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

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Authors' contributions

This work was carried out in collaboration between 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.

Original Research Article

ABSTRACT

In order to prepare amides under moderate and environment-friendly conditions using Beckmann rearrangement, we replaced traditional liquid-acid catalysts with Nafion perfluorinated sulphonic acid resins. We used diphenylketone oxime as the template substrate and carried out experimental studies to explore the optimal reaction conditions for Beckmann rearrangement. We studied the effects of reaction temperature, reaction time, catalyst dosage, and solvent type and volume on Beckmann rearrangement and established the following optimal reaction conditions: diphenylketone oxime (2 g), acetonitrile (solvent; 20 mL), Nafion (catalyst; 0.4 g), reaction temperature (70°C), and reaction time (4 h). Under these conditions, the degree of conversion of diphenylketone oxime was 36.32%, while benzanilide selectivity and yield were 44.06% and 16%, respectively. We also studied the adaptability of other substrates for Beckmann rearrangement at the optimal conditions and found that Nafion can catalyse both aromatic and aliphatic ketone oximes. Melting point, infrared, and ^{1}H and ^{13}C nuclear magnetic resonance analyses were conducted to characterise the obtained products. Reuse experiments of the catalyst showed that Nafion exhibited good recovery performance and hence is a green and promising catalyst.

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1. INTRODUCTION

Amides are very important compounds and functional groups in organic chemistry and biochemistry. These functional groups are widely used in drugs, natural products, and a large number of industrial materials, such as polymers, detergents, and lubricants. The Beckmann rearrangement reaction [1], which converts oximes to amides, has a long history; this classical reaction was first discovered by a German chemist named Beckmann in 1886, and it is of great value in organic chemistry. ε-caprolactam, the precursor of nylon-6, is prepared by the Beckmann rearrangement of cyclohexanone oxime.

The traditional Beckmann rearrangement method requires a strong acid [2-6] as the catalyst and it can be carried out only under stringent conditions. High-quality equipment is required, which drives up the cost of the reaction, and the generated wastewater is also a serious problem to the environment. Therefore, developing a moderate catalytic system for Beckmann rearrangement, which works under flexible and environment-friendly conditions, is the objective of many organic chemists [7-10].

We used diphenyl ketone as the template substrate in this study and the obtained ketone oxime was characterised. The effects of catalyst type, solvent type, reaction temperature, reaction time, catalyst dosage, and solvent volume (i.e. oxime concentration) on the Beckmann rearrangement of diphenylketone oxime were studied. Further, melting point (MP), infrared (IR), and nuclear magnetic resonance (NMR) analyses, which are qualitative in nature, were conducted along with the quantitative liquid chromatography analysis.

2. EXPERIMENTAL DETAILS

2.1 Reagents and Instruments

Diphenyl ketone, hydroxylamine hydrochloride, Nafion[TM] NR50 perfluorinated sulphonic acid resin, Amberlyst[®]15 sulphonic acid resin, *p*-toluene sulphonic acid, amino sulphonic acid, polyphosphoric acid (PPA), acetonitrile, cyclohexane, dimethyl sulphoxide, methanol, ethanol, acetone, acetophenone, *p*-chloroacetophenone, and *p*-methoxyaceto-phenone were used in this study.

A heating magnetic stirrer (78HW-1 digital display), ZX98-1 rotary evaporator, LC2130 liquid chromatograph, WRR melting point instrument, NICOLET LS10 Fourier-transform infrared spectrometer, and BRUKER AVANCE III nuclear magnetic resonance spectrometer were used for the preparation and analysis of the obtained diphenylketone oxime.
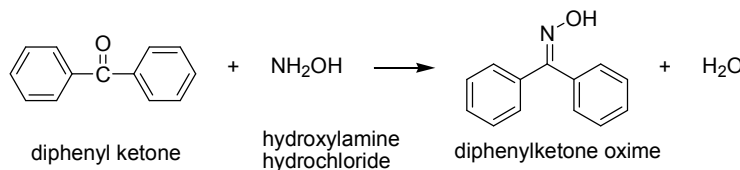
2.2 Preparation of Diphenylketone Oximes

The reaction mechanism for oxime synthesis from diphenyl ketones is shown in Scheme 1.
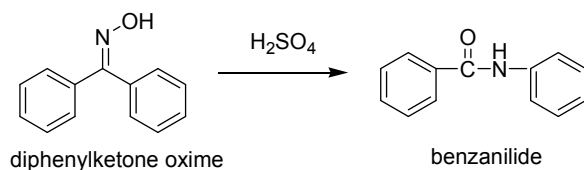
In a 125 mL round-bottomed flask, 2.5 g diphenyl ketone and 1.5 g hydroxylamine hydrochloride were dissolved in 10 mL of ethanol and 2 mL of water; to this solution, 1.6 g of sodium hydroxide was added. The mixture was stirred using a magnetic stirrer and subjected to a heating reflux for 2 h at 70°C. Later, this solution was transferred into a beaker containing 8 mL of concentrated hydrochloric acid and 50 mL of water. Under these conditions, diphenylketone oxime precipitated out as white powder crystals. After cooling, filtration, and recrystallization with ~10 mL of ethanol, a small amount of the dried products was extracted for MP determination and the rest was used for the rearrangement reaction. Diphenylketone oxime was obtained as colourless transparent needle crystals, whose MP is reported to be 142.5°C.

2.3 Diphenylketone Oxime Rearrange-ment

The Beckmann rearrangement mechanism of diphenylketone oximes is as shown in Scheme 2.

Scheme 1. Preparation of diphenylketone oximes

Scheme 2. Rearrangement of diphenylketone oxime

A typical rearrangement reaction was carried out as follows. The solvent (acetonitrile, 20 mL) was added to a 125 mL round-bottomed flask to which the substrate oxime (diphenylketone oxime, 2 g) and solid catalyst (Nafion, 0.4 g) were subsequently added. The mixture was stirred using a magnetic stirrer and subjected to a heating reflux for 2 h at 70°C. Thin-layer chromatography was conducted using a *n*-hexane and ethyl acetate (4:1) mixture to monitor the progress of the reaction. The mixture was allowed to cool down and after filtering out the solid catalyst, the solvent in the filtrate was recycled using a rotary evaporator to get the crude product. The crude product was then recrystallised with ethanol and dried. The product, benzanilide, was obtained in the form of white crystal needles, whose MP is reported to be 163°C.

2.4 Liquid Chromatography Analysis

An ultraviolet detector was used to carry out liquid chromatography under the following conditions. 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, and injection volume: 20 µL.

The oxime conversion extent, *C*, was calculated using the amounts of oxime before and after reaction and the amide selectivity, S_1, was calculated using the amount of the product and the extent of oxime conversion. The formulae used for the calculation of *C* and S_1 are as follows.

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

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

Here, m_0, m_1, and m_2 are the amounts of oxime before reaction, the residual amount of oxime after reaction, and the amide formed, respectively. The molecular weight of both diphenylketone oxime and benzanilide is 197.24.

2.5 Melting Point Determination

A sample of 1–2 mm height was used for the determination of MP using a melting point instrument.

2.6 Infrared Spectrum Analysis

The dried sample (0.005 g) was ground along with 0.005 g of KBr powder in a mortar. The obtained powder was compressed into a tablet, which was later used for infrared scanning.

2.7 Nuclear Magnetic Resonance Test

500 MHz nuclear magnetic measurement; deuterium dimethyl sulphoxide was used to dissolve the samples.

3. RESULTS AND DISCUSSION

3.1 Standard Curve of Liquid Chromatography

The peak data of the standard samples was processed by Origin; the standard curve of benzanilide is shown in Fig. 1. The linear equation for the standard curve was calculated to be Y = 205034 + 51882X and the correlation coefficient was R^2 = 0.9977, which indicates a good linear relationship between the amide concentration and chromatographic peak area in the range of measurement.

Fig. 2 depicts the standard curve of diphenylketone oxime, the linear equation of which was Y = 183614 + 48103X; the regression coefficient was R^2 = 0.9969, indicating that in the measured range, oxime concentration exhibited a good linear relationship with the peak area.

3.2 Effect of Different Catalysts on Beckmann Rearrangement

In order to investigate the effects of different catalysts on Beckmann rearrangement, we used a liquid-acid catalyst, polyphosphoric acid (PPA)

and solid sulphonic acid catalysts (*p*-toluene sulphonic acid, amino sulphonic acid, Amberlyst® 15 sulphonic acid resin, and Nafion perfluorinated sulphonic acid resin) for the rearrangement reaction; the results are shown in Table 1. The reaction with the solid catalyst employed acetonitrile as the solvent. Considering that the rearrangement reaction is exothermic, the reaction temperature was set at 70°C, a little lower than the boiling point of acetonitrile (82°C).

As can be seen in Table 1, the reaction activities of the catalysts were not the same. In the rearrangement reaction in which PPA was used as the catalyst, diphenylketone oxime conversion reached a level as high as 100%; further, the selectivity and yield of benzanilide were also high. However, the liquid-acid catalyst posed several disadvantages, such as its strong corrosive nature, toxicity, and lack of recyclability. When solid sulphonic acids were used as the catalysts, benzanilide yield zero when catalysed by amino sulphonic acid and *p*-toluene sulphonic acid; further, these two catalysts dissolved in the reaction solution and hence could not be recycled. Nafion and Amberlyst are sulphonic acids supported on resins and when they were used as catalysts, diphenylketone oxime conversion and the selectivity and yield of benzanilide were much higher; in addition, the activity of Nafion was better than that of Amberlyst. The reaction process was mild and safe; catalyst recovery after the reaction was simple and the catalyst could be used again. Therefore, we selected Nafion perfluorinated sulphonic acid resin as the catalyst for further studies.

$Y = 205034 + 51882X$
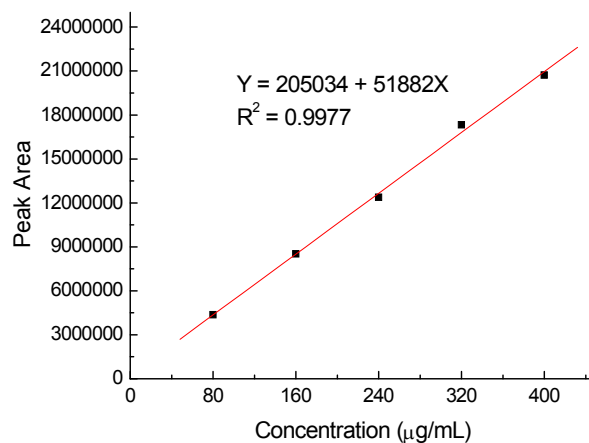$R^2 = 0.9977$

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

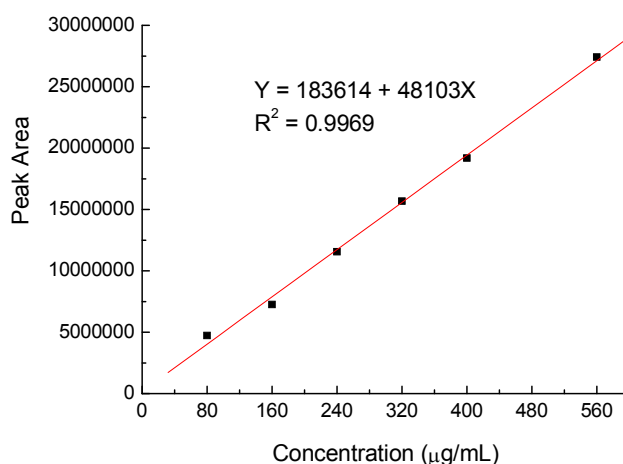$Y = 183614 + 48103X$
$R^2 = 0.9969$

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

Table 1. Effect 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 sulphonic acid [b]	1.53	0	0
P-toluene sulphonic acid [b]	2.54	0	0
Amberlyst®15 sulphonic acid resin [b]	2.96	36.75	1.09
Nafion perfluorinated sulphonic 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°C, reaction time 0.5 h.
[b] solid catalyst system: catalyst 0.2 g, acetonitrile 20 mL, reaction temperature 70°C, reaction time 2 h

3.3 Effect of Different Solvents on Beckmann Rearrangement

In order to study the effects of different solvents on the diphenylketone oxime Beckmann rearrangement, we fixed the amount of diphenylketone oxime, Nafion catalyst dosage, and reaction time at constant values and varied the solvent used. The results are shown in Table 2. The reaction temperatures were maintained at values a little lower than the boiling point of each solvent.

As can be seen from Table 2, the type of solvent had a great influence on the Beckmann rearrangement of diphenylketone oximes. A strongly polar solvent led to a higher degree of conversion. As the reaction temperatures of the reactions involving acetonitrile and cyclohexane were the same, we can compare these two solvents with each other. The degree of conversion of diphenylketone oxime and selectivity of benzanilide were relatively higher when acetonitrile was used as the solvent. This is probably due to the strong polarity of acetonitrile, which made it easier for the produced benzanilide to desorb from Nafion and dissolve in the solvent. Cyclohexane has very weak polarity and hence the degree of conversion of diphenylketone oxime and the selectivity and yield of benzanilide were the lowest (see Table 2). The same observations could be made when dimethyl sulphone (DMSO) and acetone were used as the solvents. Because we set the reaction temperature to be a little lower than the solvent's boiling point, the reaction temperature used when DMSO was used as the solvent (130°C) was too high, while the reaction temperature when acetone was used as the solvent (45°C) was too low. The reaction temperature used when acetonitrile was used as the solvent (70°C) was moderate; therefore, acetonitrile was selected as the solvent for further reactions.

3.4 Effect of Reaction Temperature on the Beckmann Rearrangement

Using acetonitrile as the solvent, we investigated the effects of reaction temperature on the Beckmann rearrangement reaction catalysed by Nafion; the results are shown in Table 3.

It can be seen from Table 3 that the reaction temperature affected the conversion of diphenylketone oxime and the selectivity of benzanilide. At low temperatures, the degree of conversion of diphenylketone oxime was very low (only 6.63% at 30°C) and it increased with an increase in the reaction temperature. The degree of conversion was 21.96% at 82°C. However, benzanilide selectivity decreased with an increase in the reaction temperature; this may be due to the high temperature speeded the reaction of oxime hydrolysis. Benzanilide yield increased initially with an increase in the reaction temperature and later stabilised. The highest yield was obtained at 70°C. Therefore, we optimised 70°C as the reaction temperature; at this temperature, the degree of conversion of diphenylketone oxime and the benzanilide selectivity were high. Further, the benzanilide yield was maximum.

3.5 Effect of Reaction Time on Beckmann Rearrangement

In order to further study the influence of different parameters on Beckmann rearrangement, we investigated the effect of reaction time on the rearrangement reaction. The results are shown in Table 4.

From Table 4, it can be seen that the degree of conversion of diphenylketone oxime was the highest when the reaction time was 4 h; as the reaction time increased, the degree of conversion stabilised. The selectivity of

benzanilide decreased with an increase in the reaction time, possibly because of the polymerisation of benzanilide at higher reaction times. Benzanilide yield was the highest when the reaction time was 4 h, after which it decreased. Therefore, we optimised the reaction time to be 4 h. At this reaction time, the conversion of diphenylketone oxime was complete, high selectivity of amide was maintained, and benzanilide yield was maximum.

3.6 Effect of Catalyst Dosage on Beckmann Rearrangement

In order to investigate the influence of catalyst dosage on the Beckmann rearrangement of diphenylketone oximes, we maintained a constant diphenylketone oxime amount, reaction temperature, and time, while varying the catalyst dosage. The results are shown in Table 5.

It can be seen from Table 5 that with an increase in the catalyst dosage, the degree of conversion

of diphenylketone oxime increased, while the selectivity of benzanilide increased initially and then decreased. The maximum value was reached at a catalyst dose of 0.4 g. Further, benzanilide yield was also maximum when the catalyst dosage was 0.4 g. Therefore, we optimised the catalyst dosage at 0.4 g.

3.7 Effect of Solvent Volume on Beckmann Rearrangement

We maintained a constant diphenylketone oxime amount and Nafion catalyst dosage to study the effect of diphenylketone oxime concentration on Beckmann rearrangement, while changing the solvent volume, the results are shown in Table 6.

From the table, it can be seen that in the tested oxime concentration range, the degree of conversion of diphenylketone oxime initially increased slowly and then decreased rapidly. This may be because at high solution concentrations, it was difficult to remove

Table 2. Effect 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

Table 3. Effect 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

Table 4. Effect 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°C

Table 5. Effect 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

benzanilide from Nafion, which reduced the amide content in the reaction solution. Changes in the oxime concentration also affected the selectivity of benzanilide. With an increase in the volume of the solvent, oxime concentration decreased and benzanilide selectivity increased. When the solvent volume was 20 mL, benzanilide selectivity increased to 44.06%. Upon further increasing the solvent volume, benzanilide selectivity increased slowly. A high benzanilide yield can be obtained at a medium oxime concentration, while at high and low oxime concentrations, amide yield decreased. Therefore, the optimum acetonitrile volume was 20 mL.

3.8 The Adaptability of Different Substrates to Beckmann Rearrangement

In order to study the generality and applicability of Nafion perfluorinated sulphonic acid resin catalysts to Beckmann rearrangement, we studied several other ketone oximes under the optimal reaction conditions. We used acetone, which is an aliphatic ketone, and acetophenone, *p*-chloroacetophenone, and *p*-methoxyaceto-phenone, which are aromatic ketones, to study the effect of different substrates on Beckmann rearrangement. The preparation and rearrangement processes of these ketone oximes were the same as those used for diphenylketone oxime. The feeding ratios used to prepare these ketone oximes and to analyse their Beckmann rearrangement reactions are

shown in Table 7. Amide yield was calculated using the amount of the recrystallised product after rearrangement and the theoretically calculated amount of the rearrangement product.

It can be seen from Table 7 that when Nafion was used as the catalyst, aromatic and aliphatic ketone oximes could undergo Beckmann rearrangement (similar to diphenylketone oxime). Further, aromatic ketone oximes exhibited higher activities than their aliphatic counterparts.

3.9 Reuse Performance of the Nafion Catalyst

Perfluorinated sulphonic acid resins are granular solids, which can be separated by filtration from the reaction solution and reused for the next reaction 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 for the first time, the degree of conversion of diphenylketone oxime and benzanilide yield reduced a little. As the number of reuse instances increased, the degree of conversion and yield decreased. A portion of the sulphonic acid resin mass was lost during the recycling and reuse processes, which may be the reason behind the decrease in the degree of conversion and yield. In general, Nafion can be recycled easily and reused.

Table 6. Effect 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

Table 7. Feeding ratios to prepare different substrate ketone oximes and to conduct their corresponding Beckmann rearrangement reactions

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°C, reaction time 4 h

Table 8. Beckmann rearrangement of diphenylketone oxime on recycled Nafion catalysts

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°C, reaction time 4 h

3.10 Characterisation of Benzanilide

The benzanilide obtained was analysed by melting point determination and IR and NMR spectroscopy. Melting point measurements indicated that the MP of benzanilide was in the range of 161.7–162.3°C, which is in accordance with the value reported in literature value (163°C); this further indicates that the sample is pure.

Fig. 3 depicts the IR spectrogram of benzanilide. The absorption peaks at 1655 cm^{-1} and 1533 cm^{-1} can be assigned to the C=O stretching vibrations and the bending vibrations of N-H in the amide group. Meanwhile, the absorption peak at 3413 cm^{-1} could be attributed to N-H stretching vibrations. The absorption peaks in between 770–730 cm^{-1} and 710–690 cm^{-1} correspond to the out-of-plane bending vibrations of C-H on the substituent benzene ring.
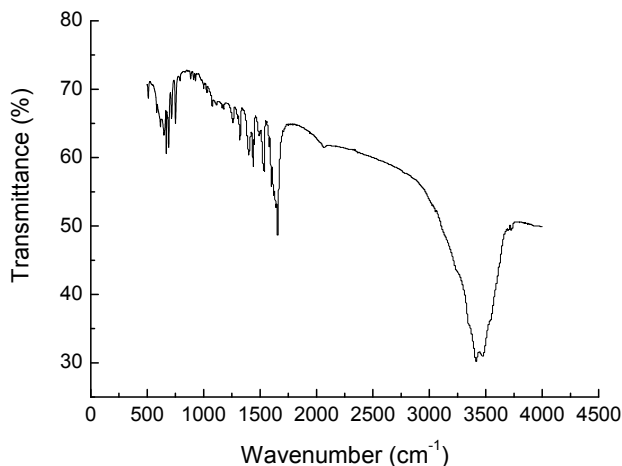
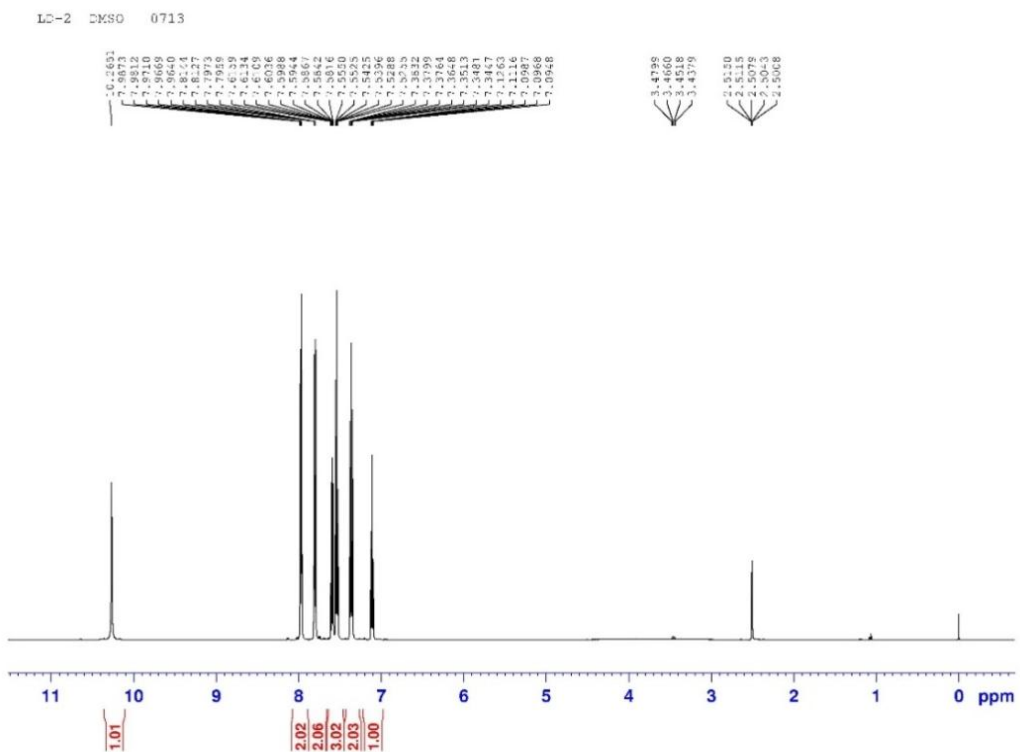**Fig. 3. IR spectrum of benzanilide**
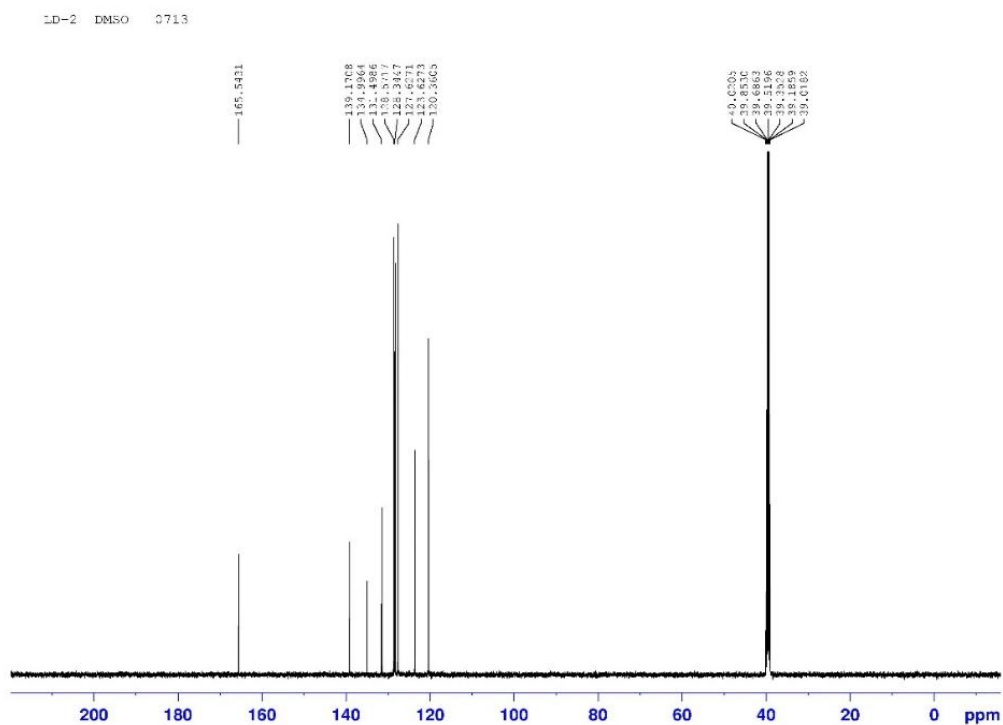
Fig. 4. ^{1}H NMR spectrum of benzanilide

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

The ^{1}H and ^{13}C NMR spectra of benzanilide are shown in Figs. 4 and 5, respectively. The peak assignment in these spectra is as follows.

^{1}H NMR (500 MHz, DMSO): δ10.27 (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), and 7.17-7.04 (m, 1H, Ar-H).

^{13}C NMR (126 MHz, DMSO): δ165.5, 139.2, 135.0, 131.5, 128.5, 127.6, 123.6, 120.4 (the heptet around δ40 corresponds with the solvent).

From the melting point, IR, and NMR results, it can be concluded that the product of the Beckmann rearrangement reaction was indeed benzanilide.

4. CONCLUSIONS

In order to prepare amides in mild and environment-friendly conditions using the Beckmann rearrangement reaction, we used Nafion perfluorinated sulphonic acid resin as the catalyst instead of traditional liquid acids to study the optimal reaction conditions with diphenylketone oxime as the template substrate. The adaptability of other substrates towards Beckmann rearrangement in the optimised conditions and the reuse performance of the catalyst were also investigated. The following conclusions could be drawn from this study.

(1) Compared to other sulphonic acid catalysts, Nafion perfluorinated sulphonic acid resin exerted a relatively positive effect on the Beckmann rearrangement reaction.
(2) When the substrate (diphenylketone oxime) amount was 2 g, the optimal reaction conditions were as follows: reaction temperature of 70 °C, reaction time of 4 h, Nafion catalyst dosage of 0.4 g, and solvent (acetonitrile) volume of 20 mL. Under these conditions, the degree of conversion of diphenylketone oxime was 36.32%, while the selectivity of benzanilide was 44.06% and the yield of benzanilide was 16%.
(3) In the presence of Nafion, aromatic and aliphatic ketone oximes could undergo Beckmann rearrangement in a manner similar to diphenylketone oxime; aromatic ketone oximes exhibited higher reaction activities than aliphatic ketone oximes.

(4) Nafion perfluorinated sulphonic acid resin catalyst can be easily separated from the solution and did not pollute the environment. Reuse studies showed that Nafion exhibited good recycling performance and hence can be considered a green and promising catalyst.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Beckmann rearrangement. Available:http://www.name-reaction.com/beckmann-rearrangement.
2. He CD, Xu ZJ. Study on Beckmann rearrangement of diphenyl methanone oxime over sulphuric acid catalyst. Journal of Anqing Teachers College (Natural Science). 2004;10(4):13-14. Chinese.
3. Zeng ZQ. Organic chemistry experiment. 2nd ed. Beijing: China Higher Education Press. 1987;223-226.
4. Li HY, Luo HA. Beckmann rearrangement of cyclohexanone oxime into caprolactam catalyzed with phosphorus pentoxide. China Synthetic Fiber Industry, 2005; 28(6):18-20. Chinese.
5. Li DM, Shi F, GuoS, Deng YQ. Highly efficient Beckmann rearrangementand dehydration of oximes. Tetrahedron Lett. 2005;46:671-674.
6. Lin CR, Yu LJ, Li S, Karton A. To bridge or not to bridge: The role of sulfuric acid in the Beckmann rearrangement. Chem Phys Lett. 2016;659:100-104.
7. Lidia DL, Giampaolo G, Andrea P. Beckmann rearrangement of oximes under very mild conditions. J Org Chem. 2002; 67:6272-6274.
8. Furuya Y, Ishihara K, Yamamoto H. Cyanuric chloride as a mild and active Beckmann rearrangement catalyst. J Am Chem Soc. 2005;127:11240-11241.
9. Wang B, Gu YL, Luo C, Yang T, Yang LM, Suo JS. Sulfamic acid as a cost-effective

and recyclable catalyst for liquid Beckmann rearrangement, a green process to produce amides from ketoximes without waste. Tetrahedron Lett. 2004;45: 3369-3372.

10. You K, Mao L, Yin D, Liu P, Luo H. Beckmann rearrangement of cyclohexa-none oxime to ε-caprolactam catalyzed by sulfonic acid resin in DMSO. Catal Commun. 2008;9:1521-1526.

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