

Homogeneous liquid-phase Beckmann rearrangement of oxime catalyzed by phosphorous pentoxide and accelerated by fluorine-containing strong acid

Hiroshi Sato^{a,*}, Hiroshi Yoshioka^a, Yusuke Izumi^b

^a Basic Chemicals Research Laboratory, Sumitomo Chemical, Sobiraki, Niihama, Ehime 792, Japan

^b Department of Life Science, Sugiyama Women Courage, Hoshigaoka-Motomachi, Chikusa, Nagoya 464, Japan

Received 11 November 1998; accepted 25 February 1999

Abstract

Phosphorous pentoxide (P_2O_5) effectively catalyzed homogeneous liquid-phase Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam in *N,N*-dimethylformamide (DMF). The turn-over number (TON) of P_2O_5 was 20. The catalytic activity was greatly increased by addition of a co-catalyst, trifluoromethane sulfonic acid, and the TON was increased to 100. The catalyst system was successfully applied to other ketoximes such as acetone oxime, acetophenone oxime, and cyclopentanone oxime. A strongly polarized pseudo-iminium cation was proposed as an active species. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Beckmann rearrangement (homogeneous liquid phase); Catalyst; Phosphorous pentoxide; Trifluoromethanesulfonic acid; Cyclohexanone oxime; ϵ -Caprolactam, DMF (solvent)

1. Introduction

Catalytic Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam has long been expected to be a clean process without by-production of a large amount of ammonium sulfate which inevitably accompanies the conventional liquid-phase Beckmann rearrangement because it requires as a catalyst a stoichiometric amount of fuming acid comprising concentrated sulfuric

acid and sulfur trioxide. For the vapor-phase Beckmann rearrangement of cyclohexanone oxime, too many heterogeneous catalysts have been proposed to refer. Typical examples are silica–alumina [1], supported boron oxide [2–5], faujasite zeolite [6–8], pentasil zeolite [9–15], Ca–A zeolite [16], titanosilicate [17,18], β -zeolite [19], mesoporous MCM-41 [20], and supported tantalum oxide [21]. In particular, Sato et al. [10–14] have reported that pentasil zeolites with no acidity, which are further treated with trimethylsilyl chloride, affords a high catalytic performance (conversion: 100%, lactam selectivity: 95%). However, the vapor-phase rearrangement over solid acid catalysts needs such a high reaction temperature as 250 to 350,

* Corresponding author. T&R Management Office, Sumitomo Chemical, 2-27-1, Shinkawa, Chuo-ku, Tokyo 104, Japan. Tel.: + 81-3-5543-5158; Fax: + 81-3-5543-5909; E-mail: satoh4@sc.sumitomo-chem.co.jp

thereby side-products which are difficult to be purified tend to be formed, and rapid catalyst deactivation is often caused due to carbon deposit.

Therefore, the homogeneous liquid-phase catalytic rearrangement process under milder reaction conditions appears to be preferable to the vapor-phase process over heterogeneous catalysts. Nevertheless, no efficient practical catalyst system has been developed for the homogeneous liquid-phase rearrangement of cyclohexanone oxime. For example, it has been reported that a Vilsmeier complex, $[\text{Me}_2\text{N}=\text{CHCl}]^+\text{SO}_4\text{H}^-$, which is obtained by the reaction of *N,N*-dimethylformamide (DMF) with chlorosulfonic acid, catalyzes the Beckmann rearrangement. However, equimolar amount of the Vilsmeier complex is required [22]. Recently, it has been reported that a Lewis acid system consisting of SbCl_5 – AgBF_6 catalyzes the Beckmann rearrangement of oxime trimethylsilyl ethers [23,24]. However, the system is not effective for the rearrangement of oxime itself. One of the authors, Sato, has reported that a transition metal catalyst system comprising tetrabutylammonium perchlorate and trifluoromethane sulfonic acid catalyzes the Beckmann rearrangement [25]. However, in this case also, the TON of the catalyst is less than 5. Furthermore, one of the authors, Izumi, has reported that an alkoxymethylene–*N,N*-dimethyliminium salt $[\text{Me}_2\text{N}=\text{CH}(\text{OR})]^+\text{X}^-$ effectively catalyzes the Beckmann rearrangement in a homogeneous liquid phase of DMF under mild condition (50 to 60°C) [26]. The alkoxymethylene–*N,N*-dimethyliminium salt is prepared in situ by reacting DMF with epichlorohydrin in the presence of a strong acid, and the TON of the iminium salt catalyst derived using heteropolyacid as a strong acid component has reached 200.

In the preceding patent literature, we have revealed a new and effective Beckmann rearrangement catalyst comprising phosphorous pentoxide (P_2O_5) and trifluoromethane sulfonic acid in a homogeneous liquid phase [27]. In this

paper, we will report a detailed scientific feature of the new catalyst.

2. Experimental

A typical example of the rearrangement reaction is as follows: A 200 ml, round-bottomed flask was purged with nitrogen and therein were placed 45 ml of dried DMF and 0.35 g (2.5 mmol) of P_2O_5 , after which the resulting mixture was heated to 60 to 120°C. At this stage, the mixture turned to be a clear homogeneous solution. Subsequently, a solution of 8.0 g (70.7 mmol) of cyclohexanone oxime in 45 ml of DMF was drop-wise added to the mixture at 60 to 120°C. The reaction was continued for 0.5 to 2 h. After completion of the reaction, a small amount of alkali was added to the reaction mixture to deactivate the catalyst. The reaction mixture was then subjected to analysis by gas chromatography. The product ϵ -caprolactam was identified by IR and ^{13}C -NMR analyses as follows: IR spectra: $\nu(\text{C}=\text{O})$ was observed at 1600 cm^{-1} , and $\nu(\text{NH})$ was observed at 3430 cm^{-1} ; ^{13}C -NMR spectra (in CDCl_3): chemical shifts characteristic for ϵ -caprolactam were observed at $\delta = 23.9, 36.8, 42.3, \text{ and } 178\text{ ppm}$ from TMS.

3. Results and discussion

3.1. Influences of aprotic polar solvents

Considering that DMF is a key solvent for the iminium salt-catalyzed rearrangement [26], we have examined various acidic compounds in DMF solvent for the catalytic rearrangement reaction of cyclohexanone oxime, and have found that P_2O_5 exhibits a catalytic cycle with a TON of more than unity. The influences of aprotic polar solvents on the rearrangement reaction over P_2O_5 catalyst are summarized in Table 1. *N,N*-Dialkyl formamide (DMF, *N,N*-diethylformamide, *N,N*-diisopropylformamide),

Table 1
Influences of aprotic polar solvents on the rearrangement reaction

Run no.	Solvent	Conversion of oxime (%)	Selectivity of lactam (%)	TON ^a (mol/mol)
1	<i>N,N</i> -Dimethylformamide	99.8	94.2	13.3
2	<i>N,N</i> -Diethyl formamide	66.5	81.2	7.6
3	<i>N,N</i> -Diisopropyl formamide	50.8	64.4	4.6
4	<i>N,N</i> -Dimethyl acetamide	62.3	74.3	6.5
5	<i>N</i> -Methyl-2-pyrrolidone	47.4	57.1	3.8
6	Dimethyl sulfoxide	61.4	61.5	5.3
7	Formamide	16.4	69.5	1.6
8	Tetramethyl urea	11.8	78.4	1.3
9	Hexamethylphosphorous triamide	16.3	74.3	1.7
cf.	Chlorobenzene	8.2	78.0	0.9

Reaction conditions: cyclohexanone oxime/ P_2O_5 = 14.4/1 (molar ratio); [oxime/DMF] = 0.8 mmol/ml; reaction: 95°C, 2 h.

^aTON: ϵ -caprolactam (mol)/ P_2O_5 (mol).

N-alkyl cyclic amide (*N*-methyl-2-pyrrolidone), and dimethylsulfoxide exhibit fairly good catalytic performances. In particular, DMF shows an excellent performance as follows: conversion of cyclohexanone oxime: 99.8%; selectivity of ϵ -caprolactam: 94.2%; TON: 13.3. Thus, in the case of the P_2O_5 catalyst also, DMF is the best choice as a solvent as in the case of the iminium-salt catalyst [26]. Therefore, in spite of the obscurity of the rearrangement mechanism over P_2O_5 catalyst, this result seems to indicate some resemblance in the rearrangement mechanism in both cases. Other solvents such as formamide, tetramethylurea, hexamethylphosphoroustriamide, and monochlorobenzene give poor results (TON \leq 1.7).

3.2. Influences of the reaction temperature on the catalytic performances of P_2O_5 catalyst

With an increase of the reaction temperature from 60 to 120°C, the catalytic activity gradually increases up to a maximum TON: 19.8 at 100°C, while the lactam selectivity slightly decreases from 91.0% (60°C) to 89.5% (120°C) (Fig. 1). Therefore, the best catalytic performance is obtained around 80 to 100°C. The most appropriate temperature is a little bit higher compared with that (50 to 60°C) of the iminium-salt catalyzed rearrangement reaction [26].

3.3. Improvement of the catalytic activity of P_2O_5

Among various acidic compounds examined for the improvement of the catalytic activity of P_2O_5 (Table 2), zinc dichloride, trifluoroacetic anhydride [(CF₃CO₂)₂O], and trifluoromethane sulfonic anhydride [(CF₃SO₃)₂O] increased the TON of P_2O_5 from 19.3 to 21.6, 22.5, and 24.6, respectively. TONs of lanthanum trioxide (16.8) and methane sulfonic acid (18.2) are slightly smaller than that of P_2O_5 . Sulfur trioxide (TON:

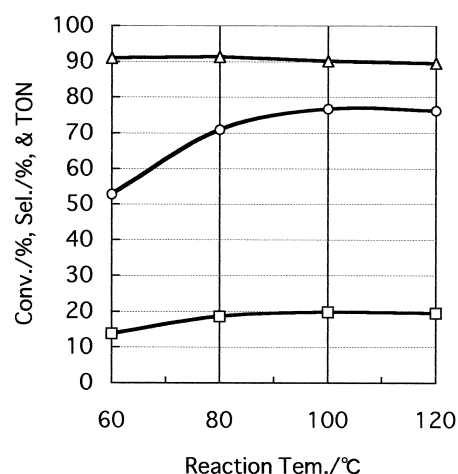


Fig. 1. Influences of the reaction temperature on the rearrangement reaction (1): P_2O_5 catalyst in DMF. (○) Conversion of oxime, (△) selectivity of lactam, (□) TON of P_2O_5 .

Table 2
Search for promoters co-operative with P₂O₅ (1): general screening

Run no.	Additives	Conversion of oxime (%)	Selectivity of lactam (%)	TON ^a (mol/mol)
1	none	77.0	87.3	19.3
2	ZnCl ₂	85.8	87.9	21.6
3	La ₂ O ₃	64.3	90.0	16.8
4	(CF ₃ CO) ₂ O	87.5	89.9	22.5
5	CH ₃ SO ₃ H	70.5	89.8	18.2
6	(CF ₃ SO ₂) ₂ O	94.4	90.8	24.6
7	SO ₃	12.8	17.2	2.2
8	LiClO ₄	23.2	100	8.4
9	Me ₂ SO ₄	42.3	84.6	10.3

Reaction conditions: cyclohexanone oxime/P₂O₅ = 70.7/2.5 (mmol); additive/P₂O₅ = 0.5 (molar ratio); [oxime/DMF] = 0.8 mmol/ml; reaction: 120°C, 0.5 h.

^aTON: ε-caprolactam (mol)/P₂O₅ (mol).

2.2), lithium perchlorate (TON: 8.4), and dimethylsulfate (TON: 10.3) suppressed the activity of P₂O₅. These results indicate that fluorine-containing strong acidic compounds tend to accelerate the catalytic activity of P₂O₅.

Therefore, in order to make clear the effect of these promoters, further detailed investigations were carried out on organic acidic compounds (Table 3) and inorganic acidic compounds (Ta-

ble 4). The ratio between substrate and catalyst (S/C ratio) was increased from 28.3 (Table 2) to 56.6 (Tables 3 and 4). Therefore, the attainable maximum TON would be 56.6 in the latter cases. Among organic acidic compounds examined (Table 3; additive/P₂O₅ molar ratio: 0.5), CF₃SO₃H and its derivatives exhibited large to moderate acceleration effects as follows: CF₃SO₃H (TON: 30.1), (CF₃SO₃)₂O (TON: 41.0),

Table 3
Search for promoters co-operative with P₂O₅ (2): organic acidic compounds

Run no.	Additives	Conversion of oxime (%)	Selectivity of lactam (%)	TON ^a (mol/mol)
1	none	38.6	90.7	19.5
2	CF ₃ SO ₃ H	58.2	92.8	30.1
3	(CF ₃ SO ₂) ₂ O	82.4	87.5	41.0
4	CF ₃ SO ₃ SiMe ₃	47.8	92.8	24.7
5	CF ₃ SO ₃ Et	42.6	92.4	22.0
6	(CF ₃ SO ₃) ₂ Sn	44.8	92.6	23.1
7	(CF ₃ CO) ₂ O	52.9	90.8	26.8
8	C ₆ H ₅ -SO ₃ H	37.5	87.5	18.3
9	CF ₃ CO ₂ H	39.3	89.1	19.5
10	<i>p</i> -CH ₃ C ₆ H ₄ -SO ₃ Me	40.6	87.2	19.7
11	<i>m</i> -NO ₂ -C ₆ H ₄ -SO ₃ H	38.0	92.0	19.5
12	CCl ₃ CO ₂ H	18.9	67.1	7.1
13	(CH ₃ CO) ₂ O	36.6	89.4	18.2
14	(CF ₃) ₂ CHOH	24.8	78.3	10.8
15	C ₆ F ₅ OH	31.4	84.4	14.8
cf.	CF ₃ SO ₃ H ^b	5.0	40.2	1.1 ^c

Reaction conditions: cyclohexanone oxime/P₂O₅ = 70.7/1.25 (mmol); additive/P₂O₅ = 0.5 (molar ratio); [oxime/DMF] = 0.8 mmol/ml; reaction: 120°C, 0.5 h.

^aTON: ε-caprolactam (mol)/P₂O₅ (mol).

^bCatalyst: CF₃SO₃H only (without P₂O₅).

^cTON: ε-caprolactam (mol)/CF₃SO₃H (mol).

Table 4
Search for promoters co-operative with P_2O_5 (3): inorganic acidic compounds

Run no.	Additives	Conversion of oxime (%)	Selectivity of lactam (%)	TON ^a (mol/mol)
1	none	38.6	90.7	19.5
2	$BF_3 \cdot OEt_2$	61.4	90.2	30.9
3	$BF_3 \cdot MeOH$	30.2	100	17.4
4	$LiBF_4$	25.7	93.0	13.3
5	$SO_3 \cdot H_2SO_4$	7.8	13.4	0.6
6	97% H_2SO_4	7.0	13.4	0.6
7	$SO_3 \cdot Py$	10.9	31.2	1.9
8	$SO_3 \cdot NMe_3$	15.0	70.8	5.9
9	FSO_3H	7.0	13.4	0.6

Reaction conditions: cyclohexanone oxime/ P_2O_5 = 70.7/1.25 (mmol); additive/ P_2O_5 = 0.5 (molar ratio); [oxime/DMF] = 0.8 mmol/ml; reaction: 120°C, 0.5 h.

^aTON: ϵ -caprolactam (mol)/ P_2O_5 (mol).

trifluoromethane sulfonic acid trimethylsilyl-ester (TON: 24.7), tin bis (trifluoromethane sulfonate) (TON: 23.1), trifluoromethane ethyl-ester (TON: 22.0). Trifluoroacetic anhydride also exhibited a moderate accelerating effect (TON: 26.8), but trifluoroacetic acid itself showed no effect. Considering that the accelerating effect of CF_3SO_3H itself is smaller than that of its anhydride, the smaller effect of trifluoroacetic acid itself than that of its anhydride can be reasonably understood. That is, these acid anhy-

drides seem to work as two molar equivalent to the acids themselves. Benzene sulfonic acid, *p*-toluene sulfonic acid methyl-ester, *m*-nitrobenzene sulfonic acid, and acetic anhydride did offer almost no effect. On the contrary, the following compounds inhibited the catalytic activity of phosphorous pentaoxide: trichloroacetic acid (TON: 7.1), 1,1,1,3,3,3-hexafluoro-2-propanol (TON: 10.8), and perfluorophenol (TON: 14.8). These results indicate that the strong

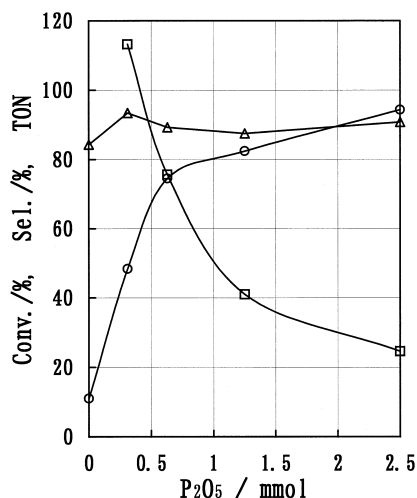


Fig. 2. Influences of the amount of P_2O_5 on the rearrangement reaction: P_2O_5 – $(CF_3SO_3)_2O$ catalyst system in DMF at 120°C. (○) Conversion of oxime, (△) selectivity of lactam, (□) TON of P_2O_5 . DMF: 45 ml; cyclohexanone oxime: 70.7 mmol; $(CF_3SO_3)_2O$: 1.25 mmol.

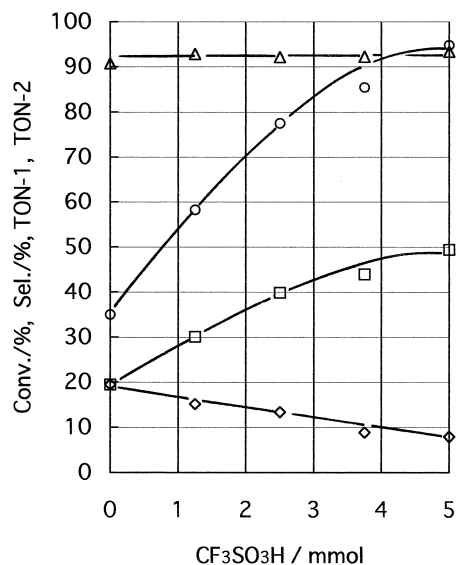


Fig. 3. Influences of the amount of CF_3SO_3H on the rearrangement reaction: P_2O_5 – CF_3SO_3H catalyst system in DMF at 120°C. (○) Conversion of oxime, (△) selectivity of lactam, (□) TON of P_2O_5 , (◇) TON of $(P_2O_5 + CF_3SO_3H)$. DMF: 45 ml; cyclohexanone oxime: 70.7 mmol; P_2O_5 : 1.25 mmol.

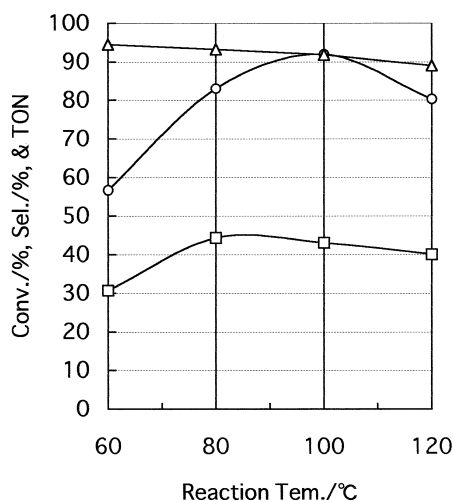


Fig. 4. Influences of the temperature on the rearrangement reaction: (○) yield of lactam, (△) selectivity of lactam, (□) TON of P_2O_5 . DMF: 90 ml; cyclohexanone oxime: 141.4 mmol; P_2O_5 : 2.5 mmol; $(CF_3SO_2)_2O$: 2.5 mmol.

acidic character of additives containing CF_3SO_3 - or CF_3CO_2 -group is necessary to accelerate the catalytic activity of P_2O_5 . It is noteworthy that, in the absence of P_2O_5 , CF_3SO_3H itself does not show any catalytic activity for the rearrangement reaction even in DMF (a control experiment in Table 3: the TON = 1.1 means a stoichiometric reaction rather than a catalytic reaction). Therefore, it is clear that P_2O_5 is an essential catalyst and CF_3SO_3H or its anhydride is a promoter co-operating with it.

Among various inorganic acidic compounds examined, only $BF_3 \cdot OEt_2$ exhibited a high accelerating effect (TON: 30.9) for P_2O_5 as shown in Table 4. Other strong acids such as fuming acid comprising sulfur trioxide and sulfuric acid, concentrated sulfuric acid, sulfur trioxide pyridine complex, and fluorosulfuric acid retarded the activity of P_2O_5 .

3.4. Detailed study on the catalyst comprising P_2O_5 and CF_3SO_3H

Taking CF_3SO_3H as a representative accelerator, the detailed feature of the catalyst compris-

ing P_2O_5 and CF_3SO_3H was examined in the following part. First of all, influences of the amount of P_2O_5 are shown in Fig. 2. With the increase of the amount of P_2O_5 , the yield of lactam increases rapidly at the initial stage, then the increase slows down after the amount of P_2O_5 exceeds 1 mmol. In accordance with these changes, the TON of P_2O_5 rapidly decreases from the initial high value of 113.2 at P_2O_5 : 0.31 mmol to TON: 41.0 at P_2O_5 : 1.25 mmol, then the TON gradually decreases till 24.6 at P_2O_5 : 2.50 mmol. The reason is not clear now why the yield of lactam gets saturated at the high catalyst concentration region. The selectivity of lactam remains constant around 90%. The influences of the amount of CF_3SO_3H are shown in Fig. 3. In this case, both the lactam yield and the TON of P_2O_5 increase almost proportionally with the increase of the amount of CF_3SO_3H .

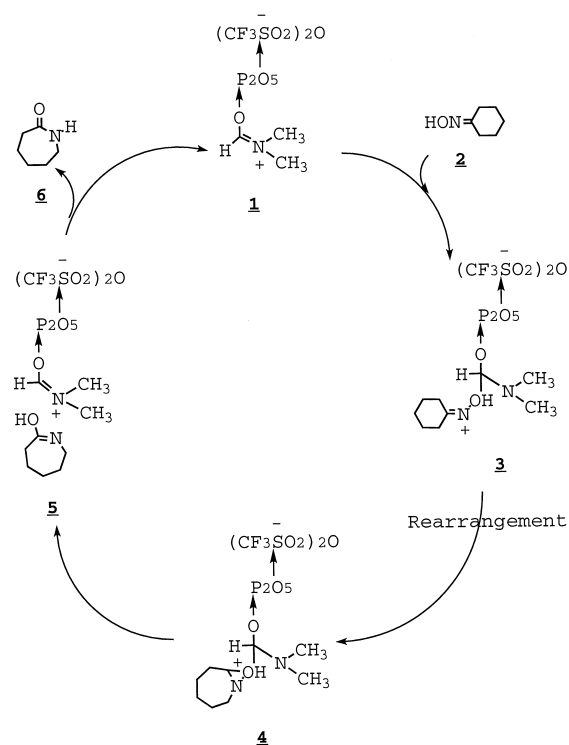


Fig. 5. Proposed reaction mechanism for the rearrangement of cyclohexanone oxime to ϵ -caprolactam catalyzed by P_2O_5 - $(CF_3SO_2)_2O$.

On the other hand, however, the TON of the combined amount of P_2O_5 and CF_3SO_3H decreases gradually with the increase of CF_3SO_3H . Therefore, the accelerating effect of CF_3SO_3H is not necessarily high enough. The influences of the reaction temperature are illustrated in Fig. 4. Both the lactam yields and the TONs of P_2O_5 are higher compared with those in Fig. 1 (P_2O_5 catalyst without a promoter). However, the tendency of the temperature effect is similar to that in Fig. 1. That is, the most favorable reaction temperature is around 80 to 100°C. A good result was obtained at 80°C: the lactam yield was 77.4%, and the TON of P_2O_5 was 44.4.

3.5. Estimation of the rearrangement mechanism catalyzed by P_2O_5

Considering the above results, we propose the following rearrangement mechanism (a pseudo-iminium cation mechanism similar to that proposed by one of authors in the preceding paper [26]) (Fig. 5): P_2O_5 coordinates to DMF and withdraws electron from it to form a partially polarized pseudo-iminium cation **1** as a rearrangement catalyst. This polarization is further strengthened by coordination of strong acidic additives such as CF_3SO_3H , $(CF_3SO_3)_2O$ or BF_3OEt_2 to P_2O_5 . Cyclohexanone oxime **2** then reacts with the catalyst **1** to form an intermediate **3** where a polarized pseudo-cyclohexyliminium cation coordinates to the catalyst. This pseudo-cation then undergoes Beckmann rearrangement to form an intermediate **4** where a polarized pseudo-cycloheptyliminium cation

Table 5
Application to the Beckmann rearrangement of other ketoxime (1): P_2O_5 catalyst

Run no.	Starting oxime	Amide product	Yield (%)
1	Acetone oxime	<i>N</i> -Methyl acetamide	5.6
2	<i>syn</i> -Acetophenone oxime	Acetanilide	12.6
3	Cyclopentanone oxime	2-Piperidone	10.9

Reaction conditions: ketoxime/ P_2O_5 = 35.5/1.25 (mmol); [oxime/DMF] = 0.8 mmol/ml; reaction: 120°C, 0.5 h.

Table 6
Application to the Beckmann rearrangement of other ketoxime (2): (P_2O_5 + CF_3SO_3H) catalyst

Run no.	Starting oxime	Amide product	Yield (%)
1	Acetone oxime	<i>N</i> -Methyl acetamide	100
2	<i>syn</i> -Acetophenone oxime	Acetanilide	22.4
3	Cyclopentanone oxime	2-Piperidone	59.5

Reaction conditions: ketoxime/ P_2O_5 / CF_3SO_3H = 35.5/1.25/1.25 (mmol); [oxime/DMF] = 0.8 mmol/ml; reaction: 120°C, 0.5 h.

coordinates to the catalyst. The intermediate **4** then affords an intermediate **5** where cycloheptyliminium alcohol coordinates to the catalyst. The intermediate **5** then liberates ϵ -caprolactam **6** and the initial catalyst **1**. Thus, a catalytic cycle is completed. Therefore, DMF works both as a catalyst precursor and as a polar solvent to dissolve the polarized catalyst.

3.6. Application to other ketone oximes

The Beckmann rearrangement catalyzed by P_2O_5 was applied to other ketoximes; acetone oxime, *syn*-acetophenone oxime, and cyclopentanone oxime. The results with these ketone oximes are very poor (yields of amide products: 5.6%, 12.6%, and 10.9%, respectively) in comparison with that (yield of ϵ -caprolactam: 67.5%) of cyclohexanone oxime as shown in Table 5. However, by addition of CF_3SO_3H , the results are greatly improved as shown in Table 6: yield of *N*-methyl acetamide: 100%, yield of 2-piperidone: 59.5%. Therefore, the accelerating effect of CF_3SO_3H is clearly shown in these cases. However, in the case of *syn*-acetophenone oxime, the yield of acetanilide is as low as 22.4%. The migration of phenyl group might be retarded in the catalyst system by the steric hindrance in the catalyst **1**.

4. Conclusions

P_2O_5 effectively catalyzed the homogeneous liquid-phase Beckmann rearrangement of cyclo-

hexanone oxime to ϵ -caprolactam in DMF. The turn-over number (TON) of P_2O_5 was 20. The catalytic activity was greatly increased by addition of fluorine-containing strong acids such as CF_3SO_3H , its derivatives, $(CF_3CO_2)_2O$, and BF_3-OEt_2 . In the case of the catalyst comprising P_2O_5 and CF_3SO_3H , the TON of P_2O_5 was increased to 100. These catalysts were successfully applied to other ketoximes such as acetone oxime and cyclopentanone oxime. The catalytic intermediate proposed for the rearrangement reaction is a strongly polarized pseudo-iminium cation **1** coordinated by P_2O_5 and fluorine-containing strong electronegative group such as trifluoro-methane sulfonyl ($CF_3SO_3^-$).

References

- [1] British Petroleum, Br. Patent No. 881927, 1961.
- [2] BASF, Ger. Patent No. 1227028, 1957.
- [3] Bayer, Jpn. Patent Kokai No. 37686, 1978.
- [4] S. Sato, K. Urabe, Y. Izumi, *J. Catal.* 102 (1986) 99.
- [5] S. Sato, S. Hasebe, H. Sakurai, K. Urabe, Y. Izumi, *Appl. Catal.* 29 (1987) 77.
- [6] P.S. Landis, P.B. Venuto, *J. Catal.* 6 (1966) 245.
- [7] T. Yashima, S. Horie, S. Saito, N. Hara, *Nippon Kagaku Kaishi* (1977) 77.
- [8] Y. Murakami, Y. Saeki, K. Ito, *Nippon Kagaku Kaishi* (1978) 21.
- [9] Mobil Oil, US Patent No. 4359421, 1982.
- [10] H. Sato, N. Ishii, K. Hirose, S. Nakamura, *Proc. 7th Int. Zeolite Conf.*, 1986, p. 755.
- [11] H. Sato, K. Hirose, M. Kitamura, Y. Nakamura, *Proc. 8th Int. Zeolite Conf.*, 1989, p. 1213.
- [12] H. Sato, K. Hirose, M. Kitamura, *Nippon Kagaku Kaishi* (1989) 548.
- [13] H. Sato, K. Hirose, Y. Nakamura, *Chem. Lett.* (1993) 1987.
- [14] H. Sato, *Catal. Rev. Sci. Eng.* 39 (4) (1997) 395.
- [15] W.F. Hoelderich, G. Heitmann, *Catal. Today* 38 (1997) 227.
- [16] T. Yashima, K. Miura, T. Komatsu, in: J. Weitkamp, H.G. Karge, H. Pfeifer, W. Hoelderich (Eds.), *Zeolite and Related Microporous Materials: State of the Art 1994*, *Studies in Surface Science and Catalysis*, Vol. 84, Elsevier, Amsterdam, 1997.
- [17] A. Thagarah, S. Sivasanker, P. Ratnasamy, *J. Catal.* 137 (1992) 252.
- [18] J. Sudhakar Reddy, R. Ravishankar, S. Sivasanker, P. Ratnasamy, *Catal. Lett.* 17 (1994) 139.
- [19] L.X. Dai, R. Hayasaka, Y. Iwaki, K. Koyano, T. Tatsumi, *Chem. Commun.* 9 (1996) 1071.
- [20] L.X. Dai, K. Koyama, T. Tatsumi, *Catal. Lett.* 53 (3–4) (1998) 211.
- [21] T. Ushikubo, K. Wada, *J. Catal.* 148 (1994) 138.
- [22] M.A. Kira, Y.M. Shaker, *Egypt. J. Chem.* 16 (1973) 551.
- [23] T. Mukaiyama, Th. Harada, *Chem. Lett.* (1991) 1653.
- [24] T. Harada, T. Ohno, S. Kobayashi, T. Mukaiyama, *Synthesis* (1991) 1216.
- [25] K. Narasaka, H. Kusama, Y. Yamashita, H. Sato, *Chem. Lett.* (1993) 489.
- [26] Y. Izumi, T. Jujita, *J. Mol. Catal. A: Chem.* 106 (1996) 43.
- [27] Y. Izumi, H. Sato, H. Yoshioka, Y. Nomura, *US Patent No.* 5,254,684, 1993 (to Sumitomo Chemical and Y. Izumi).