a**, derived from 4-phenyl-1-butene (**9**) (1 mol equiv.) in CH_2Cl_2 at −78°C was subsequently treated with the polymer-bound piperidine **6** (2.0 mol equiv. of piperidine moieties) and the suspension solution was then slowly warmed to room temperature and stirred at ambient temperature for 8 h. The filtrate was concentrated in vacuo to give the desired product **9b** in an almost pure form. Simple filtration through the short path silica gel column gave analytically pure 3-phenylpropanal (**9b**) in 94% yield



Scheme 3.

Table 2. The efficacy of the regenerated polymer **6** in quenching the ozonolysis reaction

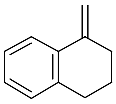
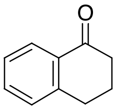
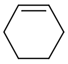
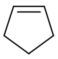
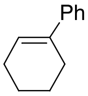
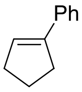
Entry	The *n*th recovered polymer (*n*=)	Time (h)	Product **9b** (%)
1	1	8	93
2	2	8	92
3	3	8	94
4	4	8	93

(entry 1, Table 1). Under similar condition, ozonide **9a** was treated with polymer-bound pyrrolidine **7** to obtain 3-phenylpropanal (**9b**) in 71% yield (entry 2). The lower yield of the aldehyde **9b** formation led us to isolate the other possible product from the resin. The insoluble resin was acidified with 1 M HCl and the filtrate was extracted with CH$_2$Cl$_2$. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated to give 3-phenylpropanoic acid (**9c**), which was then purified through a short path silica gel column. The yield of pure **9c** is 20%. Using a similar procedure, the ozonide **9a** was treated with Amberlite (IRA-400, $^-$OH form) **8** to obtain 3-phenylpropanal (**9b**) in 80% yield and carboxylic acid **9c** in 13% yield (entry 3). The data as shown in Table 1 indicate that the polymer-bound piperidine **6** is the most regioselective reagent in the reaction with monosubstituted ozonide.

The polymer-bound piperidine **6** reacted with ozonide **9a** to give the insoluble piperidinium formate **6a**. After filtration, the insoluble resin was treated with aqueous NaOH, water and methanol in sequence. The regenerated resin **6** was isolated in almost quantitative yield after drying in vacuo (Scheme 3). The first regenerated polymer-bound amine **6** was employed to react with ozonide **9a** under similar conditions. The aldehyde **9b** was isolated in 93% yield and the resin **6** was recovered in quantitative yield by our standard protocol (entry 1, Table 2). The results as shown in Table 2 also indicate that the reactivity of the polymer-bound piperidine **6** was excellent even after the fourth regeneration. The yield of the aldehyde **9b** formation was consistently above 90%. In other words, the polymer-bound piperidine **6** can be recovered using mild condition in high yield and the recovered polymeric amine can be used repeatedly without loss of reactivity.

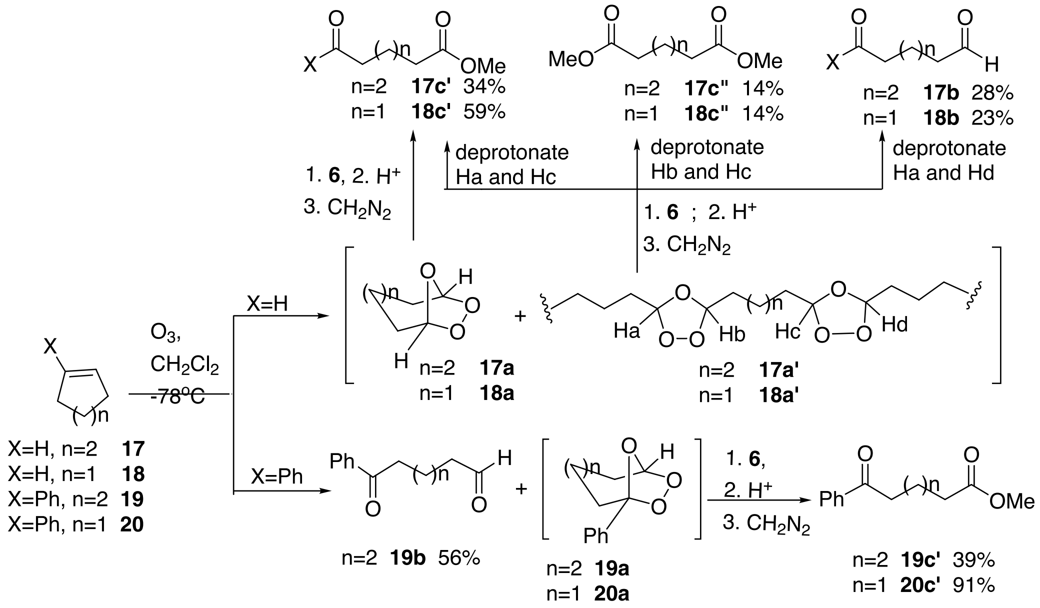
Encouraged by the results as shown in Table 2, we proceed to study the scope of this methodology in quenching the ozonolytic reaction for different alkenes. The simple terminal alkenes **9–11** gave the corresponding aldehydes **9b–11b** in excellent yields (entries 1–3, Table 3). This indicates that the polymeric amine abstracts the less substituted ozonide ring proton predominately. The yield is slightly lower in entry 2 probably due to the volatility of heptanal (**10b**). On the other hand, the benzyl acrylate **12** gave oxalic acid monobenyl ester (**12c**) instead of oxoacetic acid benzyl ester (**12b**) in excellent yields (entry 4). This result indicates that the polymeric amine predominately abstracts the more substituted ozonide ring proton, which is geminal to the carbobenzyloxy group. The electron-withdrawing property of the carbobenzyloxy group is more important than its steric effect in directing the reaction. The 1,1-disubstituted alkenes **13–16** gave the corresponding ketones in excellent yields (entries 5–8).

Table 3. The alkenes undergo ozonolysis at −78°C in CH$_2$Cl$_2$ followed by treatement with polymer amine **6** at room temperature

Entry	Starting material		Time (h)	Product		Yield (%)[a]
1	Ph(CH$_2$)$_2$CH=CH$_2$	**9**	8	Ph(CH$_2$)$_2$CHO	**9b**	94
2	Me(CH$_2$)$_5$CH=CH$_2$	**10**	8	Me(CH$_2$)$_5$CHO	**10b**	85
3	THPO(CH$_2$)$_4$CH=CH$_2$	**11**	8	THPO(CH$_2$)$_4$CHO	**11b**	94
4	PhCH$_2$O$_2$CCH=CH$_2$	**12**	7	PhCH$_2$O$_2$CCO$_2$H	**12c**	91
5	Ph(Me)C=CH$_2$	**13**	9	PhCOMe	**13b**	92
6		**14**	10		**14b**	95
7	THPOCH$_2$(Me)C=CH$_2$	**15**	8	THPOCH$_2$COMe	**15b**	93
8	PhCH$_2$O$_2$C(Me)C=CH$_2$	**16**	8	PhCH$_2$O$_2$CCOMe	**16b**	96
9		**17**	24	OHC(CH$_2$)$_4$CHO	**17b**	28
				OHC(CH$_2$)$_4$CO$_2$Me	**17c′**[b]	34
				MeO$_2$C(CH$_2$)$_4$CO$_2$Me	**17c″**[b]	14
10		**18**	24	OHC(CH$_2$)$_3$CHO	**18b**	23
				OHC(CH$_2$)$_3$CO$_2$Me	**18c′**[b]	59
				MeO$_2$C(CH$_2$)$_3$CO$_2$Me	**18c″**[b]	14
11		**19**	24	PhCO(CH$_2$)$_4$CHO	**19b**	56
				PhCO(CH$_2$)$_4$CO$_2$Me	**19c′**[b]	39
12		**20**	8	PhCO(CH$_2$)$_3$CO$_2$Me	**20c′**[b]	91

[a] Isolated yields are reported.

[b] The product was isolated as its methyl ester by treatment with diazomethane during the workup.



Scheme 4.

A cyclic alkene, cyclohexene (**17**), was treated with ozone in CH_2Cl_2 at −78°C followed by reaction with polymer-bound amine **6**. After the reaction was complete, adipaldehyde (**17b**) can only be isolated from the filtrate in 28% yield. Therefore, we tried to isolate the other products from the resin. The insoluble resin was acidified with 1 M HCl and the aqueous filtrate was extracted with CH_2Cl_2. The organic layer was then treated with CH_2N_2 and we were able to isolate methyl 6-oxohexanoate (**17c′**) and dimethyl hexanedioate (**17c″**) in 34 and 14% yields, respectively (entry 9, Table 3). The result of this reaction can be rationalized as follows. Both mono-ozonide **17a** and polymeric ozonide **17a′** are formed after the ozonolysis of cyclohexene (**17**) (Scheme 4). The deprotonation of mono-ozonide **17a** with polymeric amine **6** followed by treatment with CH_2N_2 results in the formation of aldehyde-ester **17c′** under our workup procedure. The deprotonation processes of the polymeric ozonide **17a′** are more complicated. The deprotonation of its H_a and H_c followed by treatment with CH_2N_2 result in the formation of the aldehyde-ester **17c′**. The deprotonation of ozonide ring protons H_b and H_c followed by treatment with CH_2N_2 result in the formation of the di-ester **17c″**. The deprotonation of ozonide ring protons H_a and H_d result in the formation of the di-aldehyde **17b** (Scheme 4). A similar rationale can also be applied to the case of cyclopentene (**18**). The cyclopentene gave glutaraldehyde (**18b**) (23%), methyl 5-oxopentanoate (**18c′**) (59%), and dimethyl glutarate (**18c″**) (14%), respectively (entry 10).

We found that the ozonolysis of 1-phenylcyclohexene (**19**) in CH_2Cl_2 gave a mixture of keto-aldehyde **19b** (56%) and ozonide **19a**. The ozonide **19a** can be converted to the corresponding keto-ester **19c′** in 39% yield in the same flask (entry 11). Interestingly, the ozonolysis of 1-phenylcyclopentene (**20**) gave ozonide **20a** in excellent yield. The ozonide **20a** can be converted to the corresponding keto-ester **20c′** in 91% yield (entry 12).

3. Conclusions

The polymer-supported piperidine **6** is useful to workup the ozonolytic reaction of alkenes. For simple terminal alkenes, the aldehydes can be isolated in good yields by simple filtration. For benzyl acrylate, carboxylic acids were formed as the major products and can be isolated from the polymeric resin by washing with 1 M HCl. The filtrate was then extracted with organic solvent. For 1,1-disubstituted alkenes, the corresponding ketones were formed in excellent yields. For cyclic alkenes, the product distribution depends on the ring size and its substitution pattern. The used resin can simply be washed with base to regenerate the polymeric amine. The reactivity of the regenerated polymeric amine is as good as that of the freshly prepared one. In general, polymeric piperidine **6** is a much superior reagent in comparison with those literature methods as shown in Schemes 1 and 2 in its efficiency and simplicity to workup the ozonolytic reaction.

4. Experimental

All reactions were carried out under nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Melting points were determined using a Thomas-Hoover melting point apparatus and are uncorrected. The ^1H- and ^{13}C NMR spectra were recorded on a Bruker Avance DPX400 spectrometer, and chemical shifts were given in ppm downfield from tetramethylsilane (TMS). IR spectra were taken with a Perkin–Elmer 682 spectrophotometer and only noteworthy absorptions were listed. Mass spectra were measured on a VG Trio-2000GC/MS spectrometer by electronic impact at 70 eV (unless otherwise indicated). High Resolution Mass Spectroscopy (HRMS) was measured on a JEOL JMS-HX 110 (National Hsing-Hua University) or VG-11-250J (Academia Sinica) Mass Spectrometer.

The products obtained in this study, such as 3-phenylpropanal (**9b**), heptanal (**10b**), acetophenone (**13b**), α-tetralone (**14b**), adipaldehyde (**17b**), dimethyl adipate (**17c″**), glutaraldehyde (**18b**), dimethyl glutarate (**18c″**), are commercial available. Their spectra are identical to those as shown in the Aldrich handbook.[12,13] The products, 6-(tetrahydropyran-2-yloxy)-1-hexene (**11**),[14] 5-(tetrahydropyran-2-yloxy)pentanal (**11b**),[15] oxalic acid monobenzyl ester (**12c**),[16] 1-(tetrahydropyran-2-yloxy)propan-2-one (**15b**),[17] 2-oxopropionic acid benzyl ester (**16b**),[18] methyl 5-oxoheptanoate (**17c′**),[19] 5-oxopentanoic acid methyl ester (**18c′**),[20] 6-oxo-6-phenylhexanoic acid methyl ester (**19c′**),[21] 5-oxo-5-phenylpentanoic acid methyl ester (**20c′**),[22] are known in the literature.

4.1. Procedure for the preparation of crossed-linked poly-[1-(4-vinylbenzyl)piperidine] (6)

A suspension of chloromethylated 2% cross-linked-polystyrene (contains 2.0–2.5 mmol Cl^-/g, 200–400 mesh, 4.0 g) and 1.6 mL of piperidine (16.6 mmol) in 50 mL of benzene was heated at reflux for 11 h. The reaction mixture was cooled down to room temperature and filtered through a fine-porosity Corning glass frit (4–5.5 μm) under vacuum. The resin was washed sequentially with anhydrous benzene, CH_2Cl_2, H_2O and MeOH. The washed polymer was dried in vacuum at 60°C for 5 h to give a white powder resin **6** (3.8 g) in 95% yield. Each gram of resin **6** contains approximately 2.0 mmol of nitrogen as estimated from elemental analysis.

4.2. Procedure for the preparation of crossed-linked poly-[1-(4-vinylbenzyl)pyrrolidine] (7)

A suspension of chloromethylated 2% cross-linked-polystyrene (contains 2.0–2.5 mmol Cl^-/g, 200–400 mesh, 4.0 g) and 1.7 mL of piperidine (21.1 mmol) in 50 mL of benzene was heated at reflux for 11 h. The reaction mixture was cooled to room temperature and filtered through a fine-porosity Corning glass frit (4–5.5 μm) under vacuum. The resin was washed sequentially with anhydrous benzene, CH_2Cl_2, H_2O and MeOH. The washed polymer was dried in vacuum at 60°C for 5 h to give a white powder resin **7** (3.8 g) in 96% yield. Each gram of resin **7** contains approximately 2.0 mmol of nitrogen as estimated from elemental analysis.

4.3. General procedure for the reaction of ozonide with polymer-supported amine to give carbonyl product

In a 50 mL two-neck flask, equipped with a magnetic stirrer, a drying tube and a gas dispersing tube (with porous fritted tip), were placed 20 mL of CH_2Cl_2 and 1-phenyl-1-cyclopentene **9** (100 mg, 0.8 mmol). A stream of ozone was bubbled through the solution at −78°C. Ozone treatment was terminated when the mixtures assumed a blue color. A stream of nitrogen removed excess ozone. To the solution was added polymer-supported amine **6** (760 mg, 1.5 mmol). The reaction was warmed slowly to room temperature and stirred for 8 h. The reaction mixture was filtered through sintered glass and the filtrate was concentrated to give 3-phenylpropanal (**9b**) in an almost pure form. In order to obtain the analytically pure product, short silica gel column chromatography by elution with EtOAc/hexane (1/8) was employed to give **9b** (107.1 mg, 94% yield) as a colorless oil.

4.4. General procedure for the reaction of ozonide with polymer-supported amine to give the carboxylic acid product

In a 50 mL two-neck flask, equipped with a magnetic stirrer, a drying tube and a gas dispersing tube (with porous fritted tip), were placed 20 mL of CH_2Cl_2 and 1-phenyl-1-cyclopentene **20** (207.1 mg, 1.44 mmol). A stream of ozone was bubbled through the solution at −78°C. Ozone treatment was terminated when the mixture assumed a blue color. A stream of nitrogen removed the excess ozone. To the solution was added polymer-supported amine **6** (1.4 g, 2.9 mmol). The reaction was warmed slowly to room temperature and stirred for 8 h. The reaction mixture was filtered through sintered glass. The resin was collected and washed with 1 M HCl. The filtrate was extracted with ethyl acetate. The organic layer was concentrated to about 5 mL. To the concentrated solution was added CH_2N_2 until the solution turned yellow. The solution was concentrated and purified by silica gel column chromatography by elution with EtOAc/hexane (1/1) to give **20c′** (270 mg, 91% yield) as a colorless oil.

4.5. General procedure for the regeneration of the polymer-supported amine

The polymer-bound piperidine **6** reacted with ozonide to give the corresponding carbonyl compound and the insoluble piperidinium formate **6a**. After filtration, the insoluble resin was treated with aqueous NaOH, water and methanol in sequence. The regenerated resin **6** was isolated in almost quantitative yield after drying in vacuo.

Acknowledgements

We are grateful to the National Science Council, National Chung Cheng University, and Academia Sinica for the financial support.

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