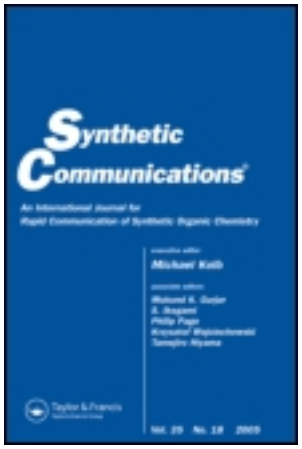

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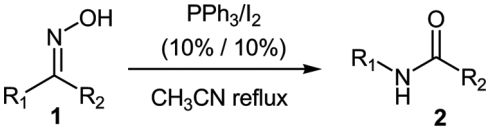
GRAPHICAL ABSTRACT



Abstract *A Beckmann rearrangement of ketoximes reaction using triphenylphosphine/iodine as an effective catalyst in acetonitrile at reflux temperature is reported. The results indicate that conversion of oximes to amides can be reached in good to excellent yields under optimal reaction conditions within several minutes. The reaction mechanism is also proposed. Supplemental materials are available for this article. Go to the publisher's online edition of* Synthetic Communications *to view the free supplemental file.*

Keywords Amide; Beckman rearrangement; iodine; ketoximes; triphenylphosphine

INTRODUCTION

Amides are important compounds for chemicals. The classical method for preparation of these compounds is conversion of ketoxime into corresponding amide, known as the Beckmann rearrangement,[1,2] which is of tremendous interest to all practicing organic chemists because the reaction insert a nitrogen into a carbon framework. It is a powerful method, particularly for manufacturing ε-caprolactam in the chemical industry. However, the conventional Beckmann rearrangement usually requires harsh conditions such as high temperature and use of an excess amount of strongly Brønsted acid such as concentrated H_2SO_4 or polyphosphoric acid (PPA), which cause serious problems such as corrosion of equipment and

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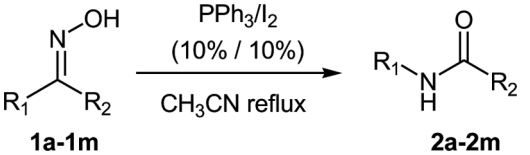
environmental pollution. To overcome these requisite harsh problems, chemists search for many methods such as vapor-phase,[3–6] solvent-free,[7–9] supercritical water,[10–13] and liquid-phase processes, such as Beckmann rearrangement catalyzed by cyanuric chloride (CNC),[14] sulfamic acid (NH_2SO_3H),[15] chlorosulfomic acid,[16] bis(2-oxo-3- oxazolidinyl)phosphinic chloride (BOP-Cl),[17] diethyl chlorophosphate (Et_2PO_3Cl),[18] $HgCl_2$,[19] bis(tri-chloromethyl) carbonate,[20] *p*-toluenesulfonic chloride (TsCl),[21] trifluoro acetic acid,[22] *p*-toluenesulfonic acid (TsOH),[2] and mesitylenesulfonyl chloride.[23,24] However, some of these methods still have disadvantages, such as toxicity of catalyst, tedious workup, vigorous reaction conditions, expensive reagents, difficulty in handing, long reaction time, and unsatisfactory yields. More recently, I_2-mediated Beckmann rearrangement[25] has been reported, which required 0.5 equivalent I_2 for optimum yields. PPh_3/NCS[26] has been reported as reaction intermediate in the Beckmann rearrangement reaction, but it needed 1.2 equivalents of PPh_3 and N-chlorosuccinimide (NCS). Therefore, it is necessary to develop a simple, clean, inexpensive catalyst system for highly efficient and selective catalytic Beckmann rearrangement process. In continuation of our previous work on applications of PPh_3 as a catalyst in an organocatalytic reaction,[27] here we report a facile method for Beckmann rearrangement of ketoximes to amides using triphenylphoshine/iodine (Ph_3P/I_2) as an efficient catalyst under mild reaction conditions.

Triphenylphosphine (Ph_3P) and iodine (I_2) are commercially available, cheap chemicals with outstanding physical properties and stability. Recently, it has been shown that Ph_3P has the prospect to be used as a substitute for conventional basic catalytic materials.[28–31] Also, I_2 is a useful acidic catalytic material. In homogeneous liquid reactions, Ph_3P/I_2 is easy to handle as a catalyst owing to its miscibility with water and unique catalytic features. Intrinsic zwitterionic property of Ph_3P/I_2 is very different from that of conventional catalysts.[32,33] All those features prompted us to explore further applications of Ph_3P/I_2 as a special catalyst in carbon–nitrogen bond-forming reactions. We report herein, for the first time, Ph_3P/I_2-catalyzed Beckmann rearrangement of ketoximes to produce corresponding amides (Scheme 1) without producing any waste.

Initially, I_2 was chosen for the catalytic Beckmann rearrangement. As shown in Table 1, the transformation cannot proceed in various solvents and different temperatures using only I_2. We also used Ph_3P as catalyst, but the results were disappointing. We studied the reaction of acetophenone oximes with Ph_3P in the presence of various electrophilic halogen sources such as N-bromosuccinimide (NBS), iodine (I_2), and CCl_4. The results are shown in Table 1. Results in Table 1 show that Ph_3P/I_2 is more efficient than Ph_3P/NBS and Ph_3P/CCl_4. The reaction of acetophenone oximes with PPh_3/I_2 occurs at reflux temperature in CH_3CN to produce phenyl acetamide in excellent yields (entries 11 and 12); however, the same reaction with Ph_3P/CCl_4 as catalyst produces phenyl acetamide only in 10% yield,



Scheme 1. Beckmann rearrangement catalyzed by PPh_3/I_2.

Table 1. Different catalysts catalyze Beckmann rearrangement of acetophenone oxime in different solvents

Entry	Catalyst (amount mol%)	Solvent (temp.)	Time (min)	Yield[a] (%)
1	I_2 (5)	DMF (rt)	180	—
2	I_2 (10)	DMF (rt)	180	—
3	I_2 (10)	CH_3CN (rt)	180	—
4	I_2 (10)	CH_3CN (reflux)	180	—
5	I_2 (10)	Acetone (rt)	180	—
6	I_2 (10)	Acetone (reflux)	180	—
7	PPh_3/I_2 (10/10)	DMF (rt)	180	—
8	PPh_3/I_2 (10/10)	DMF (reflux)	180	—
9	PPh_3/I_2 (10/10)	CH_3CN (rt)	180	20
10	PPh_3/I_2 (10/10)	Toluene (reflux)	240	20
11	PPh_3/I_2 (10/10)	CH_3CN (reflux)	5	96
12	PPh_3/I_2 (5/5)	CH_3CN (reflux)	60	90
13	PPh_3/CCl_4 (10/10)	CH_3CN (reflux)	60	10
14	PPh_3/NBS (10/10)	CH_3CN (reflux)	30	90

[a]Isolated yields.

even prolonging reaction time to 60 min. For the case of Ph_3P/NBS, the yield is good, but it needs longer reaction time.

To improve the catalytic efficiency of the Ph_3P/I_2 system in this reaction, the solvent effect was also inspected in the reaction of acetophenone oxime rearrangement. The results are summarized in Table 1 (entries 7–12). Acetonitrile as solvent gives the best result (entry 11). Considering all these results together, 10 mol% Ph_3P and 10 mol% I_2 are chosen as the optimal catalytic system and acetonitrile as solvent for Beckmann rearrangement in our study.

The generality and scope of the Ph_3P/I_2 system–catalyzed Beckmann rearrangement of ketoximes to amides were also investigated (Table 2). One can

Table 2. Beckmann rearrangement of ketoximes (**1a–1m**) to amides (**2a–2m**)[a]

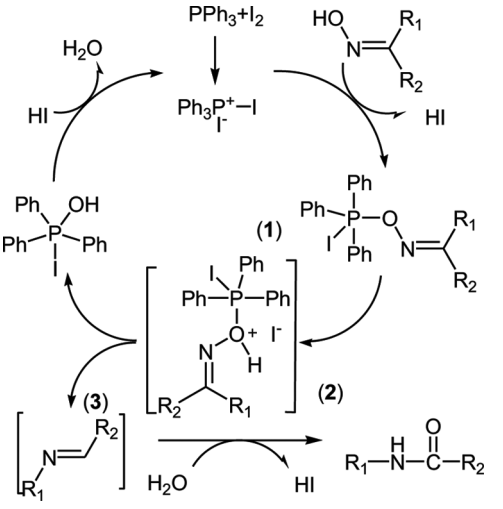
Entry	R_1	R_2	Product	Time (min)	Yield[b] (%)
1	Phenyl	Methyl	**2a**	5	96
2	4-Methoxylphenyl	Methyl	**2b**	10	96
3	4-Methylphenyl	Methyl	**2c**	10	95
4	3-Methoxylphenyl	Methyl	**2d**	10	86
5	2,4-Dimethylphenyl	Methyl	**2e**	5	93
6	2,5-Dimethoxylphenyl	Methyl	**2f**	5	94
7	1-Naphthyl	Methyl	**2g**	10	95
8	2-Naphthyl	Methyl	**2h**	10	93
9	Phenyl	Phenyl	**2i**	10	95
10	2-Chlorophenyl	Phenyl	**2j**	90	88
11	4-Chlorophenyl	Phenyl	**2k**	90	90
12	4-Aminophenyl	Methyl	**2l**	90	Trace
13	2,4-Dihydroxyl	Methyl	**2m**	90	Trace

[a]In CH_3CN, reflux, 10 mol% Ph_3P and 10 mol% I_2 as catalyst.
[b]Isolated yields.

see that excellent yields are obtained for all of ketoximes. The conversions of acetophenone oxime and substituted acetophenone oximes, for example, *p*-methyl acetophenone oxime, *p*-methoxyl acetophenone oxime, *o*-methoxyl acetophenone oxime, 2,4-dimethyl acetophenone oxime, and 2,5-dimethoxyl acetophenone oxime, to amides reach more than 90% yields (entries 1–6) within a short reaction time, even as short as 5 min. (entries 5 and 6). The results also suggest that the structures of the oximes have very little effect on the reaction. In the case of 4-chlorobenzophenone oxime and 2-chlorobenzo-phenone oxime (entries 10 and 11), they take much longer time than others. The reason for the chloride substitute reducing the reaction rate may be that the electron-withdrawing group on the aromatic ring, which has stronger electron-attracting ability, influences the migration of the aryl group. Hydroxyl and amino groups are electron-donating groups, but they are not able to rearrange in this catalytic system (entries 12 and 13), probably because the amino group in the aromatic ring can react with iodine of the Ph_3P/I_2 system, which causes the catalyst invalidation and influences the rearrangement reaction. While 2,4-dihydroxyl acetophenone oxime has acidity, it can react with triphenylphosphine, which sabotages the rearrangement.

Recently, an organocatalyst for the Beckmann rearrangement has attracted researchers, attention for its efficiency in catalytic activity and easy handling during the rearrangement.[34] Organophosphrus catalyst triphosphazene (TAPC)[35] was reported as a highly efficient catalyst for the Beckmann rearrangement by Ishihara and coworkers, and a novel mechanism was proposed to account for the new generation of organocatalytic Beckmann rearrangement. Based on this hypothesis, a similar mechanism is also described for the PPh_3/I_2-catalyzed Beckmann rearrangement, as shown in Scheme 2.

Reaction of Ph_3P with iodine gives the known electrophilic $Ph_3P \cdot I_2$ adduct,[33] which is attacked by the hydroxyl group to liberate hydrogen iodide[36,37] and intermediate (**1**). Hydrogen iodide can protonate the oxygen to give intermediate (**2**).[38]



Scheme 2. Plausible reaction path for the Beckmann rearrangement catalyzed by PPh_3/I_2.

Next, the loss of the Ph_3POHI moiety with concomitant transformation R_1 group to nitrogen atom forms the imine cationic intermediate (**3**). Finally, electrophilic $Ph_3P \cdot I_2$ adduct can be regenerated by protonating hydroxyl group of the pentacoordinated phosphorus and losing H_2O, following by iodide attack to the phosphorus. The intermediate **3** hydrated gives the final product amide and hydrogen iodide.

CONCLUSION

In conclusion, PPh_3/I_2 is a convenient catalyst system with respect to other reported catalyst systems and can be used as a valid alternative catalyst in Beckmann rearrangement to convert oximes into amides in good yields under optimal reaction conditions within several minutes.

EXPERIMENTAL

All solvents and reagents were used as obtained from commercial sources. The oximes were prepared according to standard methods, and their purities were established before utilization by melting point. Standard ^{1}H NMR and ^{13}C NMR were recorded at 300 and 75.4 MHz, from $CDCl_3$ or dimethylsulfoxide (DMSO-d_6) solutions. Ultra-high-resolution MS were obtained on a MaXis UHR-TOP instrument. All runs were conducted at least in duplicate.

A solution of ketoxime (1 mmol), 10 mol% PPh_3, and 10 mol% I_2 in MeCN was refluxed for a determined time. After completion of the reaction as monitored by thin-layer chromatography (TLC), the reaction was stopped, cooled to room temperature, and concentrated in vacuo. The residue was dissolved in EtOAc and washed with saturated sodium thiosulfate solution. The organic layer was separated, washed with NaCl saturated aqueous, and then concentrated. The resulting crude product was purified by column chromatography on silica gel to give the corresponding amide.

All products are known, which were confirmed by the melting point, ^{1}H NMR, and UHR-MS. The representative compounds also were characterized by ^{13}C NMR. All the characterized data of products were identical with those described in the literature.

N-(2,4-Dimethylphenyl)acetamide (2e)

Yield: 93%. Mp 132–133 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, $J = 7.9$ Hz, 1H), 7.08 (s, 1H), 7.00 (d, $J = 7.9$ Hz, 1H), 2.32 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H). ^{13}C NMR: δ 169.13, 135.49, 132.74, 131.43, 130.57, 127.4, 124.32, 23.67, 20.65, 17.74. UHR-MS (ESI): m/z calc. for $C_{10}H_{13}NO$ + [Na] 186.0895; found 186.0884 ($M^+ + Na$).

N-(*p*-Chlorophenyl)benzamide (2k)

Yield 90%, Mp 195–197 °C. ^{1}H NMR (300 MHz, *d*-DMSO): δ 10.34 (s, 1H), 7.98 (d, $J = 8.5$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.34–7.39, (m, 2H), 7.10–7.15(m, 1H). ^{13}C NMR: δ 165.00, 139.23, 136.88, 134.02,

130.04, 129.12, 128.92, 128.10, 124.38, 122.32, 120.95, 120.85. UHR-MS (ESI): m/z calc. for $C_{13}H_{10}ClNO + [Na]$ 254.0349; found 254.0334 ($M^+ + Na$).

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