BECKMANN REARRANGEMENT OF CYCLOHEXANONE OXIME p-TOLUENESULFONATE ON ACIDIC CATALYSTS

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The Beckmann rearrangement of cyclohexanone oxime p-toluenesulfonate has been studied using several catalysts. The reaction is catalyzed by weakly acidic sites and seems to occur by way of O-(p-toluenesulfonyl)-ϵ-caprolactim.

Была исследована Бекмановская перегруппировка п-толуолсульфоната цикло-гексаноа-оксима, используя различные катализаторы. Реакция катализируется сдабо-кислыми центрами и протекает через О-(п-толуолсулыфонил)-ϵ-капро-лактим.

The Beckmann rearrangement is a well-known reaction with widespread synthetic applications. Usual methods involve the use of strongly acidic reagents and/or high temperatures that may cause isomerization and other side reactions.

The reaction may be made easier by using the oxime tosylates as substrates and carrying it out in heterogeneous conditions /1/. This method is much milder, more selective and simpler to perform than the homogeneous reaction with product isolation usually involving only filtration and solvent evaporation.

The present work deals with the application of some solid acids as catalysts in the Beckmann rearrangement of cyclohexanone oxime p-toluenesulfonate.

As catalysts, we used neutral $\gamma-Al_2O_3$ (Merck 1077), SiO_2 (Merck 10180) and several Kearby type catalysts made gels as been previously described, viz. ammoniacal $AlPO_4$ /2/ and $\gamma-Al_2O_3/AlPO_4$ /3/ and oxiranic $AlPO_4$ /2/ and $\gamma-Al_2O_3/AlPO_4$ /3/.

The acidity of the catalysts was determined by titration with n-butylamine in nonaqueous medium in the presence of Hammett indicators and by calorimetric titration /4/. Before each titration the catalysts were pre-dried at 773 K for 3 h under 0.3 Torr vacuum.

In a typical run the necessary water was added to 1 g of pre-dried catalyst which was then covered with 5 ml of anhydrous CCl_4 and stirred for 2 h on a

Table 1

Catalyst	Acidity (meq/g)		% TsOH		Specific surface area (m^2/g)
	$H_O \leqslant 2.8$	Calorim.	0^a	50^a	
ox $AlPO_4$	0.75	0.87	13.3	26.0	251.5
am $AlPO_4$	0.31	0.37	12.5	19.3	101.0
am $Al_2O_3/AlPO_4$	0.54	0.67	15.4	27.1	224.5
ox $Al_2O_3/AlPO_4$	0.83	0.97	23.3	53.8	299.2
SiO_2	$\leqslant 0.01$	2.28	62.3	84.7	663.0
Al_2O_3	0.00	0.00	4.1	3.9	111.7

[a] μl H_2O/g catalyst

water bath at 298±1 K. Afterwards 5 ml of freshly prepared solution of cyclo-hexanone oxime tosylate in anhydrous CCl_4 (1 g tosylate/50 ml solution) was added and stirring was continued for 30 min. The yellowish slurry was then filtered and washed once with CCl_4 (5 ml) and twice with water (2 x 25 ml). The extracts were mixed and immediately titrated with standardized sodium hydroxide to determine the amount of tosylic acid formed.

Table 1 shows some textural properties of the catalysts together with the percentage of tosylic acid developed when the reaction is performed under anhydrous conditions and when water-doped catalysts are used.

In all cases, plotting the percentage of tosylic acid released versus the amount of water added per gram of catalyst produces a curve with a maximum at about 50–60 μl H_2O/g catalyst which then diminishes slowly as the amount of water increases. This is shown in Fig. 1 for SiO_2.

The straight line represents the percentage of tosylic acid formed under the same conditions in the absence of catalyst and with the corresponding amount of water.

As can be seen from the above, the reaction requires only weakly acidic sites. SiO_2 was the best catalyst because it has the largest number of this sites as shown by calorimetric titration (see Table 1).

As shown in Fig. 1, traces of water have an activating effect on the reaction. This can be explained by the conversion of Lewis acid sites into Brönsted sites in the $AlPO_4$ and $Al_2O_3/AlPO_4$ systems, both coexisting in these catalysts /5, 6/, and by the formation of Si–OH groups on the partially dehydrated surface of SiO_2 /7/. Thermogravimetric measurements have shown that at lower pretreating temperatures the catalyst surface is entirely covered with hydroxy groups, which implies weak surface acidic sites. Increasing amounts of water lead to a decrease in conversion which implies preferential adsorption of water on the catalyst.
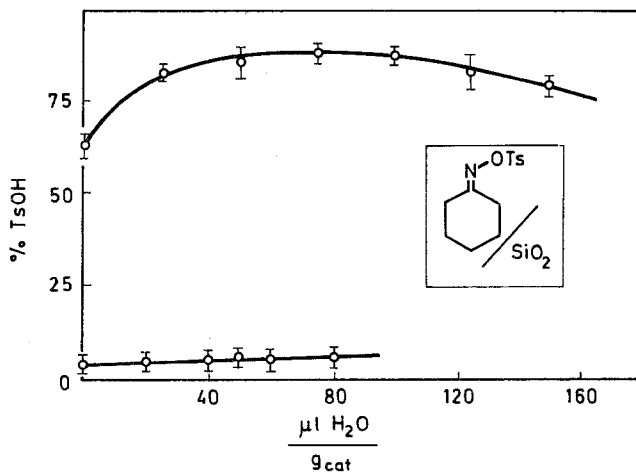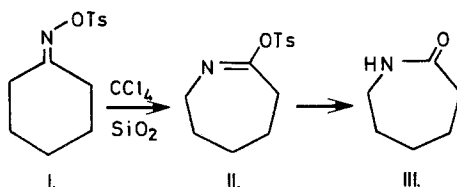
Fig. 1.

The rearrangement seems to take place through an unstable 0-(p-toluenesulfonyl)-ε-caprolactim intermediate (II).

Preparative experiments performed under anhydrous conditions using methanol as the eluant allowed us to detect II by its characteristic absorption bands in the IR spectrum /8/.

REFERENCES

1. J. Cymerman Craig, A. R. Naik: J. Amer. Chem. Soc., *81*, 3410 (1962).
2. M. A. Aramendia, J. M. Campelo, S. Esteban, C. Jimenez, J. M. Marinas, J. V. Sinisterra: Rev. Inst. Mex. Petrol, *12*, 61 (1980).
3. J. M. Campelo, J. M. Marinas, R. Perez-Ossorio: Proc. Vth Ibero-American Symp. Catal., *1*, 84 (1978).
4. K. Tanabe: Solid Acids and Bases, Kodansha Tokio, 1970.
5. I. B. Peri: Discuss. Faraday Soc., *52*, 55 (1971).
6. G. Wendt: Z. Chem., *17*, 118 (1977).
7. A. McKillop, D. W. Young: Synthesis, 401 (1979).
8. W. Z. Heldt: J. Amer. Chem. Soc., *80*, 5880 (1958).