



An efficient protocol for the eliminative deoxygenation of aliphatic and aromatic epoxides to olefins with polyphosphoric acid as a promoter



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ABSTRACT

An efficient eliminative deoxygenation reaction is reported for the conversion of aliphatic and aromatic epoxides to olefins. Polyphosphoric acid (PPA) is used in 30 mol % as a promoter to afford the products in excellent yield (85–96%) at 50 °C under neat condition. Our method has advantages such as inexpensive reagents, high yield, stereoselective product in short reaction time under eco-friendly reaction conditions.

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Introduction

Epoxide formation of organic compounds is well-known in the organic and the biologically important molecules synthesis to obtain a number of oxygen-containing products.¹ In contrast, the reverse reaction (reductive/eliminative deoxygenation) of epoxides to olefins is little-known. Some examples are NaOH/TBAB,² [Fe₄S₄(SC₆H₅)₄]²⁻,³ CpTiCl₂/Mg,⁴ PPh₃,⁵ indium-metal, Na/Hg,⁶ NaBH₄,⁷ Lil/Amberlyst-15,⁸ LReO₃/PPh₃,⁹ Co(salene)₂/Na–Hg,¹⁰ (EtO)₂P(O)–TeNa,¹¹ MoO(Et₂dtc)₂,¹² copper nanocrystals,¹³ hydrotalcite-supported gold catalyst¹⁴ and gold-silver nanoparticles,¹⁵ however, these reagents have some drawbacks like less tolerance of functional groups, low yields, long reaction time, tedious workup, and moisture sensitive reaction conditions. Therefore, an alternate eliminative deoxygenation method is of high interest.

Polyphosphoric acid (PPA) has been used extensively in different organic syntheses for example, acylation,¹⁶ alkylation,^{2b} cyclization,¹⁷ acid catalyzed reactions dehydration, rearrangements, and synthesis of polymer and *N*-containing heterocycles.¹⁸ A comparison is given with our method and recently reported methods in the eliminative deoxygenation of epoxides to olefins (Table 1).

In continuation of our interest in Lewis acid catalysts/promoter¹⁹ herein, we report an efficient protocol for the eliminative deoxygenation of aliphatic and aromatic epoxides to olefins in the presence of PPA (30 mol % loading) as a highly efficient

promoter to afford the products in excellent yields (85–96%) within 5–15 min at 50 °C under neat condition.

Results and discussion

We optimized the deoxygenation reaction conditions in the reaction of styrene oxide (1 equiv) with PPA by varying mol % and solvents (polar, non-polar, and neat condition) at different reaction conditions (Table 2). The polar solvents like DMF, ACN, NMP, and DMSO gave less yields up to 15–30% (Table 2, entries 1–3, 8 and 9), less polar solvents like THF and 1,4-dioxane gave moderate yields up to 55% (Table 2, entries 10 and 11), the non-polar solvents like hexane and heptane afforded 75–80% yield (Table 2, entries 12 and 13) and without solvent (neat reaction) gave the product in excellent yield (95%) at 50 °C using PPA (30 mol %) within 5–10 min (Table 2, entry 6). However, further increase in mol % of PPA, the reaction gave lower yields (Table 2).

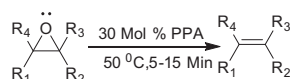
Under optimal conditions, PPA was explored for various aliphatic and aromatic epoxides (Table 3) to afford alkenes **1a–15a** in excellent yields 85–96% at 50 °C under neat condition (Table 3, entries 1–15). Like, aromatic (Table 3, entries 1–3 and 9–11), alicyclic (Table 3, entries 4, 6, and 12), aliphatic (Table 3, entries 5, 7, and 8) epoxides were transformed to alkenes in excellent yields. The carbonyl, nitro, hydroxyl, esters, and ketones groups in the deoxygenation of alicyclic epoxides (Table 3, entries 4, 12, and 13) and ether linkage in the aromatic and aliphatic epoxides (Table 3, entries 8, 9, 14, and 15) remained unaffected during the reaction. It might be the angle strain in the epoxide ring is the driving force for the reaction. We need a strong acid or base

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Table 1

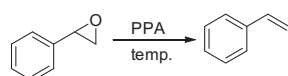
Previous methods for eliminative deoxygenation of epoxides to alkenes



Substrate	LiI/Amberlyst 15 h [yields%]	LReO ₃ /PPh ₃ h [yields%]	Co(salane) ₂ /NaHg h [yields%]	(EtO) ₂ P(O)-TeNa h [yields%]	Mo (Et ₂ dtc) ₂ h [yields%]	30 mol % PPA min [yields%]
	–	–	6 [95]	42 [88]	36 [92]	<10 [96]
	3 [85]	2 [32]	1 [95]	–	–	<10 [96]
With or without Solvent	With solvent	With solvent	With solvent	With solvent	With solvent	Without solvent

Table 2

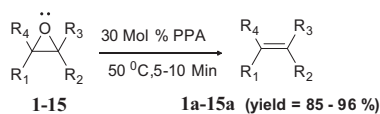
Optimized condition for the deoxygenation of styrene oxide with PPA



Entry	PPA (mol %)	Solvent	Time (min)	Temp (°C)	Yields ^a (%)
1	30	DMF	15	Reflux	15
2	30	ACN	15	Reflux	20
2	30	Ethanol	15	Reflux	30
4	10	–	15	50	20
5	20	–	15	50	50
6^a	30	–	5–10	50	95
7	40	–	10	50	85
8	30	NMP	15	Reflux	15
9	30	DMSO	10	Reflux	15
10 ^b	30	THF	5–10	Reflux	50
11 ^b	30	Dioxane	5–10	Reflux	55
12 ^c	30	Hexane	5–10	Reflux	75
13 ^c	30	Heptane	5–10	Reflux	80

^a Yield of isolated product under neat conditions.^b Less polar solvent gave moderate yield.^c Non-polar solvents gave up to 80% yields.**Table 3**

Examples of aliphatic and aromatic epoxide with PPA



Entry	Epoxides	Product	Time (min)	Yield ^a (%)
1			5	95 ^c
2			5	92
3			5	90
4			5	88
5			6	93

Table 3 (continued)

Entry	Epoxides	Product	Time (min)	Yield ^a (%)
6			5	88
7			5	85
8			6	85
9			6	88
10			10	86
11			5	96
12			5	95
13			4	84
14			3	86
15			4	84

^a Yield of isolated product, all these products are characterized by comparing their physical and chemical properties with authentic samples.²⁰^c Volatile compounds (styrene) isolated by fractional distillation (Supporting information).

condition in the case of carbonyl and nitro group oxygen participation for such reaction. Therefore, the reductive deoxygenation of epoxide occurred under optimized reaction conditions. Our method is also highly stereospecific in nature. For example, deoxygenation of *cis*-stilbene oxide gave *cis*-stilbene and *trans*-stilbene oxide to *trans*-stilbene (Table 3, entries 10 and 11) and the chemoselectivity between epoxide ring and hydroxyl group (Table 3, entry 12). All products were characterized by comparing with their physical and chemical properties of authentic samples.²⁰

Under optimal condition, we have also converted various chalcone epoxides to chalcones **1b–17b** with PPA in excellent yield (90–95%) within 5–10 min at 50 °C under neat condition without

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