CHEMISTRY LETTERS, pp. 2171-2174, 1990.

Catalytic Beckmann Rearrangement of Oximes in Homogeneous Liquid Phase

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Oximes such as cyclohexanone oxime and benzaldehyde oxime were catalytically transformed into the corresponding lactams in *N,N*-dimethylformamide solutions of alkylating reagents such as trialkyloxonium salts. Catalyst turnover attained 43 on the basis of the acid used to obtain alkylating reagent. *O*-Alkyl-*N,N*-dimethylformamidinium salt was suggested to be a catalyst species.

Catalytic rearrangement of oximes into lactams without use of stoichiometric amounts of acid promoters has long been an important subject for catalyst researchers, particularly with respect to the conversion of cyclohexanone oxime. A great number of heterogeneous catalysts have previously been proposed for the vapor-phase rearrangement of cyclohexanone oxime into ε-caprolactam.[1-11] The vapor-phase rearrangement over solid catalysts, however, needs high reaction temperatures between 250 and 350 °C, thereby lactam selectivity is not sufficiently high and catalyst deactivation often results due to carbon deposit. Liquid-phase catalytic rearrangement processes under milder reaction conditions, therefore, seem more desirable not only for affording high lactam selectivity but also for saving energy in process operation; nevertheless no efficient catalyst systems for liquid-phase rearrangement have been developed.

The author wishes to report here a novel homogeneous catalyst system for liquid-phase rearrangement of oximes. This catalyst system comprises *N,N*-dialkylformamide as a solvent and a strong alkylating reagent such as trialkyloxonium salt.

The rearrangement reaction was performed in a homogeneous liquid phase. An alkylating reagent or its precursor components, such as a combination of strong acid and epoxide, were dissolved in anhydrous *N,N*-dialkylformamide solvent, and the solution was heated at 50 °C for 1 h. Cyclohexanone oxime was then added to the solution, and heated between 48

and 65 °C for 1 h. The product ε-caprolactam was identified by ^{1}H NMR (200 MHz), and determined by GLC using a Unisole 30T column (2 m).

Table 1 demonstrates the catalytic behavior of *N,N*-dimethylformamide-alkylating reagent system for the rearrangement of cyclohexanone oxime, comparing with the result for another aprotic solvent of dimetylsulfoxide-alkylating reagent system. The oxime was converted to ε-caprolactam in high selectivity of more than 98 mol% in *N,N*-dimethylformamide, but in dimethylsulfoxide the reaction hardly proceeded. Trimethyloxonium tetrafluoroborate as an alkylating reagent gave higher catalyst turnover than methyl trifluoromethanesulfonate, a superacid ester.

Table 1. Liquid-Phase Catalytic Beckmann Rearrangement of Cyclohexanone Oxime[a)]

Alkylating reagent (mmol)	Oxime (mmol)	Solvent (ml)	Reaction temperature/°C	Oxime conversion[b)]/%	Catalyst turnover[c)]
$Me_3O^+BF_4^-$(0.67)	17.7	DMF[d)] (6)	53	17.8	4.7
$Me_3O^+BF_4^-$(1.2)	17.7	DMSO[e)](6)	52	<0.1	-
CF_3SO_3Me (0.66)	3.53	DMF[d)] (3)	65	49.4	2.6

a) Reaction time: 1 h.
b) Each selectivity to ε-caprolactam was more than 98 mole%.
c) Moles of converted oxime/moles of alkylating reagent.
d) *N,N*-Dimethylformamide. e) Dimethylsulfoxide.

Since trialkyloxonium salts are readily prepared from $BF_3 \cdot Et_2O$ and an epoxide such as epichlorohydrin,[12,13] the present catalyst system was also obtainable *in situ* by mixing *N,N*-dialkylformamide, $BF_3 \cdot Et_2O$ and epoxide, without use of isolated oxonium salts.

Table 2 summarizes the reaction results with the *in situ* prepared catalysts using different kinds of solvents. As expected, each catalyst system prepared in situ was very effective. Interestingly, only *N,N*-dialkylformamide or *N*-alkyl-*N*-arylformamide was suitable for the solvent for the rearrangement, and other polar aprotic solvents were quite inadequate. Less polar solvents such as hexane, benzene, and chlorinated hydrocarbons were also ineffectual. These solvent effects clearly imply that the active catalyst species are formed through the reactions between the alkylating reagents and *N,N*-dialkylformamide. Considering that *N,N*-dimethylformamide can be easily alkylated with a trialkyloxonium salt into

Table 2. Rearrangement of Cyclohexanone Oxime by $BF_3 \cdot Et_2O$-Epichlorohydrin-Solvent System[a)]

$BF_3 \cdot Et_2O$ (mmol)	ECH[b)] (mmol)	Oxime (mmol)	Solvent (ml)	Reaction temperature/°C	Oxime conversion[c)]/%	Catalyst turnover[d)]
1.1	5.1	17.7	DMF[e)] (6)	55	35.3	5.7
1.1	5.1	17.7	MPF[f)] (6)	52	12.7	2.0
0.54	2.0	4.42	DIPF[g)] (1.5)	48	41.9	3.4
0.58	2.0	8.84	FA[h)] (3)	55	0.0	-
1.13	5.1	17.7	DMA[i)] (6)	52	0.0	-
1.11	5.1	17.7	HMPA[j)] (6)	53	0.0	-
1.25	5.1	17.7	CH_3CN (6)	52	0.0	-
0.51	2.6	8.84	DMSO[k)] (6)	55	4.2	0.7

a) Reaction time: 1 h. b) Epichlorohydrin.
c) Each selectivity to ε-caprolactam was more than 98 mol%.
d) Moles of converted oxime/moles of $BF_3 \cdot Et_2O$.
e) *N*,*N*-Dimethylformamide. f) *N*-Methyl-*N*-phenylformamide.
g) *N*,*N*-Diisopropylformamide. h) Formamide. i) *N*,*N*-Dimethylacetamide.
j) Hexamethylphosphoramide. k) Dimethylsulfoxide.

an *O*-alkylformamidinium salt (Eq. 1),[14] the active species in the present catalyst system are probably this type of formamidinium salts.

$$Me_2NCHO + Me_3O^+BF_4^- \longrightarrow [Me_2N{=}CH(OMe)]^+BF_4^- + Me_2O \quad (1)$$

Reportedly,[15] a Vilsmeyer complex of $[Me_2N{=}CHCl]^+SO_4H^-$, which is another type of formamidinium salt and obtainable by the reaction of *N*,*N*-dimethylformamide with chlorosulfonic acid, acts as a promoting reagent for Beckmann rearrangement of oximes through its powerful electrophilic property, but an equimolar amount of the reagent is required (Eq. 2).

$$RR'C{=}NOH + [Me_2N{=}CHCl]^+SO_4H^- \longrightarrow [RCONH_2R']^+SO_3Cl^- + Me_2NCHO \quad (2)$$

In contrast, the present study revealed *O*-alkylformamidinium salt (Meerwein salt) as a possible active species could function not as a reagent but as a *catalyst* for the rearrangement reaction. The detailed reaction mechanism by the present catalyst system is now under investigation.

Another *in situ* catalyst prepared from *N*,*N*-dimethylformamide (12 ml), $BF_3 \cdot Et_2O$ (0.38 mmol) and cyclohexene oxide (1.0 mmol) in place of epichlorohydrin afforded a high turnover of 15.5, when cyclohexanone oxime (8.84 mmol) was treated at 66 °C for 1 h (conversion = 65.8%). Moreover, a combination of *N*,*N*-dimethylformamide (6 ml), epichlorohydrin (2.6 mmol), 12-tungstosilicic acid (0.14 mmol) in place of $BF_3 \cdot Et_2O$, and cyclohexanone oxime (17.7 mmol) gave a turnover of 43 on the basis of the heteropoly acid under the reaction conditions of 50 °C and 1 h (conversion = 33.8%). Such effectual modifications of epoxide and acid components in *in situ* catalyst preparation suggest a great possibility of further improvement in the catalyst turnover.

The present catalyst system such as *N*,*N*-dimethylformamide-$BF_3 \cdot Et_2O$-epichlorohydrin is also capable of rearranging other types of oximes. For example, acetaldehyde oxime (a mixture of *syn* and *anti* isomers) and *syn*-benzaldehyde oxime were transformed into a mixture of *N*-methylformamide and acetamide (total turnover=3.6), and *N*-phenylacetamide (turnover=2.8) respectively.

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(Received September 3, 1990)