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Beckmann Rearrangement Catalyzed by the Combined Use of Tetrabutylammonium Perrhenate(VII) and Trifluoromethanesulfonic Acid

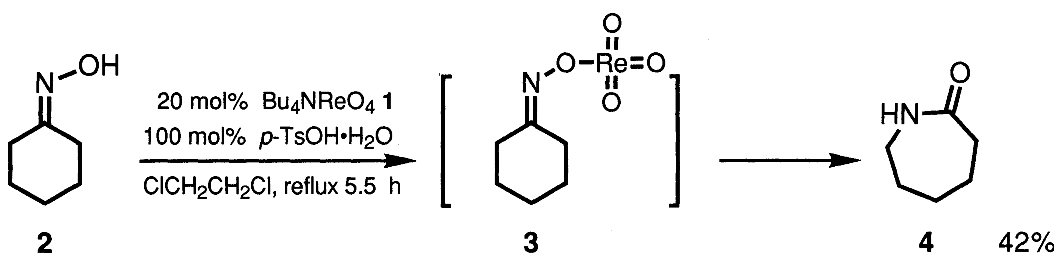
Koichi NARASAKA, Hiroyuki KUSAMA, Yuko YAMASHITA, and Hiroshi SATO†
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
†Ehime Research Laboratory, Sumitomo Chemical Co., Ltd., 5-1, Sobiraki-cho, Niihama, Ehime 792

Beckmann rearrangement of oximes is catalyzed with tetrabutylammonium perrhenate(VII), trifluoromethanesulfonic acid and hydroxylamine hydrochloride in nitromethane under azeotropic conditions, giving amides in high yield.

Beckmann rearrangement is often used to transform oximes to amides or lactams in organic synthesis, and is also applied to the production of ε-caprolactam in the industrial process.1) This reaction generally requires the use of excess amount of strong Brønsted acids, which causes serious problems such as decomposition of the product and formation of a large quantity of salts by neutralization. Therefore, it is strongly desired to exploit an efficient catalytic method of this rearrangement. Although there have been reported various kinds of heterogeneous catalysts for the vapor-phase process,2) only two catalytic methods (*O*-alkyl-*N*,*N*-dimethylformamidinium salt3) and antimony (V) salt4)) have been developed in the liquid-phase process.

We have recently reported 1,3-rearrangement of allylic and propargylic alcohols which proceeded *via* the corresponding perrhenic acid esters by the treatment of the alcohols with tetrabutylammonium perrhenate (Bu_4NReO_4, **1**)5) and *p*-toluenesulfonic acid (*p*-$TsOH \cdot H_2O$).6) This result suggested us that the Beckmann rearrangement of oximes would proceed catalytically by employimg Bu_4NReO_4 and Brønsted acid *via* the formation of the oxime perrhenate such as **3**.

At first, the Beckmann rearrangement of cyclohexanone oxime (**2**) was tried and the treatment of **2** with 20 mol% of **1** and 100 mol% of *p*-$TsOH \cdot H_2O$ in refluxing 1,2-dichloroethane gave ε-caprolactam **4** in 42% yield. In the absence of **1**, the reaction did not proceed at all. When the acetate of the oxime **2** was employed instead of the oxime, Beckmann rearrangement hardly occurred with the catalysts under the same reaction conditions. These results indicated strongly that the reaction proceeds *via* the oxime perrhenate **3** as expected.



The screening of the reaction conditions (Table 1) revealed that ε-caprolactam **4** was obtained in good yield by using only a catalytic amount of trifluoromethanesulfonic acid[7] instead of p-TsOH•H_2O (Table 1, Entry 2). The use of the solvents having small donor number such as nitromethane and dichloroethane considerably improved the yield of the lactam **4** as compared with the use of acetonitrile or *N*,*N*-dimethylformamide (DMF).[8] In particular, the reaction proceeded very smoothly in nitromethane (Table 2). Presumably, nitromethane may capture the rearranged intermediate, the iminium cation, effectively by forming the nitronate (Fig. 1), which is easily hydrolyzed to afford ε-caprolactam.

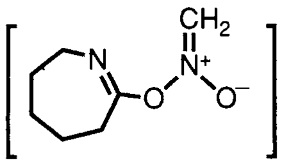


Fig. 1.

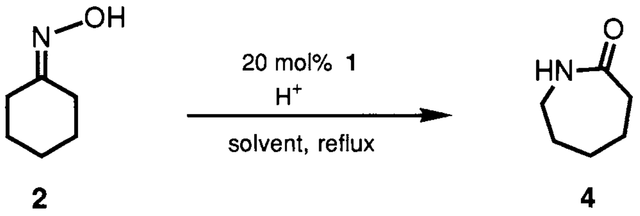


Table 1. Effect of Brønsted Acid[a)]

Entry	Brønsted acid (mol%)	Time / h	Yield of 4 / %
1	*p*-TsOH•H_2O (100)	5.5	42
2	CF_3SO_3H (20)	8	68
3	CF_3SO_3H (40)	5	71
4	H_2SO_4 (100)	5.5	13

a) All the reactions were carried out in refluxing 1,2-dichloroethane.

Table 2. Effect of Solvent[a)]

Entry	Solvent	Time / h	Yield of 4 / %
1	CH_3NO_2	1	85
2	CH_3CN	7	44
3	$ClCH_2CH_2Cl$	8	68
4	DMF (100 °C)	5	10

a) 20 mol% of CF_3SO_3H was used.

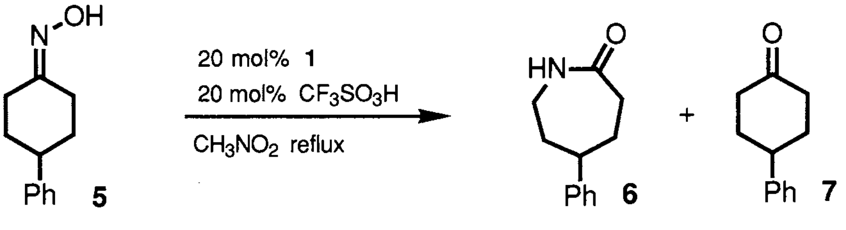


Table 3. Effect of Hydroxylamine Hydrochloride

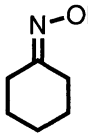
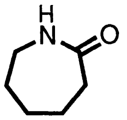
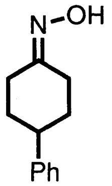
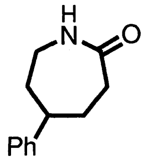
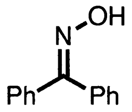
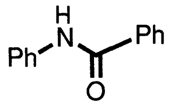
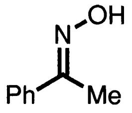
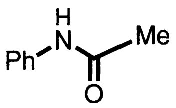
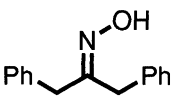
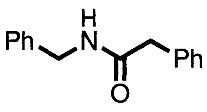
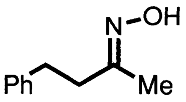
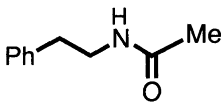
Entry	$H_2NOH•HCl$	Condition	Time / h	Yield of 6 / %	Yield of 7 / %
1	none	reflux	1	79	16
2	50 mol%	reflux	2.5	91	0
3	50 mol%	azeotropic	1	91	0

By the reaction in nitromethane, the oxime **2** was entirely consumed, but the yield of **4** was less than 90%. Since the hydrolysis of the oxime **2** to cyclohexanone was supposed to proceed as a side reaction, the reaction of 4-phenylcyclohexanone oxime (**5**) was tried under the same reaction conditions to detect the hydrolyzed product. In fact, 4-phenylcyclohexanone (**7**) was isolated in 16% yield along with the corresponding lactam **6** in 79% yield by the reaction in nitromethane (Table 3, Entry 1).

The hydrolysis could not be suppressed by adding dehydrating agents such as anhydrous sodium sulfate or acetic anhydride. The reaction of **5** was then carried out in the presence of 50 mol% of $H_2NOH{\bullet}HCl$, expecting the *in situ* conversion of the generated ketone **7** to the oxime **5**. The lactam **6** was obtained in 91% yield and the ketone **7** was not detected (Table 3, Entry 2). Furthermore, the reaction was accelerated by azeotropic removal of water (Table 3, Entry 3).

The catalytic Beckmann rearrangement of several oximes was examined under the above reaction conditions, and the results were summarized in Table 4. In each case, the reaction proceeded smoothly with the azeotropic removal of water to give the corresponding amide in high yield.[9)]

Table 4. The Beckmann Rearrangement of Oximes [a)]

Entry	Substrate	$H_2NOH{\bullet}HCl$ (mol%)	Time	Product	Yield/%
1		50	1.5 h		84
2		50	1 h		91
3		50	20 min		98
4		20	1 h		94
5		20	40 min		88
6		20	2 h		88

a) All the reactions were carried out by the use of 20 mol% of **1** and CF_3SO_3H in nitromethane under azeotropic conditions.

The representative experimental procedure (Table 4, Entry 5) is as follows: To a solution of dibenzyl ketone oxime (225 mg, 1.00 mmol), Bu_4NReO_4 (99.5 mg, 0.20 mmol), and trifluoromethanesulfonic acid (32.8 mg, 0.21 mmol) in CH_3NO_2 (6 ml) at room temperature was added $H_2NOH•HCl$ (15.2 mg, 0.21 mmol). The mixture was refluxed for 40 min under the azeotropic condition using Molecular Sieves 4A as a dehydrating reagent and then was quenched with saturated aqueous sodium hydrogen carbonate. The mixture was extracted three times with dichloromethane and the combined extracts were washed with brine and dried over anhydrous sodium sulfate. After the solvent was removed *in vacuo*, the crude materials were purified by thin-layer chromatography (silica gel, benzene : methanol = 95 : 5) to give *N*-benzylphenylacetamide (198 mg, 88% yield).

References

1) R. E. Gawly, *Org. React.*, **35**, 1 (1988), and references cited therein.
2) Y. Izumi, S. Sato, and K. Urabe, *Chem. Lett.*, **1983**, 1649, and references cited therein.
3) Y. Izumi, *Chem. Lett.*, **1990**, 2171.
4) T. Mukaiyama and T. Harada, *Chem. Lett.*, **1991**, 1653; T. Harada, T. Ohno, S. Kobayashi, and T. Mukaiyama, *Synthesis*, **1991**, 1216.
5) Tetrabutylammonium perrhenate (**1**) was purchased from Aldrich Chemical Co., Inc. and was purified by recrystallization from methanol - ether.
6) K. Narasaka, H. Kusama, and Y. Hayashi, *Chem. Lett.*, **1991**, 1413; *Tetrahedron*, **48**, 2059 (1992).
7) In the absence of **1**, the reaction hardly proceeded even by the use of trifluoromethanesulfonic acid.
8) Donor number: $ClCH_2CH_2Cl$ 0, CH_3NO_2 2.7, CH_3CN 14.1, DMF 26.6. Concerning donor ability of solvents, see; V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions," Plenum, New York (1978).
9) All spectral data were in good agreement with those of the literatures.

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