

Transformation of diols in the presence of heteropoly acids under homogeneous and heterogeneous conditions

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Abstract

1,2-Diols (1,2-propanediol, isomeric 2,3-butanediols and 2,3-dimethyl-2,3-butanediol) readily undergo the pinacol rearrangement to yield the corresponding carbonyl compounds (propanal, 2-butanone and 3,3-dimethyl-2-butanone, respectively) in the presence of heteropoly acids ($H_4[SiMo_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$ and $H_3[PW_{12}O_{40}]$). The selectivity depends on the acid strength and the form of the heteropoly acid catalyst (transformation under homogeneous conditions or in the presence of heteropoly acid supported on silica). Heat treatment of supported $H_3[PW_{12}O_{40}]$ results in a highly stable catalyst, due to the strong interaction between the acid and the support. A similar stabilization of $H_4[SiMo_{12}O_{40}]$ could not be achieved. The highly selective formation of cyclic ethers, characteristic of the dehydration of higher diol homologues (1,4-butanediol, isomeric 2,5-hexanediols, 2,5-dimethyl-2,5-hexanediol, 1,5-pentanediol and 1,6-hexanediol) is also catalyzed by heteropoly acids. This cyclodehydration occurs by a stereospecific intramolecular S_N2 mechanism.

Keywords: Heteropoly acids; Diols; Pinacol rearrangement; Cyclodehydration

1. Introduction

Heteropoly acids are new catalysts that are widely used in organic transformations. They can be applied in reactions requiring electrophilic catalysis (alkylation, acylation, isomerization, hydration and dehydration), and also promote oxidations [1]. They have already been introduced into large-scale industrial processes (hydration of alkenes, oxidation of methacrolein and polymerization of tetrahydrofuran). As a consequence of some unique properties (multi-

functional character, heterogeneous, pseudo-liquid, homogeneous and phase-transfer catalysis) and favorable technological features (easy recovery and environmentally safer handling), there is still growing interest in the exploration of new applications.

The elimination of alcoholic hydroxyl groups is an interesting and important reaction amongst the electrophilic transformations, since many different products (alkenes, dienes, ethers and carbonyl compounds) may be formed, depending on the reaction conditions and the structure of the starting materials. Diols can readily undergo electrophilic dehydration reactions under homogeneous (H_2SO_4 , H_3PO_4 , etc.) and het-

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erogeneous (Al_2O_3 , $\text{Ca}_3(\text{PO})_4$, zeolites, Nafion-H, etc.) conditions [2–4]. However, very few data are to be found in the literature concerning the heteropoly acid-catalyzed dehydration of these compounds. In fact, only a single paper reports a kinetic study of the dehydration of 1,4-butanediol to produce tetrahydrofuran [5].

As a result, a systematic study of this subject was undertaken. The major goals were (i) to collect data concerning the interaction of diols and heteropoly acids, (ii) to compare these reactions under homogeneous and heterogeneous conditions, and (iii) to find reaction conditions resulting in selective transformations.

2. Experimental

2.1. Materials

All the diols studied (1,2-propanediol, 2,3-butanediol, 2,3-dimethyl-2,3-butanediol, 2,4-pentanediol, 3-methyl-2,4-pentanediol, 1,4-butanediol, 2,5-hexanediol, 2,5-dimethyl-2,5-hexanediol, 1,5-pentanediol and 1,6-hexanediol) were Fluka products with a purity of at least 98%, and were used as received. 2,3-Butanediol was separated into the racemic and *meso* isomers by fractional distillation of the corresponding cyclic ketals formed with acetone. A similar procedure allowed separation of the isomeric 2,5-hexanediols through distillation of the cyclic formals. $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]$ (denoted as SiMo_{12}) was synthesized according to the literature [6]. $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ (PMo_{12}) was purchased from Aldrich, $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ (SiW_{12}) from Riedel-de Haen, and $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ (PW_{12}) from Serva. Supported heteropoly acids were prepared by impregnating Kieselgel (Aldrich, Type 62, 60–200 mesh, exhibiting no activity alone) with an appropriate amount of a 0.01 molar aqueous solution of the acid to achieve a final loading of 10%. The slurry was evaporated to dryness under vacuum, followed by a 4-h calcination at 170°C or 300°C [7,8]. Catalyst samples with an

additional water treatment (room temperature, 1 h) were also prepared.

2.2. Methods

Reactions in the homogeneous phase were carried out by reacting a mixture of 0.02 mol of diol and heteropoly acid corresponding to a catalyst quantity of 0.1 mol% at 150–180°C and collecting the products that distilled off (MethI). Supported catalysts were also used in a similar way. Reactions were usually complete in 30–60 min depending on the reactivity of the diol. A customary vertical fixed-bed reactor (length: 160 mm, inner diameter: 20 mm) electrically heated with a split-tube furnace was used for heterogeneous reactions (MethII). 1 g of the supported heteropoly acid was kept at 200°C for 1 h before the diol was introduced with a syringe pump at a feeding rate of 1.5 g h⁻¹. Except when noted, conversions were 100%.

2.3. Analysis

The reaction products (homogenized by adding an appropriate amount of diglyme) were analyzed by GC and GC–MS. The product distribution was determined with a Hewlett-Packard GC (50-m HP-1 capillary column, FID). The GC–MS investigations were performed on an HP-5890 GC instrument, using the same column coupled with an HP-5970 mass selective detector. Individual compounds were identified by comparison with authentic samples or by using an MS library search method. Heteropoly acids were characterized by differential scanning calorimetry (DSC; Perkin-Elmer DSC2 instrument).

3. Results and discussion

The acidity of the four heteropoly acids used in the present study changes in the sequence $\text{PW}_{12} > \text{SiW}_{12} > \text{PMo}_{12} > \text{SiMo}_{12}$ [9]. As a result, all diols were studied in the presence of the

Table 1
Selectivities of the dehydration of 1,2-diols in the presence of PW_{12}

1,2-Propanediol		2,3-Butanediol (isomeric mixture)		2,3-Dimethyl-2,3-butanediol	
MethII ^a		MethII ^a		MethI	
Propanal	64	2-Methyl propanal	14	2,3-Dimethyl-1,3-butadiene	21
Corresponding dioxolanes	32	2-Butanone	86	3,3-Dimethyl-2-butanone	79

^a PW_{12} -on-silica, calcined at 170°C.

strongest (PW_{12}) and the weakest acid ($SiMo_{12}$). When it seemed necessary, however, all four heteropoly acids were tested to establish more accurate correlations between acid strength and activity/selectivity.

Preliminary studies with 1,3-diols showed that these compounds underwent very complex transformations (formation of dienes, saturated and unsaturated alcohols and carbonyl compounds). This seems to be a general pattern characteristic of the dehydration of 1,3-diols in the presence of highly active electrophilic catalysts [2,3]. Since all our attempts to find reaction conditions resulting in selective reactions failed, no further studies were conducted with these compounds.

1,2-Diols, in contrast, underwent more selective transformations. All four heteropoly acids studied exhibited high activity in the transformation of 1,2-diols, with the exception of 1,2-ethanediol which was unreactive. The main products were carbonyl compounds formed in the pinacol rearrangement (Table 1, values are in mol%). The best selectivities were achieved with PW_{12} . The pinacol rearrangement, i.e. the

formation of carbonyl compounds through the elimination of water and concomitant 1,2 rearrangement occurs with high selectivity both in the homogeneous phase and with heterogeneous catalysts. The data in Table 2 (first four columns) indicate that increasing acid strength results in a higher selectivity of the pinacol rearrangement in the dehydration of 2,3-dimethyl-2,3-butanediol. Side-reactions include fragmentation to acetone (in the presence of weaker acids) and 1,2-elimination to produce dienes. This is in agreement with earlier observations that active sites of low acidity catalyze 1,2-elimination over pillared clays [10].

Heterogeneous catalysts were also studied in the transformation of 2,3-dimethyl-2,3-butanediol (MethI). After heat treatment at 300°C, PW_{12} -on-silica exhibited the same activity as the homogeneous catalyst, whereas the selectivity decreased considerably (Table 2, column 5). The activity after water etching was slightly lower, but the selectivity was again similar to that in the homogeneous reaction (Table 2, column 6). It has recently been shown [8] that heat treatment of a silica-supported het-

Table 2
Selectivity of the dehydration of 2,3-dimethyl-2,3-butanediol (MethI, 150°C)

	$SiMo_{12}$	PMo_{12}	SiW_{12}	PW_{12}	PW_{12} -on-silica		$SiMo_{12}$ -on-silica ^a
					HT	WE	
2,3-Dimethyl-1-butene	17	10					
2,3-Dimethyl-1,3-butadiene	15	20	29	22	45	25	34
Acetone	15	27					8
3,3-Dimethyl-2-butanone	44	43	71	78	55	75	58
Unidentified	9						

HT = heat treated at 300°C, WE = water etched, reaction at 165°C.

^a Calcined at 170°C, reaction at 165°C, 27% conversion.

Table 3
Selectivity of the dehydration of 2,3-butanediol (isomeric mixture)

	SiMo ₁₂		SiMo ₁₂ /SiO ₂ ^a		PW ₁₂		PW ₁₂ /SiO ₂ ^a		PW ₁₂ /SiO ₂ ^b		PW ₁₂ /SiO ₂ ^c	
	MethI		MethII		MethI		MethII		MethII		MethII	
			S _{1n}	S ₅ ^d			S _{1n}	S ₁₅	S _{1n}	S ₁₅	S _{1n} ^e	
1,3-Butadiene	0.5		2	5	0.5		0.5	1	0.5		1.5	
2-Methylpropanal ⁺ corresponding dioxolanes	0.5 + 6		10 + 1	3 + 9	0.5 + 12		14 + 0	9 + 6	14 + 0		5 + 12	
2-Butanone ⁺ corresponding dioxolanes	19 + 66		78 + 5	61 + 16	45 + 41		85.5 + 0	82 + 2	86.5 + 0		76.5 + 5	
3-Butene-2-ol			2									
Unidentified	8		2	6								

^a Calcined at 170°C.

^b Heat treated at 300°C.

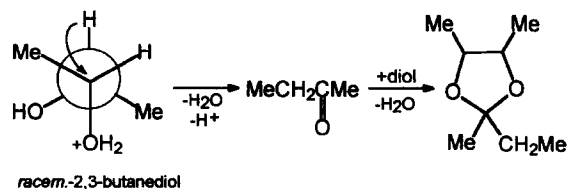
^c Heat treated (300°C) and etched with water.

^d 20% conversion.

^e 25% conversion.

S_{1n} = initial selectivity, S₅ and S₁₅ = selectivities after the addition of 5 g or 15 g of diol, respectively.

eropoly acid results in the formation of an amorphous heteropoly acid due to a strong interaction between the acid and the support. Subsequent water etching was found to remove the unchanged crystalline heteropoly acid. In the light of these observations, the decrease in the selectivity of dehydration may be attributed to the formation of mixed acid sites as a result of heat treatment. Water etching appears to ensure a more uniform active site distribution, though with lower activity. In sharp contrast, the activity of SiMo₁₂-on-silica after treatment at 170°C was markedly lower, and heat treatment at 300°C followed by water etching resulted in a completely inactive catalyst. DSC studies revealed a notable difference of the two heat-treated samples of PW₁₂-on-silica. An endothermic peak present at about 400°C after treatment at 170°C disappeared after high-temperature treatment. This may be indicative of the presence of a more stable surface species formed on PW₁₂-



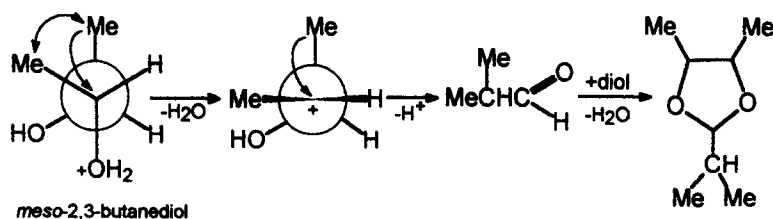
Scheme 1. The E2 transition state which indicates the favored hydride migration leading to the formation of 2-butanone in the dehydration of *racem.*-2,3-butanediol.

on-silica. In contrast, no similar phenomenon was observed with heat-treated SiMo₁₂-on-silica.

Interesting changes in selectivity were also observed in the dehydration of 2,3-butanediol. This compound yields 2-butanone with high selectivity under heterogeneous conditions (Table 3). In the homogeneous system, though the pinacol rearrangement was still the main reaction, the secondary transformation of carbonyl compounds with the unreacted starting diol led to the formation of dioxolanes (Table 3). The best selectivity was achieved with PW₁₂ under heterogeneous conditions. In the transformation of the individual isomers, the racemic compound exhibited the highest selectivity for ketone formation. This is attributed to a favorable transition state without Me–Me gauche interaction for hydride migration (Scheme 1), and the

Table 4
Selectivity of the dehydration of isomeric 2,3-butanediols in the presence of PW₁₂

	<i>meso</i>		<i>racemic</i>	
	MethI	MethII	MethI	MethII
1,3-Butadiene	1			
2-Methylpropanal + corresponding dioxolanes	1 + 39	0 + 3	21 + 0	4 + 0
2-Butanone + corresponding dioxolanes	53 + 3	32 + 63	79 + 0	96 + 0
Unidentified	3	2		



Scheme 2. The E1 transition state which indicates the favored methyl migration leading to the formation of 2-methylpropanal in the dehydration of *meso*-2,3-butanediol.

high migratory aptitude of the hydride anion [3]. In contrast, aldehyde formation from the *meso* isomer was found to be surprisingly high (Table 4). This was only observed in the presence of PW_{12} which is the strongest of the four acids. This indicates that in the transformation of the *meso* isomer an open carbocation may be involved. Once it is formed a significant relief from the unfavorable steric interaction of the methyl groups takes place resulting in an increased selectivity of 2-methylpropanal (Scheme 2).

The activity and stability of the supported heteropoly acids were also studied in the transformation of 2,3-butanediol. In prolonged catalytic tests, PW_{12} -on-silica samples after calcination at 170°C or 300°C exhibited very similar activities (Table 3). A slight change in selectiv-

ity, involving the appearance of dioxolanes in longer runs, however, is indicative of some deactivation. It seems certain that strong acidic sites involved in the pinacol rearrangement slowly lose their activity, whereas weaker sites are still able to catalyze acetal formation. The activity of the water-etched catalyst was significantly lower due to the removal of heteropoly acid from the support. The deactivation of $SiMo_{12}$ -on-silica was much more pronounced. A sharp decrease in conversion was observed after the transformation of 5 g of diol over the catalyst calcined at 170°C. Moreover, the heat-treated and water-etched catalysts exhibited only negligible activity.

Higher diol homologues (1,4-, 1,5- and 1,6-diols) can be dehydrated under either homogeneous or heterogeneous conditions to produce

Table 5
Selectivities of cyclodehydration of 1,4-, 1,5- and 1,6-diols

	$SiMo_{12}$		PMo_{12}	SiW_{12}	PW_{12}	
	MethI ^a	MethII			MethI	MethII
1,4-Butanediol	99	99	99	99	99	98
racem.-2,5-Hexanediol	100 ^b					
<i>meso</i> -2,5-Hexanediol	100 ^c				100 ^c	100 ^c
2,5-Dimethyl-2,5-hexanediol	98		96	92	99	
1,5-Pentanediol	100		100	100	99	
1,6-Hexanediol	94 ^d		92 ^e	92 ^f	93 ^g	

^a Reaction with 0.4 mol% of catalyst.

^b *cis*-2,5-Dimethyltetrahydrofuran.

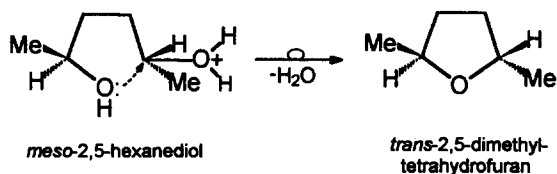
^c *trans*-2,5-Dimethyltetrahydrofuran.

^d 34% conversion; 4% 2-ethyltetrahydrofuran, 2% 2-methyltetrahydropyran, 88% oxacycloheptane.

^e 10% 2-ethyltetrahydrofuran, 12% 2-methyltetrahydropyran, 70% oxacycloheptane.

^f 14% 2-ethyltetrahydrofuran, 15% 2-methyltetrahydropyran, 63% oxacycloheptane.

^g 15% 2-ethyltetrahydrofuran, 14% 2-methyltetrahydropyran, 64% oxacycloheptane.



Scheme 3. The intramolecular S_N2 mechanism for the stereospecific cyclodehydration of *meso*-2,5-hexanediol to yield *trans*-2,5-dimethyltetrahydrofuran with inversion.

the corresponding cyclic ethers in high yield with excellent selectivity (Table 5). The only exception is 1,6-hexanediol, which, in addition to oxacycloheptane, yields five- and six-membered cyclic ethers. In this case, the weaker acid SiMo_{12} gives higher selectivity due to its limited ability to induce ring contraction through carbocationic processes. Cyclodehydration is the main reaction, even when 2,5-dimethyl-2,5-hexanediol is treated with heteropoly acids. This is unexpected since ditertiary 1,4- and 1,5-diols usually yield considerable amounts of dienes in the presence of mineral acids [11]. Cyclic ether formation is completely stereospecific, giving *cis*-2,5-dimethyltetrahydrofuran from racem.-2,5-hexanediol and *trans*-2,5-dimethyltetrahydrofuran from *meso*-2,5-hexanediol. This is in accordance with an intramolecular S_N2 mechanism (Scheme 3) and excludes the involvement of the open carbocation [12,13].

Working with SiMo_{12} we always encountered the formation of the well-known heteropoly blue. This is due to its susceptibility to reduction, resulting in slow deactivation. This phenomenon was more pronounced in the transformation of 1,2-diols where some of the products can easily be oxidized with concomitant reduction of the catalyst. In contrast, when applied in cyclodehydrations, SiMo_{12} maintained its activity for a much longer period since reduction in these systems is much slower. These observations indicate that, in agreement with literature findings [14], the activity of heteropoly blue in acid-catalyzed reactions is smaller than that of the parent heteropoly acid. This is attributed to the increased basicity of the

reduced heteropoly anion resulting in a decreased acidity.

4. Conclusion

Heteropoly acids are excellent catalysts in the dehydration of 1,2, 1,4-, 1,5- and 1,6-diols. 1,2-Diols undergo the pinacol rearrangement, whereas cyclodehydration is the main reaction for the other diols. The selectivity of these transformations increases with increasing acid strength. Heteropoly acids exhibit very similar activities and selectivities when used either under homogeneous conditions or in the heterogeneous form. In the homogeneous phase, however, secondary reactions can affect the selectivity.

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