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The Catalytic Beckmann Rearrangement of Ketoxime Trimethylsilyl Ethers Using an Antimony(V) Salt

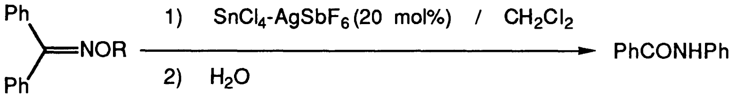
Teruaki MUKAIYAMA and Tsunehiro HARADA
Department of Applied Chemistry, Faculty of Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

In the presence of a catalytic amount of an antimony(V) salt generated from antimony(v) chloride and silver antimonate, the Beckmann rearrangement of several ketoxime trimethylsilyl ethers proceeds smoothly to give the corresponding amides or lactams in good yields.

The Beckmann rearrangement is a fundamental and useful reaction, long recognized as an extremely valuable and versatile method for the preparation of amides or lactams, and often employed even in the industrial processes.[1) However, the reaction generally requires at least an equimolar amount of activators such as strong acids including Lewis acids.[1,2) In the vapor phase process, there have been reported a few examples that were promoted by a catalytic amount of activators such as boria-hydroxyapatite[3) under rather drastic conditions. Therefore, it was strongly desired to explore an efficient catalyst which could promote the Beckmann rearrangement under mild conditions. Recently, we have found that a catalytic amount of tin(IV) species, easily prepared in situ from $SnCl_4$ and $AgClO_4$, realizes the highly stereoselective glycosylation reaction between a simple glycosyl donner, 1-O-acetyl glucose, and silyl alkoxides, and also garium(III) species for the catalytic Friedel-Crafts acylation.[4) In this communication, we would like to describe the Beckmann rearrangement performed under mild condition using a catalytic amount of such active species as an antimony(v) salt.

First, the Beckmann rearrangement of benzophenone oxime derivatives was tried by taking tin(IV) species generated from $SnCl_4$ and $AgSbF_6$ as a catalyst. As shown in Table 1, only in the case of trimethylsilyl ether, the reaction did proceed smoothly in CH_2Cl_2 at refluxing temperature to give the corresponding amide in good yield.

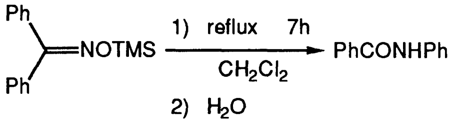
Table 1. The Beckmann Rearrangement of Benzophenone Oxime Derivatives



Entry	R	Temperature	Time/h	Yield/%
1	H	reflux	7	trace
2	Ac	reflux	7	48
3	TMS	rt	overnight	47
4	TMS	reflux	7	71
5	Me	reflux	7	trace

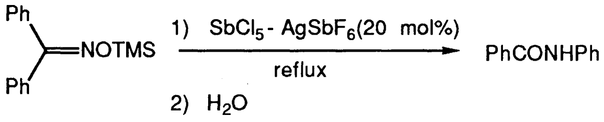
Next, several Lewis acids and solvents were examined employing the above mentioned reaction as a model. As shown in Table 2, neither $TiCl_4$ nor $SnCl_4$ alone did catalyze the reaction, and nor $AgSbF_6$ did either. On the contrary, the reaction proceeded smoothly to give the corresponding amide in 71-78% yields when active species generated from $SnCl_4$ or $SbCl_5$ and $AgSbF_6$ was employed respectively. A better result was obtained in the case of the combined use of $SbCl_5$ and $AgSbF_6$.

Table 2. Effect of Catalyst



Entry	Catalyst(20 mol%)	Yield/%
1	$SnCl_4$ + $AgSbF_6$	71
2	$TiCl_4$ + $AgSbF_6$	24
3	$AlCl_3$ + $AgSbF_6$	49
4	$SbCl_5$ + $AgSbF_6$	78
5	$TiCl_4$	2
6	$SnCl_4$	no reaction
7	$AgSbF_6$	19

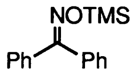
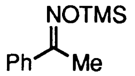
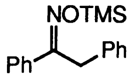
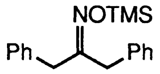
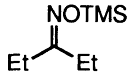
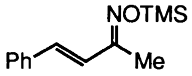
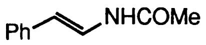
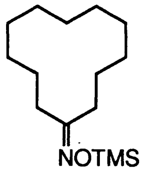
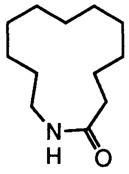
Table 3. Effect of Solvent



Entry	Solvent	Reaction time/h	Yield/%
1	CH_2Cl_2	7	78
2	Et_2O	7	53
3	CH_2ClCH_2Cl	3	98
4	CH_3CN	3	91
5	C_6H_6	3	87

Several examples of the present Beckmann rearrangement are demonstrated in Table 4. In every case, the reaction proceeds smoothly at refluxing temperature in CH_3CN to give the corresponding amides or lactams in good yields. In the case of benzophenone oxime trimethylsilyl ether, 1,2-dichloroethane was shown to be an effective solvent, while, in the case of other oxime trimethylsilyl ethers, CH_3CN was the best solvent.

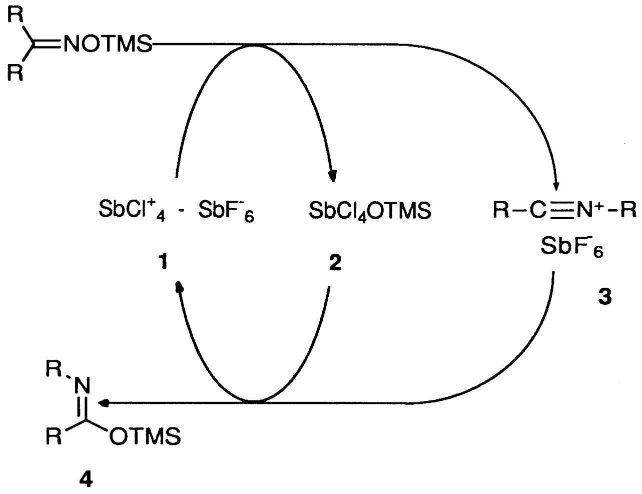
Table 4. The Beckmann Rearrangement of Several Ketoxime Trimethylsilyl Ethers[a)]

Entry	Substrate	Product	Solvent	Temperature	Time/h	Yield/%
1		PhNHCOPh	CH_2ClCH_2Cl	reflux	3	98
2		PhNHCOMe	CH_3CN	reflux	3	83
3		$PhNHCOCH_2Ph$	CH_3CN	reflux	3	83
4		$PhCH_2NHCOCH_2Ph$	CH_3CN	reflux	3	74
5		EtNHCOEt	CH_3CN	reflux	3	50
6			CH_3CN	40 °C	6	65
7			CH_3CN	reflux	3	77

a) Catalyst : $SbCl_5$ + $AgSbF_6$ (20 mol%).

The catalytic cycle of this rearrangement is postulated as shown in Scheme 1. The antimony(V) species activates a trimethylsilyloxy group of oxime moiety, followed by rearrangement of R anti to the trimethylsilyloxy function to form the cation stabilized by antimonate anion(**3**) and CH_3CN. Then the ion pair(**3**) reacts with initially formed tetrachloro(trimethylsilyloxy)antimony(**2**) to give the desired imino trimethylsilyl ether(**4**) along with a regeneration of the catalyst(**1**).

A typical experimental procedure for the Beckmann rearrangement of benzophenone oxime trimethylsilyl ether is as follows; a CH_2Cl_2 solution of 0.5 M antimony(v) chloride(0.12 ml) was added to a silver hexafluoroantimonate(20.6 mg, 0.06 mmol) solution of 1,2-dichloroethane under ice cooling with the protection from the light. After stirring for 1 h, a 1,2-dichloroethane(1.5 ml) solution of benzophenone oxime trimethylsilyl ether(80.8 mg, 0.3 mmol) was added at rt. After refluxing for 3 h, the mixture was quenched with aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4. After the evaporation of the solvents, the residue was purified by preparative TLC to afford 58.2 mg(98%) of benzanilide, mp 163-165 °C.



Scheme 1. The catalytic cycle.

References

1) R. E. Gawley, *Org. React.*, **35**, 1(1988), and references cited therein.

2) J. C. Jochims, S. Hehl, and S. Herzberger, *Synthesis*, **1990**, 1128, and references cited therein.

3) Y. Izumi, S. Sato, and K. Urabe, *Chem. Lett.*, **1983**, 1649, and references cited therein.

4) T. Mukaiyama, M. Katsurada, and T. Takashima, *Chem. Lett.*, **1991**, 985; T. Mukaiyama, T. Ohno, T. Nishimura, S. Suda, and S. Kobayashi, *ibid.*, **1991**, 1059, and references cited therein.

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