Study on the Application of Beckmann Rearrangement in the Synthesis of Amides from Oximes

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ABSTRACT

In order to prepare amide under more moderate, environment-friendly condition with Beckmann rearrangement, we replaced the traditional liquid acid catalyst with Nafion perfluorinated sulfonic acid resin. We used diphenylketone oxime as for the template substrate, and carried out the experiments to explore the optimal reaction conditions of the Beckmann rearrangement. We studied the effects of reaction temperature, reaction time, catalyst dosage, solvent kinds and volume on Beckmann rearrangement, and established the following optimal reaction conditions: diphenylketone oxime 2 g, solvent acetonitrile 20 mL, catalyst Nafion 0.4 g, reaction temperature 70 °C, reaction time 4 h. Under this conditions, the conversion of diphenylketone oxime was 36.32%, benzanilide selectivity was 44.06%, and benzanilide yield was 16.00%. We also studied the adaptability of other different substrates to Beckmann rearrangement under this optimal conditions, and found Nafion can catalyze not only aromatic ketone oxime but also aliphatic one. Melting point measurement, infrared spectrum, ^{1}H and ^{13}C nuclear magnetic resonance spectrum test had been used to characterize the product. The reuse experiment of catalyst showed that Nafion had good recovery performance, and was a green and promising catalyst.

Keywords: Beckmann rearrangement; diphenylketone oxime; Amide; Nafion.

1. INTRODUCTION

Amide is a very important compound and also a very important functional group in organic chemistry and biochemistry. Such functional group is widely used in drugs, natural products and a large number of industrial materials such as polymers, detergents and lubricants. Beckmann rearrangement reaction [1], that is, oxime as the initial material to synthesize amide, has a long history. This classic reaction was first discovered by a German chemist named Beckmann in 1886 and has very important value in organic synthesis. ε-caprolactam, the precursor of nylon-6 synthesis, is prepared through Beckmann rearrangement of cyclohexanone oxime.

The traditional Beckmann rearrangement method needs strong acid [2-6] as the catalyst, and it can be carried out only under stringent conditions. The equipment is high level required and the cost is expensive, the waste water generated is also a serious problem to the environment. Therefore, seeking for a moderate catalytic system and achieving

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Beckmann rearrangement under a more concise and environment-friendly condition are the objective of many organic chemists [7-10].

We took diphenyl ketone as template substrate, obtained the corresponding ketone oxime, and investigated the effects of catalyst kinds, solvent kinds, reaction temperature, reaction time, catalyst dosage, solvent volume (i.e. oxime concentration) on the Beckmann rearrangement of diphenylketone oxime, with melting point measurement, infrared spectrum (IR) and nuclear magnetic resonance (NMR) method for the qualitative methods, liquid chromatography for the quantitative method.

2. EXPERIMENTAL DETAILS

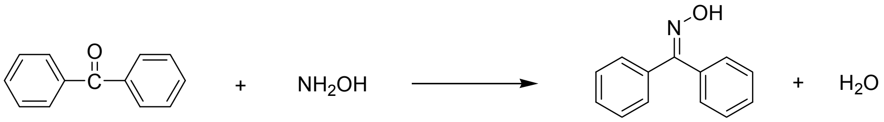
2.1 Reagents and instruments

Diphenyl ketone, hydroxylamine hydrochloride, Nafion^{TM} NR50 perfluorinated sulfonic acid resin, Amberlyst®15 sulfonic acid resin, *p*-toluene sulfonic acid, amino sulfonic acid, polyphosphoric acid (PPA), acetonitrile, cyclohexane, dimethyl sulfoxide, methanol, ethanol, acetone, acetophenone, *p*-chloroacetophenone, *p*-methoxyacetophenone.

78HW-1 digital display heating magnetic stirrer, ZX98-1 rotary evaporator, LC2130 liquid chromatograph, WRR melting point instrument, NICOLET LS10 Fourier transform infrared spectrometer, BRUKER AVANCE III nuclear magnetic resonance spectrometer.

2.2 preparation of diphenylketone oxime

The equation for the formation of oxime from diphenyl ketone is shown as follows:

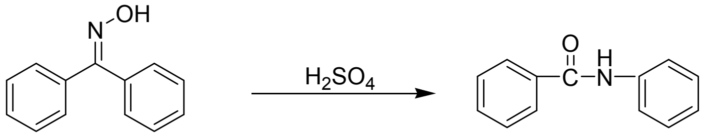


Scheme 1 Preparation of diphenylketone oxime

In a 125 mL round bottom flask, dissolving 2.5 g diphenyl ketone and 1.5 g hydroxylamine hydrochloride in 10 mL ethanol and 2 mL water, and then adding 1.6 g sodium hydroxide. Magnetic stirring and heating reflux for 2 h at 70 °C. Then transferring the solution into a beaker containing 8 mL concentrated hydrochloric acid and 50 mL water, so the diphenylketone oxime was precipitated out as white powder crystals. After cooling, filtration and recrystallization with about 10 mL ethanol, a small amount of the dried products was left for melting point determination, the rest was used for the rearrangement reaction. Diphenylketone oxime was a colorless transparent needle crystal, the literature value of melting point is142.5 °C.

2.3 Diphenylketone oxime rearrangement

The Beckmann rearrangement equation of diphenylketone oxime is as follows:



Scheme 2 Rearrangement of diphenylketone oxime

A typical rearrangement reaction was as follows: adding solvent (acetonitrile, 20 mL) to a 125 mL round bottom flask, then adding the substrate oxime(diphenylketone oxime, 2 g) and solid catalyst (Nafion, 0.4 g) respectively. Magnetic stirring and heating reflux for 2 h at 70 °C (thin layer chromatography monitoring the reaction progress, *n*-hexane: ethyl acetate =4:1). Keep stirring to cool down. Filtrating out the solid catalyst, the solvent in the filtrate was recycled by the rotary evaporator to get the crude product, recrystallization with ethanol, drying. The product benzanilide was white needle crystal, the literature value of melting point is 163 °C.

2.4 Liquid chromatography analysis

Ultraviolet detector, the liquid chromatography conditions were as follows:

Chromatographic column: C18, 250 mm×4.6 mm×5 μm, mobile phase: methanol/distilled water =60:40 (V/V), detection wavelength: 254 nm, flow rate: 1.0 mL·min^{-1}, column temperature: 30 °C, injection volume: 20 μL.

The oxime conversion C was calculated by the amount of the oxime remaining after the reaction and the amount before the reaction, the amide selectivity S_1 was calculated according to the amount of the product and the amount of oxime conversion, the formula is as follows:

$$C = \frac{m_0 - m_1}{m_0} \times 100\%$$

$$S_1 = \frac{m_2 \quad * 197.24}{(m_0 - m_1) * 197.24} \times 100\%$$

In the formula, C: the conversion of oxime, S_1: the selectivity of amide.

m_0, m_1, m_2: the amount of oxime before reaction, the residual oxime after reaction, and the amide formed.

197.24, 197.24: the molecular weight of diphenylketone oxime and benzanilide.

2.5 Melting point determination

Sample of 1-2 mm height, determining with melting point instrument.

2.6 Infrared spectrum analysis

Adding the dried sample 0.005 g into a mortar, then mixing with 0.005 g KBr powder, grinding, tablet compressing, scanning the sample.

2.7 Nuclear magnetic resonance test

500 M nuclear magnetic measurement, deuterium dimethylsulfoxide dissolved the samples.

3. RESULTS AND DISCUSSION

3.1 Standard curve of liquid chromatography

The peak data of standard samples were processed by Origin, the standard curve of benzanilide is shown in Fig. 1. The linear equation was Y=205034+51882X, correlation coefficient R=0.99885, indicating that there was a good linear relationship between the amide concentration and the chromatographic peak area in the range of measurement.

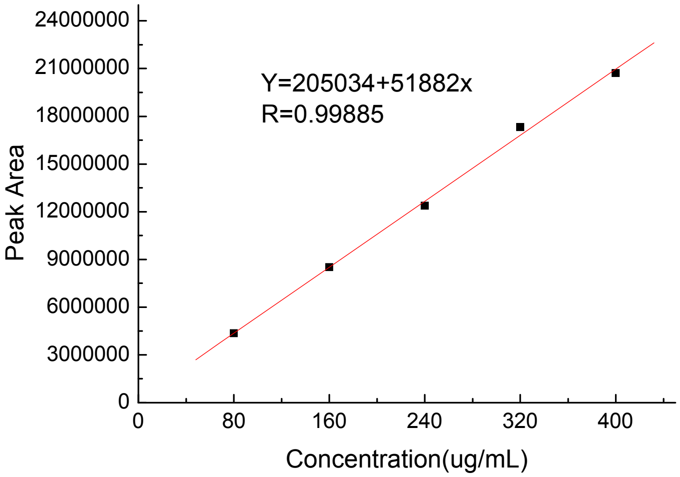


Fig. 1. The standard curve for liquid chromatography of benzanilide

Fig. 2 is the standard curve of diphenylketone oxime, the linear equation was Y=183614+48103X, R=0.99847, indicating that in the measurement range, the oxime concentration was also in good linear relation with the peak area.

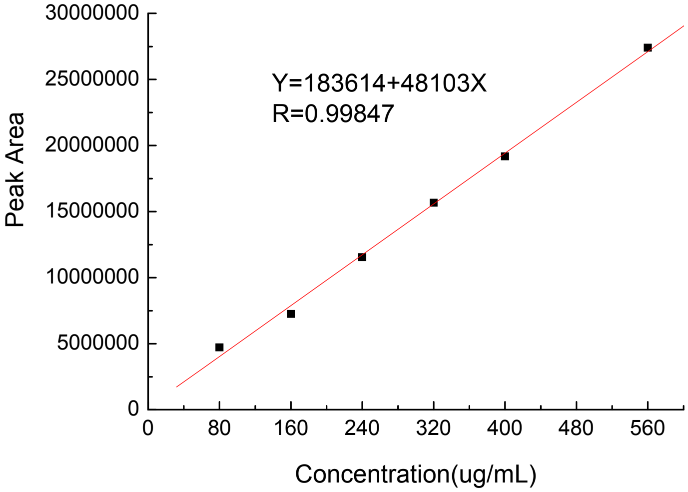


Fig. 2. The standard curve for liquid chromatography of diphenylketone oxime

3.2 Effects of different catalysts on Beckmann rearrangement

In order to investigate the effects of different catalysts on Beckmann rearrangement, we used with liquid acid polyphosphoric acid (PPA), and solid sulfonic acid *p*-toluene sulfonic acid, amino sulfonic acid, Amberlyst® 15 sulfonic acid resin, Nafion perfluorinated sulfonic acid resin as catalyst respectively for rearrangement reaction, the results are shown in table 1. The reaction with solid catalyst employed acetonitrile as the solvent. Considering the rearrangement is an exothermic reaction, the reaction temperature was selected at 70 °C, a bit lower than the boiling point 82 °C of acetonitrile.

As can be seen from table 1, the rearrangement reaction activity on different catalysts was not the same. In the rearrangement reaction of PPA as catalyst, the conversion of diphenylketone oxime reached 100%, the selectivity and the yield of benzanilide were also high. However, using liquid acid in the experiment existed the disadvantages, such as strong corrosive, toxic, cannot be recycled, and so on. When the solid sulfonic acid used as catalyst, the yield of benzanilide was zero when catalyzed by amino sulfonic acid and *p*-toluene sulfonic acid, and these two catalysts were dissolved in the reaction solution, cannot achieving the purpose of recycling the catalyst. Nafion and Amberlyst are sulfonic acid supported on resin, when they were used as catalysts, the diphenylketone oxime conversion, the selectivity and yield of benzanilide were all higher than the above two, and the activity on Nafion was better than that of Amberlyst. The reaction process was mild and safe, the recovery process of catalyst after the reaction was simple and catalyst can be used again, so we selected Nafion perfluorinated sulfonic acid resin as catalyst.

Table 1. Effects of different catalysts on the Beckmann rearrangement of diphenylketone oxime

Catalyst	**Conversion of diphenylketone oxime (%)**	**Selectivity of benzanilide (%)**	**Yield of benzanilide (%)**
PPA [a]	100	68.69	68.69
Amino sulfonic acid [b]	1.53	0	0
P-toluene sulfonic acid [b]	2.54	0	0
Amberlyst®15 sulfonic acid resin [b]	2.96	36.75	1.09
Nafion perfluorinated sulfonic acid resin [b]	16.44	43.26	7.11

** Reaction conditions: diphenylketone oxime 2.0 g.*

[a] *liquid acid catalyst system: PPA 25 mL, solvent free, reaction temperature 100 ℃, reaction time 0.5 h.*

[b] *solid catalyst system: catalyst 0.2 g, acetonitrile 20 mL, reaction temperature 70 ℃, reaction time 2 h.*

3.3 Effects of different solvents on Beckmann rearrangement

In order to study the effects of different solvents on diphenylketone oxime Beckmann rearrangement, we fixed the amount of diphenylketone oxime, Nafion catalyst dosage and reaction time, the results are showed in table 2. The reaction temperatures were a bit lower than the boiling points of each solvent.

As can be seen from table 2, the solvent had a great influence on the Beckmann rearrangement of diphenylketone oxime. A solvent with strong polarity had a higher conversion of diphenylketone oxime. We can compare the reaction of acetonitrile and cyclohexane as the solvents, the reaction temperatures of these two were the same. While acetonitrile was used as solvent, the conversion of diphenylketone oxime and the selectivity of benzanilide were relatively higher compared to the other. This is probably due to the strong polarity of acetonitrile, which made it easier for benzanilide produced to be desorbed from Nafion and dissolved in solvents, thus improving the conversion of diphenylketone oxime and the selectivity of benzanilide. The cyclohexane had very weak polarity, so the conversion of diphenylketone oxime, the selectivity and yield of benzanilide were the lowest. The same effect happened with dimethyl sulfone (DMSO) and acetone used as solvents. Because we chose the reaction temperature a little lower than the solvent's boiling point, the 130 °C of DMSO was too high while the 45 °C of acetone was too low, the 70 °C of acetonitrile was the moderate reaction temperature, so acetonitrile was selected as the solvent for the reaction.

Table 2. Effects of different solvents on the Beckmann rearrangement of diphenylketone oxime

Solvent	Boiling point (°C)	Dielectric constant ε	Reaction temperature (°C)	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
Cyclohexane	81	2.02	70	4.06	22.05	0.90
Acetone	56	20.7	45	6.93	46.64	3.23
Acetonitrile	82	37.5	70	16.44	43.26	7.11
Dimethyl sulfone	189	48.9	130	13.31	49.85	6.63

** Reaction conditions: diphenylketone oxime 2.0 g, Nafion 0.2 g, solvent 20 mL, reaction time 2 h.*

3.4 Effects of reaction temperature on Beckmann rearrangement

Using acetonitrile as solvent, we investigated the effects of reaction temperature on the Beckmann rearrangement of diphenylketone oxime catalyzed by Nafion, the results are shown in table 3.

It can be seen from table 3, the reaction temperature affected the conversion of diphenylketone oxime and the selectivity of benzanilide. At low temperature, the conversion of diphenylketone oxime was very low, only 6.63% at 30 °C, and it increased with the increase of reaction temperature, the value was 21.96% at 82 °C. But benzanilide selectivity decreased with reaction temperature increased, this may be due to the high temperature increased the competition of oxime hydrolysis reaction compared to the oxime rearrangement. The yield of benzanilide increased with the increase of reaction temperature first, and then leveled off, it reached highest at 70 °C. So we chose 70 °C for the rearrangement reaction temperature, this not only ensured the diphenylketone oxime conversion and benzanilide selectivity were higher, but also could receive the maximum benzanilide yield.

Table 3. Effects of reaction temperature on the Beckmann rearrangement of diphenylketone oxime

Reaction temperature (°C)	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
30	6.63	77.90	5.16
50	8.50	63.88	5.43
70	16.44	43.26	7.11
82	21.96	30.23	6.64

** Reaction conditions: diphenylketone oxime 2.0 g, Nafion 0.2 g, acetonitrile 20 mL, reaction time 2 h.*

3.5 Effects of reaction time on Beckmann rearrangement

In order to further study the influence factors of Beckmann rearrangement, we investigated the effects of reaction time on rearrangement reaction. The results are shown in table 4.

From table 4, it can be seen that the conversion of diphenylketone oxime had tended to be the highest when the reaction time was 4 h, and to be stable as the reaction time prolonged. During the reaction, the selectivity of benzanilide decreased with time, possibly because of the polymerization reaction of benzanilide with time prolonged. The yield of benzanilide reached the highest at 4 h, and then decreased. Therefore, we chose the reaction time of 4 h, which ensured that the conversion of diphenylketone oxime was complete, the higher selectivity of amide was maintained, and the yield of benzanilide was the largest.

Table 4. Effects of reaction time on the Beckmann rearrangement of diphenylketone oxime

Reaction time (h)	**Conversion of diphenylketone oxime (%)**	**Selectivity of benzanilide (%)**	**Yield of benzanilide (%)**
2	16.44	43.26	7.11
3	20.56	40.65	8.36
4	29.35	34.98	10.27
5	29.40	27.67	8.13
6	29.64	16.53	4.90

** Reaction conditions: diphenylketone oxime 2.0 g, Nafion 0.2 g, acetonitrile 20 mL, reaction temperature 70 ℃.*

3.6 Effects of catalyst dosage on Beckmann rearrangement

In order to investigate the influences of catalyst dosage on the Beckmann rearrangement of diphenylketone oxime, we fixed diphenylketone oxime amount, reaction temperature and time. The results are shown in table 5.

It can be seen from table 5, that with the increase of catalyst dosage, the conversion of diphenylketone oxime increased, while the selectivity of benzanilide increased first and then decreased, reaching the maximum value at 0.4 g. The yield of benzanilide reached the maximum when the catalyst dosage was 0.4 g. Therefore, we chose the most suitable catalyst dosage of 0.4 g.

Table 5. Effects of catalyst dosage on the Beckmann rearrangement of diphenylketone oxime

Nafion (g)	**Conversion of diphenylketone oxime (%)**	**Selectivity of benzanilide (%)**	**Yield of benzanilide (%)**
0.2	29.35	34.98	10.27
0.3	32.75	38.87	12.73
0.4	36.32	44.06	16.00
0.5	39.21	36.68	14.38
0.6	40.09	30.24	12.12

** Reaction conditions: diphenylketone oxime 2.0 g, acetonitrile 20 mL, reaction temperature 70 ℃, reaction time 4 h.*

3.7 Effects of solvent volume on Beckmann rearrangement

We fixed diphenylketone oxime amount and Nafion catalyst dosage to study the effects of diphenylketone oxime concentration on Beckmann rearrangement by changing solvent volume, the results are shown in table 6.

From table 6, it was known that in the range of oxime concentration investigated, the conversion of diphenylketone oxime first increased slowly and then decreased rapidly. This may be due to the higher concentration of reaction solution resulting in the difficulty in removing benzanilide from Nafion, thus reducing the content of amide in the reaction solution. The change of oxime concentration also affected the selectivity of benzanilide. Along with increasing the volume of solvent, oxime concentration decreased, benzanilide selectivity increased. When the solvent volume was 20 mL, it reached 44.06%. Further increasing the solvent volume, the selectivity of benzanilide increased slowly. Higher yield of benzanilide can be obtained at the medium oxime concentration, while the higher and lower oxime concentration all decreased the yield of amide. Therefore, the optimum volume of the added acetonitrile was 20 mL.

Table 6. Effects of solvent volume on the Beckmann rearrangement of diphenylketone oxime

Acetonitrile (mL)	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
10	34.98	9.06	3.17
15	36.01	30.89	11.12
20	36.32	44.06	16.00
25	20.78	50.65	10.53
30	13.30	59.57	7.92

** Reaction conditions: diphenylketone oxime 2.0 g, Nafion 0.4 g, reaction temperature 70 ℃, reaction time 4 h.*

3.8 The adaptability of different substrates to Beckmann rearrangement

In order to study the generality and applicability to Beckmann rearrangement of Nafion perfluorinated sulfonic acid resin catalyst, we made further research of other typical ketone oximes under the optimal reaction conditions. We used acetone as the aliphatic ketone, and acetophenone, *p*-chloroacetophenone, *p*-methoxyacetophenone as the aromatic ketone to study the effect of other different substrates on Beckmann rearrangement. The processes of preparation and rearrangement of other ketone oxime were the same as those of diphenylketone oxime, the feeding ratios to prepare other ketone oxime and the Beckmann rearrangement of other ketone oxime are shown in Table 7, the yield of amide was calculated by the recrystallized product amount after rearrangement reaction and the theoretical amount of rearrangement product.

Table 7. Feeding ratios to prepare different substrates ketone oxime and their Beckmann rearrangement

Substrate(R_1COR_2)	R_1	R_2	Preparation of ketone oxime [a]		Rearrangement of ketone oxime [b]
			Molecular weight	Moles (mmol)	Yield of amide (%)
Acetone	CH_3	CH_3	58.08	50	6.76
Acetophenone	C_6H_5	CH_3	120.15	50	12.85
p-Chloroacetophenone	*p*-ClC_6H_4	CH_3	154.60	50	10.87
p-Methoxyacetophenone	*p*-$(CH_3O)C_6H_4$	CH_3	150.17	50	13.43
diphenylketone	C_6H_5	C_6H_5			16.00

** [a] Preparation of other ketone oxime: hydroxylamine hydrochloride 75 mmol, sodium hydroxide 0.225 mol.*

[b] Reaction conditions of ketone oxime rearrangement: ketone oxime 2.0 g, Nafion 0.4 g, acetonitrile 20 mL, reaction temperature 70 ℃, reaction time 4 h.

It can be seen from table 7, that under the catalysis of Nafion, aromatic and aliphatic ketone oxime could carry out Beckmann rearrangement reaction as well as diphenylketone oxime, and aromatic ketone oximes had higher activities than aliphatic one.

3.9 Reuse performance of Nafion catalyst

Perfluorinated sulfonic acid resin is granular solid, which can be separated by filtration from reaction solution, and can be used for the reaction of the next batch by simple processing. Therefore, the reuse performance of Nafion was investigated in this study, and the results are shown in table 8.

From table 8, we can see that when Nafion was reused the first time, the conversion of diphenylketone oxime and yield of benzanilide both dropped a little. As the numbers of reuse increased, the conversion and yield decreased. The mass of sulfonic acid resin was lost in the process of recycling and reuse, which may be the cause of the decrease in conversion and yield. In general, Nafion catalyst can be recycled easily and can still be used again.

Table 8. The Beckmann rearrangement of diphenylketone oxime on the recycled Nafion catalyst

Catalyst	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
Fresh	36.32	44.06	16.00
First run recycled	34.67	45.87	15.90
Second run recycled	29.64	40.43	11.98
Third run recycled	25.87	38.98	10.08

** Reaction conditions: diphenylketone oxime 2.0 g, Nafion 0.4 g, acetonitrile 20 mL, reaction temperature 70 ℃, reaction time 4 h.*

3.10 Characterization of benzanilide

The benzanilide obtained was analyzed by melting point determination, IR and NMR test, respectively.

The melting point measurement showed that the mp of benzanilide was 161.7-162.3 °C, which was in accordance with the literature value of 163 °C, indicating that the sample was pure.

Fig. 3 is IR spectrogram of benzanilide. It can be seen that the absorption peak of 1655 cm^{-1} and 1533 cm^{-1}, which were assigned to the stretching vibration of C=O and the bending vibration of N-H in amide. And the absorption peak of 3413 cm^{-1} was the stretching vibration peak of N-H. The absorption peak of 770-730 cm^{-1} and 710-690 cm^{-1} was the out-of-plane bending vibration peak of C-H on the substituent benzene ring.

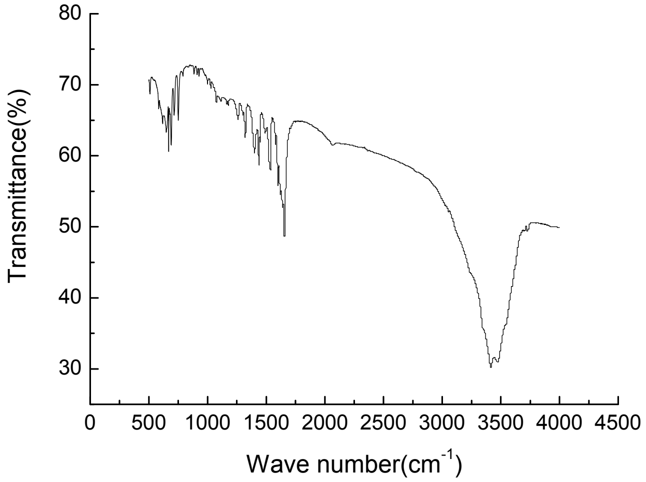


Fig. 3. IR spectrogram of benzanilide

The ^{1}H and ^{13}C NMR spectrogram of benzanilide are shown in Fig. 4 and 5. Among them:

^{1}H NMR (500MHz, DMSO): δ 10.27 (s, 1H, N-H), 7.97 (dt, J = 3.5, 2.3 Hz, 2H, Ar-H), 7.81 (dd, J = 8.5, 1.0 Hz, 2H, Ar-H), 7.65-7.57 (m, 1H, Ar-H), 7.57-7.49 (m, 2H, Ar-H), 7.41-7.30 (m, 2H, Ar-H), 7.17-7.04 (m, 1H, Ar-H).

^{13}C NMR (126MHz, DMSO): δ165.5, 139.2, 135.0, 131.5, 128.5, 127.6, 123.6, 120.4 (the heptet of around 40 was the peak of solvent).

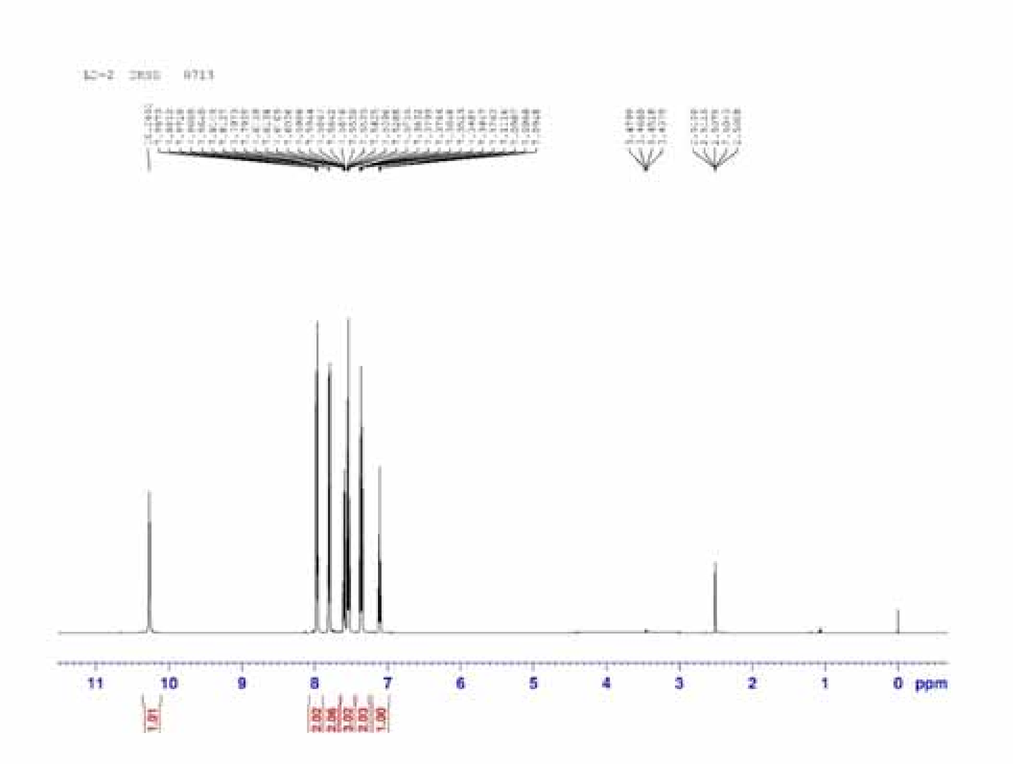


Fig. 4. ^{1}H NMR spectrogram of benzanilide

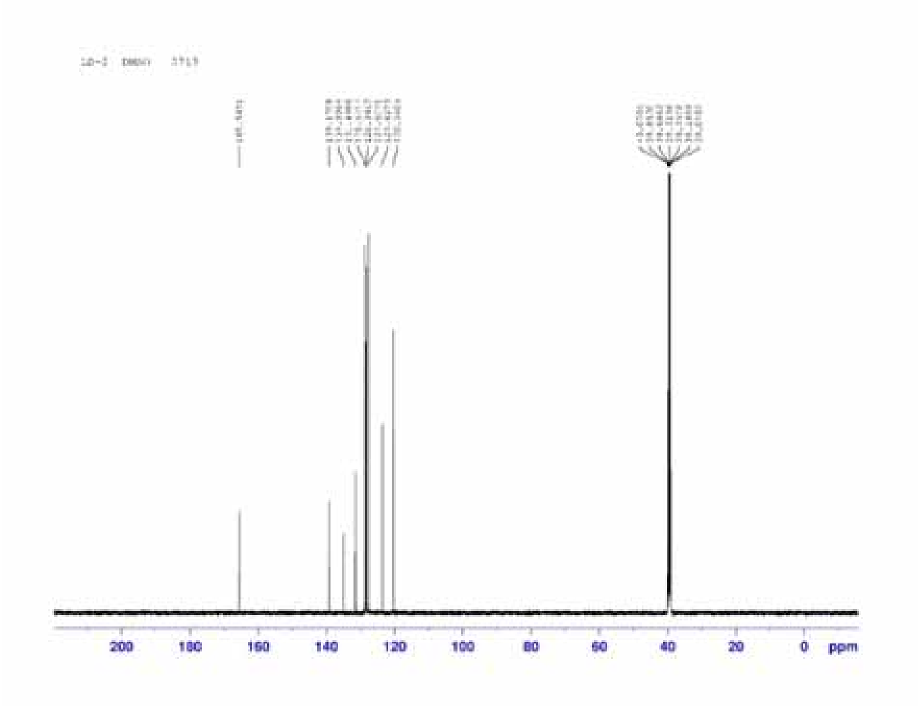


Fig. 5. ^{13}C NMR spectrogram of benzanilide

Combined with the identification of melting point determination, IR and NMR test, it can be concluded that the product of Beckmann rearrangement was indeed benzanilide.

4. CONCLUSION

In order to prepare amide in a more mild and friendly environment with Beckmann rearrangement reaction, we used Nafion perfluorinated sulfonic acid resin instead of the traditional liquid acid catalyst to study the optimal reaction conditions with diphenylketone oxime as template substrate. The adaptability of other different substrates to Beckmann rearrangement under the optimal conditions and the reuse performance of the catalyst were also investigated. The following conclusions are obtained:

(1) Compared with the other sulfonic acid catalysts, the Nafion Perfluorinated sulfonic acid resin had a relatively good effect on Beckmann rearrangement.

(2) When the substrate diphenylketone oxime was in amount of 2 g, the optimal reaction conditions were as follows: reaction temperature 70 °C, reaction time 4 h, Nafion catalyst dosage 0.4 g, solvent acetonitrile volume 20 mL. Under this condition, the conversion of diphenylketone oxime was 36.32%, the selectivity of benzanilide was 44.06%, and the yield of benzanilide was 16.00%.

(3) In the presence of Nafion, aromatic and aliphatic ketone oxime could occur Beckmann rearrangement as well as diphenylketone oxime, the aromatic ketone oximes had higher reaction activities than aliphatic one.

(4) The Nafion Perfluorinated sulfonic acid resin catalyst can be easily separated from the solution and had no pollution to the environment. The reuse experiment showed that Nafion had a good recycling performance. It was a green and promising catalyst.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration of all authors. Author YZ designed the study. All authors contributed in practical work and managed the analysis of the study. Author DL wrote the first draft of the manuscript. All authors read and approved the final manuscript.

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