

PREPARATION OF 2-METHYL-2-OXAZOLINE BY CYCLODEHYDRATION ON OXIDE CATALYSTS

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The possibilities of preparing 2-methyl-2-oxazoline were studied on oxide catalysts, at normal pressure, in a tube flow-reactor, via the ring-closure reaction of 2-acetylaminoethanol. The mechanism of the process is discussed.

Introduction

A number of different cyclization methods are known for the preparation of oxazolines [1]. However, much less attention has been devoted to the study of this ring-closure under heterogeneous catalytic conditions. The experiments of SEELIGER and THIER [2] showed that in the presence of Al_2O_3 catalyst at 320–375 °C and 10–20 torr various 2- and 2,5-disubstituted 2-oxazolines (and 5,6-dihydro-4*H*-1,3-oxazines) can be prepared from *N*-acylaminoalcohols (Fig. 1). With a slight modification of their method, and employing the laboratory-scale continuous reactor technique operating at atmospheric pressure, which we have long been using to investigate oxygen-containing organic compounds [3], we have examined numerous different, mainly industrial oxide catalysts in an attempt to generalize the above cyclodehydration transformation under continuous conditions in the presence of electrophilic catalysts. The chosen catalysts or their individual components are known dehydrating agents, used in other processes (see *e.g.* [4, 5]). Examinations were also carried out with an acetic acid — 2-aminoethanol mixture under similar conditions, with a view to studying the possibility of achieving the overall transformation in one step.

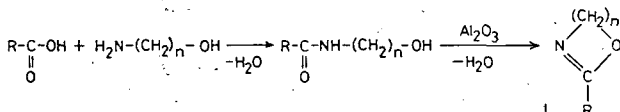


Fig. 1. Preparation of 2-oxazoline and 5,6-dihydro-4*H*-1,3-oxazines from *N*-acylaminoalcohols, $n = 2, 3$

Experimental

The catalysts used were as follows:

γ - Al_2O_3 : catalyst RB-13 prepared by the Organic Chemical Industrial Research Institute (Budapest). Before use, it was activated for 1 hour at 350 °C in a current of air.

ThO_2/Al_2O_3 : prepared on the basis of reference [6].

$ThO_2/pumice$: prepared in accordance with reference [7].

Cr_2O_3/ZnO : Leuna (GDR) catalyst L-616; specific surface area: 15 m²/g.

$CuO/ZnO/Cr_2O_3$: Leuna (GDR) catalyst L-1930. Its reduced form was prepared by reduction in a stream of hydrogen (50 ml/min) for 1 hour each at 200, 250, 300 and 350 °C. Specific surface area: 40 m²/g.

$CuO/ZnO/Al_2O_3$: Leuna (GDR) catalyst L-1950; specific surface area: 45 m²/g.

NiO/MgO : Leuna (GDR) catalyst L-9024; specific surface area: 1 m²/g.

$Bi_2O_3/MoO_3/SiO_2$: Leuna (GDR) catalyst L-9421; specific surface area: 55 m²/g.

2 ml of catalysts with a particle size of 1–2 mm was used in a reactor tube with an internal diameter of 20 mm.

The 2-acetylminoethanol was prepared on the basis of reference [2] (b.p.: 140–142 °C/1 mm Hg; [8] b.p.: 120 °C/0.03 mm Hg).

Product analysis was performed with a CHROM 41 gas-chromatography apparatus, with 2.4 m long 15% CWAX 1500 (130 °C) and Apiezon L (180 °C) columns (solid support: silanized Merck Kieselguhr with a particle size of 0.2–0.3 mm) in hydrogen as carrier gas. The 2-methyl-2-oxazoline was identified on the basis of its IR spectrum (UNICAM SP 200 instrument).

Discussion

The experimental results listed in Table I show that all of the catalysts employed in this study are suitable for the synthesis of 2-methyl-2-oxazoline. The yields obtained with γ - Al_2O_3 were lower than that reported in the literature [2], but at the same time equivalent or better results than on Al_2O_3 were achieved on some other catalysts, at comparatively low temperatures (L-1980, 280 °C; L-1950, 300 °C; ThO_2/Al_2O_3 , 250–300 °C; $ThO_2/pumice$, 300 °C). The data obtained by means of preparative working-up reveal that 2-methyl-2-oxazoline may be prepared in a yield of ca. 60% with the above method and the following catalysts: Al_2O_3 , L-9421, L-1930, L-1950 and both supported ThO_2 catalysts. On certain catalysts, and mainly at higher temperatures, the transformation was accompanied by the formation of resinous products.

Table II contains the results of the experiments carried out with the acetic acid–2-aminoethanol mixture. It may be seen from the data that, even on γ - Al_2O_3 as catalyst, which gives the best result, with this method the yields obtained with 2-acetylminoethanol can not be achieved, *i.e.* if the ring-closure is attempted in this way, the process is of little use practically.

The occurrence of the cyclodehydration could be explained merely by the participation of the acidic centres of the catalysts. It has been demonstrated, however, that

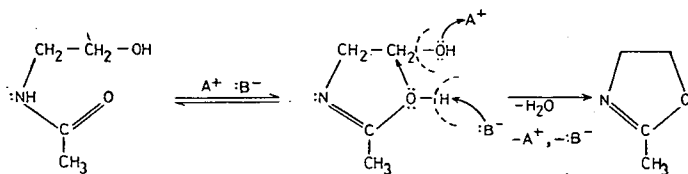


Fig. 2. Formation of 2-methyl-2-oxazoline

Table I

Ring-closure reaction of 2-acetylaminooethanol on various oxide catalysts

Catalysts	Temperature (°C)	Space velocity (ml liquid. ml ⁻¹ catalyst space. hr ⁻¹)	Yield of 2-methyl-2-oxazoline* (%)
γ -Al ₂ O ₃	350	0.95	76
	350	3.3	72
	350	3.3	56**
ThO ₂ /Al ₂ O ₃	250	3.65	77
	300	3.65	84
	300	3.65	66**
	350	3.65	75
ThO ₂ /pumice	250	3.65	32
	300	3.65	80
L-616	350	6.65	61
	400	6.65	44
L-1930	250	3.65	67
	280	3.65	71
	300	3.65	55
	350	3.65	58
L-1930 (reduced form)	250	3.65	65
	350	3.65	39
L-1950	300	3.65	79
	300	3.65	60**
	350	3.65	71
L-9024	350	6.65	44
	390	6.65	65
L-9421	350	6.65	58
	390	3.3	68
	390	3.3	57**

* Values obtained by GC determination. Yield = $\frac{\text{2-methyl-2-oxazoline (mole)}}{\text{2-acetylaminooethanol (mole)}}$

** Preparative working-up

Table II

Preparation of 2-methyl-2-oxazoline on oxide catalysts from a 1:1 molar mixture of acetic acid and 2-aminoethanol

Catalysts	Temperature (°C)	Space velocity	Yield of 2-methyl-2-oxazoline* (%)
γ -Al ₂ O ₃	350	10.35	41
	350	10.35	28**
	350	1.9	40
L-616	350	3.3	20
	400	3.3	15
L-9024	350	3.65	24
	390	3.65	46
L-9421	350	3.3	19
	390	3.3	23

*, ** See Table I.

in other dehydration reactions both the acidic and the basic centres play a role [4, 9]. Accordingly, the mechanism of the transformation may be outlined as in Fig. 2, with the simultaneous participation of the acidic and the basic centres, via the imino-hydrin tautomeric form of the starting compound.

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СИНТЕЗ 2-МЕТИЛ-2-ОКСАЗОЛИНА МЕТОДОМ ЦИКЛОДЕГИДРАТАЦИИ НА ОКИСНЫХ КАТАЛИЗАТОРАХ

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Изучены возможности синтеза 2-метил-2-оксазолина на окисных катализаторах при нормальных давлениях в трубчатом проточном реакторе при циклообразовании 2-ацетиламиноэтанола. Обсуждается механизм происходящей реакции.