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Transformation of organic compounds in the presence of metal complexes

V *. Cyclization of aminoalcohols on a ruthenium complex

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Abstract

In the presence of $RuCl_2(PPh_3)_3$ as catalyst at 150–180 °C, N-substituted aminoalcohols are cyclized to N-substituted azacycloalkanes in good yields.

Introduction

In the presence of oxide catalysts under forcing reaction conditions, diols can be cyclized with primary amines to form azacycloalkanes [1,2]. Similarly, certain aminoalcohols undergo cyclization on alumina at 300 °C [3,4]. Japanese authors recently investigated the reactions of 1,4- and 1,5-diols with primary amines in the presence of Ru complexes, from which they isolated N-substituted azacycloalkanes [5,6]. They explained the reaction in terms of a dehydrogenation–hydrogenation mechanism, and succeeded in isolating an aminoalcohol as an intermediate [5]. Here we report on a study of the reactions of some aminoalcohols under conditions similar to those used previously.

Results and discussion

The cyclizations of several aminoalcohols in the presence of $RuCl_2(PPH_3)_3$ as catalyst (Table 1) were carried out. The reactions of some diols and aniline were also studied (Table 2) and were then compared with published findings [5].

It was found that the expected cyclization did not occur in the case of the 1,3-aminoalcohols. Instead, a substance of higher molecular mass was formed (which has as yet not been identified) as in the reaction of 1,3-diols and amines.

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Table 1

Conversion of aminoalcohols **1** to azacycloalkanes **2**.

Entry	Aminoalcohol **1**		Temp. (°C)	Product **2**		Yield [a] (%)
	R	*n*		R	*n*	
1	n-Bu	1	180	n-Bu	1	0
2	Ph	1	150	Ph	1	0
3	i-Pr	2	180	i-Pr	2	70
4	Ph	2	150	Ph	2	88
5	n-Bu	3	180	n-Bu	3	71
6	Ph	3	150	Ph	3	90
7	n-Bu	4	180	n-Bu	4	71

[a] By GC.

Table 2

Reaction of diols with aniline

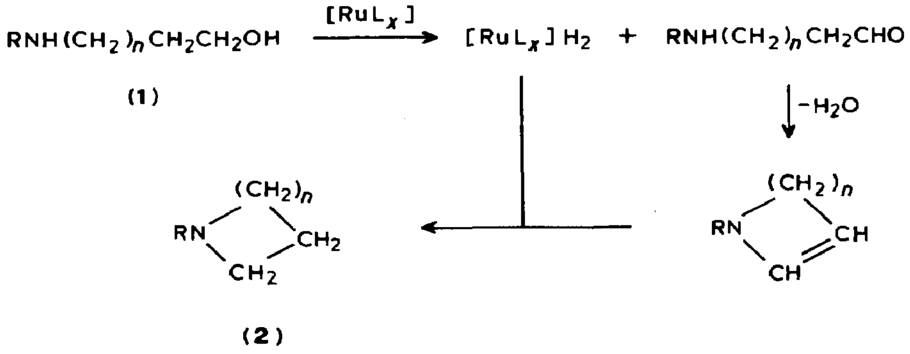
Entry	Diol	Temperature (°C)	Product 2		Yield (%)	
			R	n	our [a]	[5,6]
1	1,3-propandiol	180	Ph	1	0	–
2	1,4-butandiol	140	Ph	2	92	85
3	1,5-pentandiol	150	Ph	3	100	89
4	1,6-hexandiol	180	Ph	4	57	–

[a] By GC.

If substituent R in aminoalcohol **1** is an alkyl group, the cyclization requires a higher temperature. The process takes place by the route shown in Scheme 1, which is supported by the good dehydrogenation-hydrogenation ability of $RuCl_2(PPh_3)_3$ [7].

Experimental

A mixture of aminoalcohols (2.5 mmol) (2 ml), anhydrous dioxane (2 ml) and $RuCl_2(PPh_3)_3$ (10 mg) was heated for 5 h in a nitrogen atmosphere in a sealed glass



Scheme 1.

tube. After cooling, the reaction mixture was subjected to gas and thin-layer chromatography. The reactions between the diols and aniline were carried out as described previously [5]. Gas chromatographic examinations were made with a Chrom 4 (Czechoslovakia) chromatograph, coupled with a Digint 34 u integrator (Chinoin, Budapest), on a 1.2 m 10% Reoplex/Chromosorb P column equipped with a flame ionization detector. Nitrogen was the carrier gas. The thin-layer chromatographic examinations carried out on a Kieselgel (Merck) plate with a layer thickness of 0.5 mm, in a solvent mixture of benzene/ethanol (80/20) or in certain cases benzene/pentane [8]/ethanol (60/20/20); development by use of the Draggendorf reagent.

The starting aminoalcohols and the expected N-substituted azacycloalkanes were synthesized by published procedures. [9–15]. The diols and amines were purchased from Fluka. The $RuCl_2(PPh_3)_3$ was obtained from Strem. The dioxane was dehydrated in the usual way and was distilled under nitrogen.

Acknowledgements

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