

Catalytic Beckmann Rearrangement of Cyclododecanone Oxime

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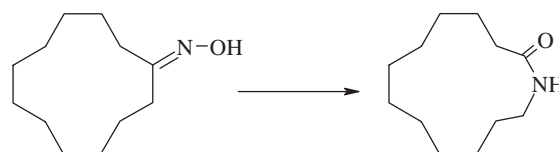
The catalytic Beckmann rearrangement of cyclododecanone oxime (CDOX) was investigated in silane–nitrile–solvent systems. We have found that chlorosilanes, such as trimethylchlorosilane and tetrachlorosilane, are effective catalysts to produce ω -lauro lactam (LRL) at 100 °C. Tetrachlorosilane is the most active catalyst, and hydrocarbon solvents such as cyclohexane, hexane, and decane are suitable for the system. Nitriles such as acetonitrile and benzonitrile would play an important role as a remover of silane species from the produced LRL–silane salt.

The Beckmann rearrangement of ketoximes such as CDOX is an important reaction to produce LRL for the production of Nylon-12 (Scheme 1). LRL is industrially produced using fuming sulfuric acid catalyst in the Beckmann rearrangement of CDOX, and the produced LRL–sulfate adduct is neutralized with ammonia to produce ammonium sulfate. Efficient catalyst systems are required for the reduction of waste ammonium sulfate and for the simplification of the process.

In the liquid-phase Beckmann rearrangement of CDOX, solid catalysts such as zeolites and heteropolyacid cesium salt have been reported.^{1–4} One of the answers to the question of how to reduce the use of sulfuric acid is to apply the vapor-phase process: β -zeolite is proposed as a catalyst in a vapor-phase reaction at 320 °C.⁵

In the liquid-phase Beckmann rearrangement of CDOX, homogeneous catalysts, which effectively work in specific solvents such as acetonitrile^{6–8} and nitromethane,⁶ are reported. In the Beckmann rearrangement of cyclohexanone oxime, solid catalysts have been proposed by several research groups.^{9–13} In the successful reports of the Beckmann rearrangement, various liquid-phase processes have employed nitrile solvents such as acetonitrile^{4,6–10,14} and benzonitrile^{3,11–14} since 2002. There is a report of the effect of solvent in the homogeneous Beckmann rearrangement of cyclohexanone oxime:¹⁴ linear correlation between dielectric constant of the solvent and the initial reaction rate. However, the role of nitriles in the liquid-phase Beckmann rearrangement has not been clarified. In this paper, we examined the Beckmann rearrangement of CDOX using silane–nitrile catalyst systems with various solvents to elucidate the effect of nitriles in the liquid phase, and found that LRL was selectively formed from CDOX in silane–nitrile–hexane systems.

Commercially available reagents were purchased from Wako Pure Chemical Industries Ltd., Tokyo Chemical Industries Co., Ltd., or Kokusan Chemical Co., Ltd., while CDOX was supplied by Ube Industries Ltd. The Beckmann rearrangement of CDOX was performed in a pressure vessel with a volume of 50 cm³. The reactor vessel with catalyst (0.19 mmol), CDOX (1.0 g, 5.1 mmol), and solvent (10 g) was placed in an oven at 100 °C. After the prescribed period, the vessel was cooled at 0 °C. The reaction mixture recovered was analyzed on a gas



Scheme 1.

Table 1. Effect of solvents in the Beckmann rearrangement of CDOX at 100 °C for 2 h^a

Entry	Solvent	Conversion /mol %	Selectivity/mol %		TON
			LRL	CD	
Catalyst: Me ₃ SiCl					
1	MeCN	100	90.0	8.5	23.6
2	EtCN	99.1	94.9	0.1	24.7
3	PhCN	96.1	95.8	1.8	24.7
4	MeNO ₂	12.9	0	65.0	0
5	Me ₂ NCHO	29.1	0	43.6	0
Catalyst: SiCl ₄					
6	MeCN	100	97.7	0.6	26.2
7	Et ₂ NCHO	24.4	38.4	20.0	2.5
8	CHCl ₃	9.6	49.6	18.8	1.3
9	<i>n</i> -Hexane	31.0	0	7.4	0
10	MeCN ^b	75.4	95.8	3.9	336

^aSolvent: 10 g, catalyst/CDOX: 0.19/5.1 (mmol/mmol). ^bReacted at 130 °C for 6 h, catalyst/CDOX: 0.011/5.1 (mmol/mmol).

chromatograph (FID-GC, Shimadzu GC-8A), using a 60-m capillary column (TC-WAX, GL Science, Japan).

Table 1 shows the effect of solvents on the Beckmann rearrangement of CDOX catalyzed by chlorotrimethylsilane, Me₃SiCl, and tetrachlorosilane, SiCl₄, at 100 °C. The silanes effectively worked as a catalyst to produce selectively LRL with high turnover number, TON, in nitrile solvents (Entries 1–3 and 6). The results are in good harmony with the previous reports: nitriles are the specific solvents for the Beckmann rearrangement.^{3,4,6–14} The large TON promises that this catalytic system could drastically reduce catalyst waste (Entry 10).

Table 2 lists the conversion of CDOX in benzonitrile solvent using various catalyst candidates. Acidic halides and silane compounds were effective catalysts for the rearrangement. In particular, SiCl₄ is the most active and selective catalyst among the candidates we tested: it completed the Beckmann rearrangement of CDOX at 100 °C in 2 h (Entry 14). Although HCl showed TON larger than 1, HCl was less active than chlorosilanes (Entry 15). Other compounds without halogen, such as acetic anhydride, sulfuric acid, ethoxytrimethylsilane, and triethylsilane, were not effective (Entries 1–4). These findings suggest that chlorosilanes produce silyl cations as active species.

Table 2. Catalytic conversion of CDOX at 100 °C for 2 h^a

Entry	Catalyst	Conversion /mol %	Selectivity/mol %		TON
			LRL	CD	
1	(CH ₃ CO) ₂ O ^b	30.0	6.3	14.0	0.5
2	H ₂ SO ₄	41.4	20.8	26.3	2.0
3	Me ₃ SiOEt	2.8	0	88.6	0
4	Et ₃ SiH	14.5	0	36.8	0
5	CH ₃ COCl	67.6	81.7	12.6	14.8
6	C ₆ H ₅ COCl	75.5	82.8	6.3	16.6
7	Me ₃ SiBr	54.8	85.3	5.7	12.9
8	Me ₃ SiCl ^c	50.9	85.6	4.6	11.7
9	Me ₂ SiCl ₂	99.9	96.9	0.7	25.9
10	MeSiCl ₃	97.8	94.4	2.0	24.7
11	EtSiCl ₃	99.5	95.9	0.8	25.6
12	PhSiCl ₃	99.9	97.3	0.5	26.1
13	SiCl ₄ ^c	81.7	97.8	1.0	21.4
14	SiCl ₄	100	98.0	0.6	26.3
15	HCl ^d	92.9	77.4	4.4	3.2

^aSolvent, PhCN: 10 g, catalyst/CDOX/PhCN: 0.19/5.1/96 (mmol/mmol/mmol). ^bReacted for 20 h. ^cReacted for 1 h. ^dHCl dissolved in 1,4-dioxane was used as catalyst with the ratio of HCl/CDOX/PhCN/1,4-dioxane: 1.14/5.1/96/3.41 (mmol/mmol/mmol/mmol).

Table 3. Effect of cosolvent in the conversion of CDOX catalyzed by SiCl₄ with MeCN at 100 °C for 2 h^a

Entry	Co-solvent	Conversion /mol %	Selectivity/mol %		TON
			LRL	CD	
1	MeCN	100	97.7	0.6	26.2
2	<i>n</i> -Hexane	95.1	95.4	2.1	24.3
3	<i>n</i> -Decane	85.9	94.6	2.6	21.8
4	Cyclohexane	94.1	95.2	1.1	24.0
5	1,4-Dioxane	46.2	79.5	4.9	9.8
6	THF	52.8	64.9	3.3	9.2
7	Acetone	43.0	55.2	24.9	6.4
8	Ethyl acetate	24.9	77.1	22.3	5.1
9	Benzene	23.4	67.2	9.9	4.2
10	Ethanol	53.7	15.1	38.4	2.2
11	Cyclohexene	100	0	0	0

^aMeCN/solvent: 1.0/9.0 (g/g), SiCl₄/CDOX/MeCN: 0.19/5.1/24 (mmol/mmol/mmol).

To elucidate the role of nitrile solvent, whether it is simple solvent or not, we tested several cosolvents with acetonitrile in the rearrangement (Table 3). The cosolvents listed in Table 3 except cyclohexene (Entry 11) work as a medium with TON > 1. Saturated hydrocarbons such as *n*-hexane and cyclohexane are the most effective cosolvents with acetonitrile (Entries 2 and 4). This indicates that toxic solvent nitriles could be reduced by diluting with *n*-hexane.

Even under the conditions of Table 3, excess acetonitrile against CDOX is used in the tests. In silane–nitrile–hexane, acetonitrile is not a simple solvent: it probably acts as a reactant or cocatalyst. Then, small amounts of nitriles are added into the mixture of silane–CDOX–hexane to clarify quantitative effects of nitriles on the Beckmann rearrangement. Table 4 shows the effect of additive benzonitrile in the conversion of CDOX in *n*-hexane solvent. At the same amount of benzonitrile as SiCl₄, the

Table 4. Effect of additive PhCN in the reaction of CDOX for 2 h^a

Entry	Temperature /°C	Conversion /mol %	Selectivity/mol %		TON
			LRL	CD	
1	100 ^b	38.2	8.6	16.5	0.88
2	100 ^{b,c}	41.5	9.1	5.5	1.01
3	100 ^d	63.3	54.5	2.3	9.2
4	120 ^d	87.1	95.9	3.4	22.4
5	130 ^d	99.2	96.7	2.3	25.7

^aPhCN + *n*-hexane: 10 g. ^bSiCl₄/CDOX/PhCN: 0.19/5.1/0.19 (mmol/mmol/mmol). ^cReacted for 8 h. ^dSiCl₄/CDOX/PhCN: 0.19/5.1/5.1 (mmol/mmol/mmol).

yield of LRL is the same as the amount of benzonitrile added (Entries 1 and 2). At the same amount of benzonitrile as CDOX, the yield of LRL is also the same as the amount of benzonitrile added: the silane works as a catalyst (Entry 5). This indicates that equimolar nitrile to CDOX is needed to accomplish the catalytic cycle. This indicates that nitrile works as a remover of catalyst species from the LRL–silane adduct to regenerate the catalyst species, silanes.

Additionally, we have tried to apply the most active SiCl₄–benzonitrile catalytic system to the Beckmann rearrangement of cyclohexanone oxime. Unfortunately, SiCl₄ did not work as a catalyst for the rearrangement: an equimolar amount of SiCl₄ to the oxime was needed to produce ϵ -caprolactum. The reactivities are different among the oximes, CDOX and cyclohexanone oxime.^{4,6–8}

We concluded that chlorosilanes, such as Me₃SiCl and SiCl₄, were effective for the production of LRL in the Beckmann rearrangement of CDOX in silane–nitrile–solvent systems at 100 °C. SiCl₄ is the most active catalyst, and hydrocarbon solvents such as cyclohexane and *n*-hexane are suitable for the system. Nitriles such as acetonitrile and benzonitrile were required for the same amount of CDOX for the LRL formation. We speculate that the nitriles would play an important role in that they remove silane species from the produced LRL–silane adduct to reproduce the catalyst silane species during catalysis.

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