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Silica-supported Phosphorus Chloride: An Efficient and Recyclable Catalyst for Beckmann Rearrangement of Ketoximes and Dehydration of Aldoximes Under Microwave Irradiation

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Abstract Silica-supported phosphorus chloride has been proved to be an efficient and recyclable catalyst for Beckmann rearrangement of a variety of ketoximes and dehydration of various aldoximes in anhydrous THF under microwave irradiation. This protocol has advantages of high conversion, high selectivity, short reaction time, no environmental pollution, and simple work-up procedure.

Keywords Beckmann rearrangement · Dehydration · Silica-supported phosphorus chloride · Oxime · Microwave irradiation

1 Introduction

The Beckmann rearrangement of ketoximes to the corresponding amides and dehydration of aldoximes to corresponding nitriles are common methods in organic chemistry and are topics of current interest [1]. The conventional Beckmann rearrangement of ketoximes and dehydration of aldoximes usually require the use of strong Bronsted or Lewis acids, i.e. concentrated sulfuric acid [2], trifluoromethanesulfonic acid [3], and polyphosphoric acid [4], which always cause the environmental problems because of the difficulty in separation.

Recently, Beckmann rearrangement of ketoximes was reported to utilize many kinds of catalysts, such as $BF_3{\cdot}Et_2O$, [5] $InCl_3$, [6] $Ga(OTf)_3$, [7] BPO_4, [8] BOP–Cl [9], $AlCl_3{\cdot}$ H_2O–KI, [10] cyanuric chloride [11], sulfamic acid [12] and oxalic acid [13]. The dehydration of aldoximes was also reported to conduct by using $ClSO_3H$, [14] $Ga(OTf)_3$, [15] zeolite, [16] ZnO/CH_3COCl, [17] KF/Al_2O_3, [18] $[RuCl_2(p\text{-cymene})]_2$, [19] and $Cu(OAc)_2$ [20] as catalysts. However, some of the catalysts used were corrosive and still difficult to isolate from the systems after the reactions.

Very recently, SiO_2-supported catalysts such as SiO_2-supported sulfuric acid [21] and MoO_3 [22] have been reported, which could efficiently resolve the separation problem and therefore eliminate the pollution caused by the above catalysts.

In addition, Beckmann rearrangement of ketoximes and dehydration of aldoximes were also reported to conduct under microwave irradiation condition, [23] which could significantly accelerate the reaction rate.

In continuation of our research on silica-supported catalysts for the important chemical transformation [21a] in this paper, we report silica-supported phosphorus chloride as an efficient and recyclable catalyst for Beckmann rearrangement of ketoximes and dehydration of aldoximes under microwave irradiation.

2 Experimental

^{1}H NMR spectra were recorded on a Mercury Plus-400 instrument using $CDCl_3$ as solvents and Me_4Si as internal standard. Elemental analyses were performed on a Vario E1 Elemental Analysis instrument. IR spectra were recorded using KBr pellets on a Digilab FTS 3000 FTIR spectrophotometer. The selectivities and conversions were determined by a Shimadzu GC 2010 equipped with 15 m–0.50 mm RTX-1 capillary column and FID detector or by Shimadzu 1671-CHA HPLC with UV–Vis detector.

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Microwave reactions were conducted using a modified microwave oven fitted with a condenser. Oximes were prepared by standard methods.

2.1 Preparation of Silica-supported Phosphorus Chloride

To phosphorus trichloride (5 mL) in a three-necked flask (50 mL) equipped with a condenser, silica gel (80–200 mesh, 2 g), which was predried at 100 °C in vacuum, was added in portions under stirring. HCl gas was gradually released from the reaction vessel. After the addition, the mixture was stirred for 48 h at room temperature. Then, excess phosphorus trichloride was evaporated off and the residue was washed by CH_2Cl_2 (10 mL) to give a white solid (2.26 g) as product, which was stored in a desiccator until use. The catalyst loading capacity of silica gel was calculated to be about 1.1 mmol/g .

2.2 General Procedure for Beckmann Rearrangement of Ketoximes and Dehydration of Aldoximes

In a round-bottomed flask (50 mL), oxime (1 mmol), THF (4 mL) and silica-supported phosphorus chloride (182 mg, 0.2 mmol) were added respectively. Then the flask was transferred into the modified microwave oven fitted with a condenser, and subjected to microwave irradiation at the power of 195 W for the appropriate time indicated in Tables 2 and 3. The progress of the reaction was monitored by TLC (petroleum ether:ethyl acetate = 2:1 as eluent) or GC. After completion of the reaction, the catalyst was filtered off and the filtrate was evaporated to remove the solvent under reduced pressure, and the residue was purified by recrystallization or chromatography to give product. All products were characterized by comparison of their melting points, IR, and ^{1}H NMR spectra with those of authentic samples. The conversions and selectivities were determined by GC or HPLC. The analytical data for representative products are given below:

N-Phenylbenzamide (Table 2, entry 12): m.p.: 163–164.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.87 (m, 10H, Ph-H), 7.90 (brs, 1H, NH). IR (KBr) v = 3344 (N–H), 1655 (C=O). Anal. Calcd. for C_8H_7NO: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.07; H, 5.70; N, 7.01.

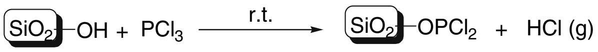
4-Methoxybenzonitrile (Table 3, entry 2): m.p.: 57–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.94 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H). IR (KBr) v = 2,216 ($C\equiv N$). Anal. Calcd. for $C_{13}H_{11}NO$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.05; H, 5.22; N, 10.44.

3 Results and Discussion

The silica-supported phosphorus chloride was prepared by reaction of preconditioned silica gel with excess phosphorus trichloride (Scheme 1). Silica gel was first dried at 100 °C in vacuum to remove excess water without dehydrating the silanol groups [24]. Then silica gel reacted with excess phosphorus trichloride at room temperature to give silica-supported phosphorus chloride as the product in high yield after the release of hydrogen chloride gas. Morrow and coworker's investigation indicated that phosphorus trichloride initially physically adsorbed on silica at room temperature *via* an interaction with surface silanol groups. Following prolonged contact over several hours, it dissociated to yield the chemisorbed SiOP-containing species $SiOPCl_2$ [25].

IR spectra of silica gel and silica-supported phosphorus chloride are shown in Fig. 1. The depression of 3,441 cm^{-1} absorption plus disappearance of 1632, 972 cm^{-1} bands of silica gel indicate consumption of silanol groups and $SiOPCl_2$ formation at the silica gel surface. The loading capacity of silica gel was calculated by analyses and found to be 1.1 mmol/g.

In the course of our study, benzophenone oxime was selected as a model substrate to examine the feasibility of Beckmann rearrangement using silica-supported phosphorus chloride as catalyst. Although Beckmann rearrangement of benzophenone oxime could be directly catalyzed by phosphorus trichloride, and the conversion of benzophenone oxime was almost 100%, the selectivity to corresponding amide was only 13%. However, it was found that silica-supported phosphorus chloride could efficiently catalyze Beckmann rearrangement of benzophenone oxime to give the corresponding amide in high conversion and selectivity under appropriate conditions. In order to optimize the reaction conditions for the Beckmann reaction, different amount of catalyst (from 5 to 30 mol%) in THF was tested. It was found that 20 mol% of silica-supported phosphorus chloride was the optimal amount for Beckmann rearrangement of benzophenone oxime (Fig. 2). The reaction was also tested at different microwave power level from 65to 650 W. It was observed that 195 W of power level was to be the most promising for the reaction because lower power level gave the poor yield and higher power level led to the carbonization of substrate (Fig. 3). The optimal reaction time was also investigated. It was found that the Beckmann rearrangement of benzophenone oxime



Scheme 1

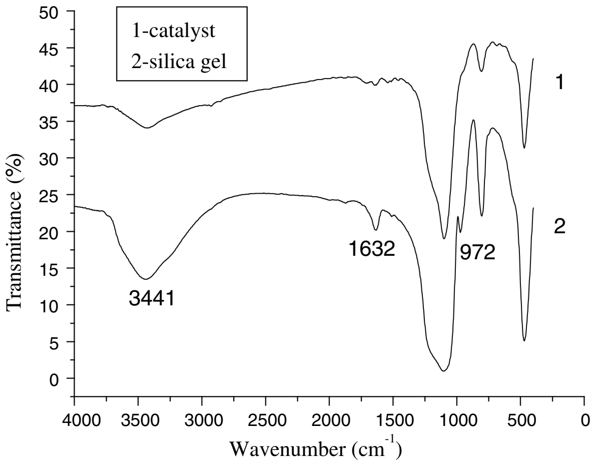


Fig. 1 The IR spectra of Silica-supported phosphorus chloride (1) and silica gel (2)

could be completed within 6 min under microwave irradiation to give the corresponding amide in excellent yield.

The solvent effect on the Beckmann rearrangement catalyzed by silica-supported phosphorus chloride under microwave irradiation was also investigated. Several solvents including polar and non-polar solvents were tested for the reaction and the results are summarized in Table 1. In toluene, the conversion of the substrate was proved to be good, but the selectivity to amide was only 64%. In acetonitrile or acetone, the selectivity to amide was proved to be good, but the conversion of the substrate was low. In addition, the reaction hardly proceeded in ethanol or water. However, the reaction in carbon tetrachloride, methylene chloride, DMF, THF and *n*-hexane afforded the corresponding amide in 99% selectivity with nearly complete conversion. Considering the ease of product separation, THF was selected to be the solvent of choice (Table 1).

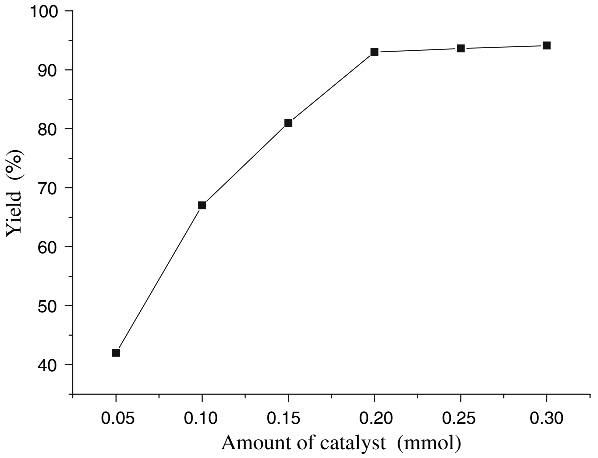


Fig. 2 The effect of amount of silica-supported phosphorus chloride on the yield of Beckmann rearrangement of benzophenone oxime (1 mmol)

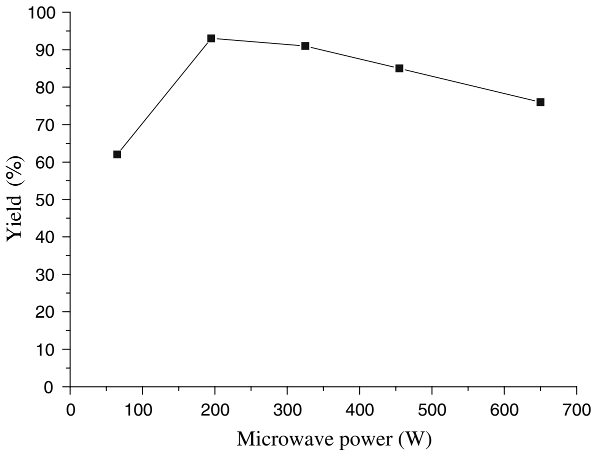


Fig. 3 The effect of microwave power on the yield of Beckmann rearrangement of benzophenone oxime catalyzed by silica-supported phosphorus chloride

The catalyst was easily separated from the reaction system, and reused for three consecutive runs, and no obvious diminishing activity was observed (the conversions and selectivities were 98% and 99% for 1st run; 99% and 100% for 2nd run; 91% and 95% for 3rd run; 86% and 83% for 4th run).

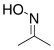
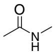
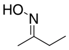
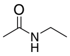
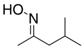
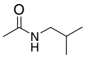
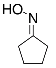
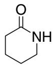
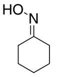
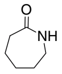
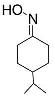
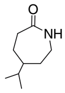
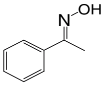
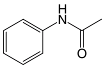
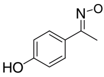
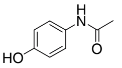
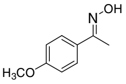
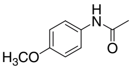
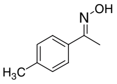
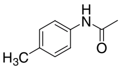
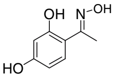
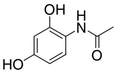
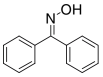
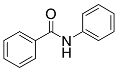
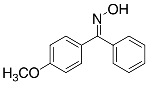
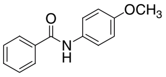
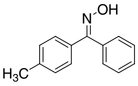
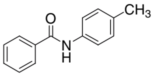
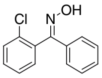
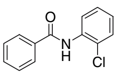
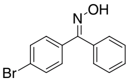
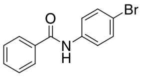
To explore the generality and scope of the Beckmann rearrangement catalyzed by silica-supported phosphorus chloride, a series of representative ketoximes as substrates were examined in THF under microwave irradiation (Table 2). Not only aromatic but also aliphatic ketoximes were smoothly rearranged under given condition. In particular, the rearrangement of most substrates was completed within 8 min. Hydroxy, methoxy, halo and nitro groups in oximes were tolerable under this condition. In the cases of unsymmetrical ketoximes, the reactions were selective and only one amide was produced for each ketoxime. For aliphatic ketoximes, the selectivities were

Table 1 Silica-supported phosphorus chloride catalyzed Beckmann rearrangement of benzophenone oxime in different solvents

Entry	Solvent	Conversion (%)[a]	Selectivity (%)[a]
1	DMF	99	99
2	THF	99	99
3	CH_2Cl_2	99	99
4	*n*-Hexane	99	99
5	CCl_4	96	99
6	MeCN	51	99
7	PhMe	99	64
8	Me_2CO	32	99
9	EtOH	–	–
10	H_2O	–	–

[a] Conversions and selectivities were determined by GC

Table 2 Microwave-assisted Beckmann rearrangement of ketoximes catalyzed by silica-supported phosphorus chloride

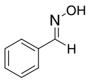
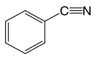
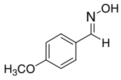
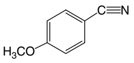
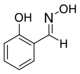
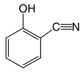
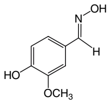
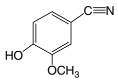
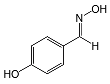
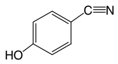
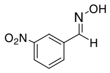
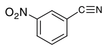
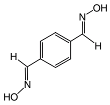
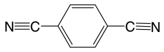
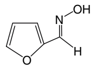
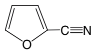
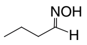
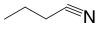
Entry	Substrate	Product[a]	Time (min)	Conversion (%)[b]	Selectivity (%)[b]
1			6	80	98
2			6	88	99
3			6	92	98
4			3	97	100
5			6	79	72
6			6	89	83
7			6	96	98
8			6	98	99
9			6	99	99
10			6	99	99
11			4	90	99
12			6	98	99
13			4	100	98
14			4	99	100
15			8	90	66
16			8	45	95

[a] All products were characterized by comparison of their melting points, IR, and ^{1}H NMR spectra with those of authentic samples

[b] Conversions and selectivities were determined by GC

almost quantitative except cyclohexanone oxime (72%) and 4-isopropylcyclohexanone oxime (83%). The conversions of acetone oxime, butanone oxime and 4-methyl-2-pentanone oxime (entries 1–3) increased with the increase of carbon chain. Cyclopentanone oxime (entry 4) provided more excellent conversion than cyclohexanone oxime and 4-isopropylcyclohexanone oxime. The conversions of acetophenone oxime, *p*-methylacetophenone oxime, *p*-methoxylacetophenone oxime and *p*-hydroxyacetophenone oxime were all nearly 100% (entries 7–10) except

Table 3 Microwave-assisted dehydration of aldoximes catalyzed by silica-supported phosphorus chloride

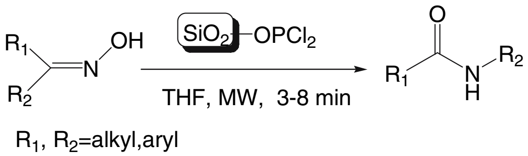
Entry	Substrate	Product[a]	Time (min)	Conversion (%)[b]	Selectivity (%)[b]
1			6	78	96
2			4	90	98
3			8	55	98
4			2	85	94
5			6	92	98
6			6	64	93
7			4	74	97
8			6	72	92
9			6	83	87

[a] All products were characterized by comparison of their melting points, IR, and ^{1}H NMR spectra with those of authentic samples

[b] Conversions and selectivities were determined by GC

2,4-dihydroxylacetophenone oxime (90%) because of the steric hindrance (entry 11). For aromatic ketoximes, the Beckmann rearrangement of benzophenone oxime and substituted benzophenone oximes bearing methyl and methoxy groups could give up to 98% conversions and selectivities, and no by-products were detected (entries 12–14). However, for substituted benzophenone oximes bearing electron-withdrawing groups (chloro and bromo), the conversions or selectivities were obviously decreased (entries 15, 16) (Scheme 2).

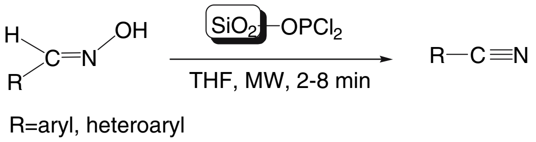
In contrast, aldoximes could also catalyzed by silica-supported phosphorus chloride using the similar reaction conditions to ketoximes, but the dehydration products, nitriles, were obtained in high yields (Table 3). Aromatic aldoximes with different substituents on the ring, such as methoxy, nitro and hydroxyl, could tolerate dehydration reactions (entries 1–6). Most substrates could afford nitriles in excellent conversion and selectivity except *m*-nitrobenzaldehyde- and *o*-hydroxybenzaldehyde oxime, which gave corresponding nitriles in moderate conversions. This could possibly be due to the electron-withdrawing effect of the former, and steric hindrance of the latter. This method was also suitable for the dialdoxime (entry 7), heterocyclic aldoxime (entry 8), and aliphatic aldoxime (entry 9) (Scheme 3).



Scheme 2

4 Conclusion

An efficient and rapid method for Beckmann rearrangement of ketoximes and dehydration of aldoximes have been



Scheme 3

developed by using recyclable and reusable silica-supported phosphorus chloride as catalyst under microwave irradiation. This protocol has advantages of high conversion, high selectivity, short reaction time, no environmental pollution, and simple work-up procedure.

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References

1. Smith BM, March J (2001) Advanced organic chemistry, 5th ed. John Wiley & Sons: New York, p 1415 and references therein
2. Nguyen MT, Raspoet G, Vanquickenborne LG (1997) J Chem Soc Perkin Trans 2:821
3. Kusama H, Yamashita Y, Narasaka K (1995) Bull Chem Soc Jpn 68:373
4. Hill RK, Mckinnie BG, Conley RT, Darby PS, Vanhalbeek H, Holt EM (1988) Tetrahedron 44:3405
5. Iglesias-Arteaga MA, Alvarado-Nuno AA (2006) Tetrahedron Lett 47:5351
6. Yoo KH, Choi EB, Lee HK, Yeon GH, Yang HC, Pak CS (2006) Synthesis 1599
7. Yan P, Batamack P, Prakash GKS, Olah G (2005) Catal Lett 103:165
8. Tsuji H, Setoyama T (2005) Chem Lett 34:1232
9. Zhu MZ, Cha CT, Deng WP, Shi XX (2006) Tetrahedron Lett 47:4861
10. Boruah M, Konwar D (2002) J Org Chem 67:7138
11. Furuya Y, Ishihara K, Yamamoto H (2005) J Am Chem Soc 127:11240
12. Wang B, Gu YL, Luo C, Yang T, Yang LM, Suo JS (2004) Tetrahedron Lett 45:3369
13. Chandrasekhar S, Gopalaiah K (2003) Tetrahedron Lett 44:7437
14. Li DM, Shi F, Guo S, Deng YQ (2005) Tetrahedron Lett 46:671
15. Yan P, Batamack P, Prakash GKS, Olah GA (2005) Catal Lett 101:141
16. Thomas B, Prathapan S, Sugunan S (2005) Microporous Mesoporous Mater 79:21
17. Sarvari MH (2005) Synthesis 787
18. Movassagh B, Shokri S (2005) Synth Commun 35:887
19. Yang SH, Chang S (2001) Org Lett 3:4209
20. Attanasi O, Palma P, Serra-Zanetti F (1983) Synthesis 741
21. (a) Li Z, Ding RB, Lu Z, Xiao SX, Ma XL (2006) J Mol Catal A: Chem 250:100 (b) Wang XG, Chen CC, Chen SY, Mou Y, Cheng SF (2005) Appl Catal A: Gen 281:47
22. Dongare MK, Bhagwat VV, Ramana CV, Gurjar MK (2004) Tetrahedron Lett 45:4759
23. (a) Curtis MP, Bunnelle WH, Pagano TG, Gopalakrishnan M, Faghih R (2006) Synth Commun 36:321; (b) Moghaddam FM, Rad AAR, Zali-Boinee H (2004) Synth Commun 34:2071; (c) Thakur AJ, Boruah A, Prajapati D, Sandhu JS (2000) Synth Commun 30:2105; (d) Feng JC, Liu B, Dai L, Bian NS (1998) Chin Chem Lett 9:795; (e) Loupy A, Regnier S (1999) Tetrahedron Lett 40:6221; (f) Hegedues A, Cwik A, Hell Z, Horvath Z, Esek A, Uzsoki M (2002) Green Chem 4:618; (g) Lingaiah N, Narender R (2002) Synth Commun 32:2391; (h) Dewan S, Singh R (2003) Synth Commun 33:3085; (i) Kumar HS, Mohanty PK, Kumar MS, Yadav JS (1997) Synth Commun 27:1327
24. Xu T, Kob N, Drago RS (1997) J Am Chem Soc 119:12231
25. Morrow BA, Lang SJ (1994) Langmuir 10:756