

Catalysis of terpene rearrangements by zirconium phosphates and zirconium organo-substituted phosphonates

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Abstract

Vapour phase catalysis of the dehydration of cyclohexanol, nerol and geraniol and of the thermal rearrangement of α -pinene by unsubstituted zirconium phosphates has been compared with similar catalysis effected by organically pillared zirconium phosphates and with catalysis by alumina. Many of the observed differences in reaction rates can be rationalised by consideration of the acidity and surface area of the catalysts but, in a few cases, differences in reaction pathway appear to be related to the topography of the catalyst. An increase in the proportion of cyclic products from dehydration of nerol relative to that of geraniol can be attributed to attachment of an alcohol in a suitable conformation for cyclisation to a strongly acidic catalyst surface. In contrast, the formation of α -fenchene from α -pinene on the surface of a pillared catalyst cannot be explained by any simple relationship of this type; in this instance, the change is probably controlled by the stereochemistry of the catalyst at the reaction site. © 1998 Elsevier Science B.V.

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1. Introduction

Polymeric inorganic metal (IV) phosphates exist as layered structures containing both Brønsted and Lewis acid sites, which make them valuable for a number of acid-catalysed reactions such as dehydration, addition, isomerisation, polymerisation and alkylation [1a,1b]. Most of the phosphate-type catalysts used up to now have been simple metal phosphates. However, other studies on polymeric metal (IV) phosphates has led to development of alkyl- and

aryl-substituted phosphates and to covalently pillared phosphates. In these materials, the layers are held apart by pendant organic groups or by organic pillars [2]. These organo-substituted metal (IV) phosphates show considerable specificity towards intercalation and adsorption of a variety of organic molecules; they have been used for molecular recognition studies [3] but, to date, have found little use as catalysts. Relative to simple polymeric metal (IV) phosphates, those containing organic functionalities reduce the normally high thermal stability of the all inorganic compounds but compensate for this by affording increased surface areas available for catalysis. This is especially so for those organo-substituted materials in which the con-

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centration of pendant groups or pillars has been adjusted so as to produce cavities in the inter-layer regions. By changing the stereochemistry of the catalyst surface both externally and within the cavitated regions, stereocontrol of sorption of substrates should be possible so as to modify any reaction pathways open to a substrate. Because the surfaces and porosity of polymeric organo-substituted metal (IV) phosphates are readily and reproducibly modifiable during their preparation, the possibility is opened up for 'tailoring' a range of catalysts to suit specific reactions. The work described here represents first steps towards understanding this relationship between control of reaction pathway and stereochemical features of a range of simple and organo-substituted zirconium phosphates and phosphonates.

For this preliminary investigation, three simple reactions have been monitored for a range of catalyst structures. The first, dehydration of cyclohexanol, offers a simple, most basic standard since it yields either cyclohexene or methylcyclopentene; the latter more stable compound arises from a reactive intermediate which rearranges to the more stable cyclopentene. In addition to simple dehydration, the alcohols, nerol and geraniol, afford the possibility of cyclisation accompanying the expected dehydration. Acid-catalysed dehydration with rearrangement means that the stability of alkenes on these catalysts must be examined also and, to this end, variations to the known pathways for rearrangement of α -pinene were investigated. Rearrangement of α -pinene gives a complex mixture

of ring expanded products together with formation of monocyclic and acyclic materials. The range of products offers maximum scope for control of reaction pathways and hence selectivity by a catalyst [4]. The catalysts used in these studies were crystalline zirconium phosphate and amorphous polymeric zirconium salts of phosphoric acid and vinylphosphonic acid. Additionally, a series of pillared polymers was examined also: zirconium 4,4'-biphenyl-bis-phosphonate, zirconium 4,4'-biphenyl-bis-monophosphate, mixed zirconium 4,4'-biphenyl-bis-monophosphate/monohydrogenphosphate and mixed zirconium 4,4'-dimethylbiphenyl- α , α' -bis-phosphonate/monohydrogenphosphate.

2. Experimental

2.1. Characterisation of catalysts

The results of the various determinations are given in Table 1. Measurements of acid strength distribution were carried out by titration with butylamine. Immediately after drying them at 110°C, samples of catalyst (0.2 g) were suspended in petroleum ether (b.p. 60–80°C, dried over KOH and distilled; 2 ml) and titrated with a solution of butylamine (0.25 M), using as indicators benzalacetophenone ($pK_a = -5.6$), dicinnamylacetone ($pK_a = -3.0$), 4-dimethylaminoazobenzene ($pK_a = +3.3$) and methyl red ($pK_a = +4.8$). Surface areas were determined by a standard BET method on a Micrometrics 2000 instrument, using nitrogen as sorbent gas.

Table 1
Physical properties of catalysts

Catalyst ^a	Surface area (m ² /g)	Particle size (μ m)	Interlayer spacing (Å)	Amount of acid (meq/g)			
				$H_0 \leq 4.8$	$H_0 \leq 3.3$	$H_0 \leq -3.0$	$H_0 \leq -5.6$
ZrP (126:11)	8.4	1.0	7.6	6.88	0.17	0	0
ZrPA	278	45.7	—	1.67	0.98	0.58	0.39
ZrVPC	127	127	16.6	0.51	0.49	0	0
ZrBP/BOPA	90	52.6	13.3	2.08	1.61	0.51	0
ZrBP/PA	370	5.9	—	—	—	—	—

^aThe full names and abbreviations for the catalysts are given in Section 2.

Particle sizes were determined with a Malvern Particle sizer, using laser diffraction. X-ray powder spectra were recorded on a Phillips 1050 diffractometer, modified to computer controlled data acquisition by Hiltonbrooks.

2.2. Gas phase reactions

These were effected in a glass reactor tube (250 × 23 mm) in which catalyst (0.1 g; previously dried at 110°C for 16 h) was sprinkled over loosely-packed glass wool, the tube being shaken gently to distribute the powder as evenly as possible. The substrate to be examined (0.5 g) was placed in a two-necked flask maintained at 150°C and was swept through the reactor tube held at either 150 or 250°C in a flow of nitrogen gas (0.5 l/min); this gave a contact time of 15 s with a weight hourly space velocity of 150. Before entering the reactor tube, the gas stream with entrained substrate was preheated to 120°C. The products of reaction were collected first in a U-tube cooled to 0°C and then in a second U-tube cooled with liquid nitrogen. The trapped effluents were examined by GC or GC/MS, using an OV351 capillary column (25 m × 0.3 mm).

2.3. Preparation of zirconium catalysts

2.3.1. Amorphous zirconium phosphate (ZrPA)

This was prepared similarly to a previously described method [5]. Aqueous H₃PO₄ (54 ml; 54.2 g/l) was added rapidly to a well stirred aqueous solution of ZrOCl₂ · 8H₂O (55.6 ml; 129 g/l). After stirring the resulting gelatinous suspension for 15 min at room temperature, it was washed several times with large volumes of distilled water followed by decantation after allowing the suspension to settle out. Finally, the amorphous gel was centrifuged off and dried at 50°C. The product was converted entirely to its protonic form by immersion in aqueous HNO₃ (1 M) for 24 h. After centrifugation, the zirconium phosphate was washed several times with distilled water until the wash water reached pH 4–5. It was then dried at 110°C overnight.

2.3.2. Crystalline zirconium phosphate (ZrP[126:11])

Amorphous zirconium phosphate (2 g) was refluxed for 126 h in orthophosphoric acid (100 ml; 11M). The resulting crystalline phosphate was filtered and washed with distilled water until the filtrate reached pH 4–5; the residue was dried at 110°C overnight [6].

2.3.3. Zirconium bis-vinylphosphonate (ZrVPC)

To a solution of vinylphosphonic acid (CH₂:CHPO₃H₂; 7.2 g) in water (33 ml) was added with stirring a solution of ZrOCl₂ · 8H₂O (8 g) in water (53 ml). A white precipitate formed immediately. The reaction mixture was refluxed gently for 5 days and then cooled to room temperature [7]. The resulting solid was isolated by centrifugation, washed several times with distilled water and then acetone and was finally dried under vacuum (1 mm Hg) at 55°C to yield 55 g of product. Found: C, 14.9; H, 2.0; P, 19.1; Zr, 29.9. Calc. for ZrC₄H₆O₆P₂: C, 15.8; H 1.9; P, 20.4; Zr, 30.0%.

2.3.4. Zirconium 4,4'-biphenyl-bis-phosphonate (ZrBPA)

To a solution of 4,4'-biphenyl-bis-phosphonic acid (1 g) in HCl (50 ml of a solution containing 15 ml aqueous 9M HCl in 35 ml methanol) was added a solution of ZrOCl₂ · 8H₂O (0.7 g) in water (5 ml). The precipitate that formed immediately was stirred under gentle reflux for 2 h [8a,8b]. The reaction mixture was cooled to room temperature and centrifuged to give a white solid which was washed several times in distilled water and then acetone and was finally dried under vacuum (1 mm Hg) at 55°C to give a white solid (0.65 g); ν_{\max} 1389 cm⁻¹, characteristic of P–C stretching.

2.3.5. Zirconium 4,4'-biphenyl-bis-monophosphate (ZrBOPA)

To a solution of 4,4'-biphenyl-bis-monophosphate (1.06 g) in MeOH/H₂O 50 ml; 10:40 v/v) was added a solution of ZrOCl₂ · 8H₂O (0.62 g)

in water (5 ml). A white precipitate formed rapidly and the reaction mixture was refluxed gently for 2 h. After cooling the mixture to room temperature, the resulting solid was isolated by centrifugation and washing with water and acetone, as described above. After drying the solid at 1 mm Hg and 55°C overnight, the yield was 0.82 g; ν_{\max} 1496 cm^{-1} , characteristic of P–O–C stretching. Found: C, 32.9; H, 2.0; P, 13.8; Zr, 19.4. Calc. for $\text{ZrC}_{12}\text{H}_8\text{O}_8\text{P}_2$: C, 33.2; H 1.8; P, 14.3; Zr, 21.0%.

2.3.6. Zirconium (mixed) 4,4'-biphenyl-bis-phosphonate / 4,4'-biphenyl-bis-monophosphate (ZrBP / BOPA)

This was prepared as for ZrBPA and Zr-BOPA by adding a solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1.92 g) in water (10 ml) to a mixture of 4,4'-biphenyl-bis-monophosphate (1.25 g) in $\text{MeOH}/\text{H}_2\text{O}$ (50 ml; 10:40 v/v) and 4,4'-biphenyl-bis-phosphonic acid (1.37 g) in HCl (50 ml of a mixture of aqueous 9 M HCl:MeOH, 15:35 v/v) to give a white solid after refluxing, washing and drying, as above. Yield, 1.28 g; ν_{\max} 1389, 1496 cm^{-1} , characteristic of P–C and P–O–C stretching. Found: C, 31.3; H, 2.5; P, 12.4; Zr, 19.7. Calc. for $\text{ZrC}_{12}\text{H}_8\text{O}_7\text{P}_2$: C, 34.5; H 1.9; P, 14.8; Zr, 21.8%.

2.3.7. Zirconium (mixed) 4,4'-biphenyl-bis-phosphonate / bis-monohydrogenphosphate (ZrBP / PA)

This was prepared by selective hydrolysis of the phosphate linkages in the above mixed ZrBP/BOPA [9]. The latter (1.08 g) was refluxed with conc. HBr for 168 h to give a solid which was isolated by centrifugation. After washing it several times with distilled water and then acetone, the residual solid was dried at 1 mm Hg and 55°C overnight to yield a brown powder (0.89 g); ν_{\max} 1389 cm^{-1} , characteristic of P–C stretching and a small band at 1497 cm^{-1} due to some residual phosphate. Found: C, 24.1; H, 1.9; P, 12.4; Zr, 19.9. Calc. for $\text{ZrC}_6\text{H}_5\text{O}_7\text{P}_2$: C, 21.0; H 1.5; P, 18.1 Zr, 26.6%.

2.3.8. Zirconium (mixed) 4,4'-dimethyl- α,α' -bis-phosphonate / 4,4'-biphenyl-bis-monophosphate (ZrDP / BOPA)

To a mixture of 4,4'-biphenyl-bis-monophosphate (0.27 g) in $\text{MeOH}/\text{H}_2\text{O}$ (10 ml; 1:4 v/v) and 4,4'-dimethyl- α,α' -bis-phosphonic acid (0.28 g) in HCl (25 ml; aqueous 9M HCl:MeOH, 1:4 v/v) was added a solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.52 g) in water (5 ml), with stirring. The white precipitate that formed immediately was refluxed gently in the reaction medium for 2 h and then cooled to room temperature. The white solid was separated by centrifugation and washing with water and acetone as above for Zr-BOPA. On drying under vacuum at 55°C overnight, a white solid was isolated (0.62 g); ν_{\max} 1497 cm^{-1} , characteristic of P–O–C stretching. Found: C, 34.8; H, 3.0; P, 12.1; Zr, 19.4. $\text{ZrC}_{13}\text{H}_{10}\text{O}_7\text{P}_2$ requires C, 36.1; H 2.3; P, 14.3; Zr, 21.1%.

2.3.9. Zirconium (mixed) 4,4'-dimethylbiphenyl- α,α' -bis-phosphonate / bis-monohydrogenphosphate (ZrDP / PA)

This was prepared by hydrolysis of the above mixed phosphonate/phosphate (ZrDP/BOPA) by refluxing a sample (1.78 g) with conc. HBr for 168 h. After cooling the brown mixture to room temperature, the resulting solid was isolated by centrifugation and then washed with water to pH 5–6 before being washed with acetone and drying under vacuum at 55°C overnight. Yield 1.43 g; ν_{\max} 1497 cm^{-1} , characteristic of P–O–C stretching. Found: C, 28.3; H, 2.5; P, 14.3; Zr, 21.7. $\text{ZrC}_7\text{H}_7\text{O}_7\text{P}_2$ requires C, 23.6; H 2.0; P, 17.4; Zr, 25.6%.

2.3.10. 4,4'-Biphenyl-bis-phosphonic acid

A mixture of diethyl 4-iodobenzenephosphonate (1.96 g) and finely divided copper were heated to 240°C under argon for 4 h [10]. After cooling the mixture to room temperature, the resulting solid was ground with CH_2Cl_2 and filtered through a short column of Celite. After evaporation of the solvent from the

eluate, the residue was refluxed with HCl (10% aqueous) for 2 h. The resulting mixture was filtered and H₂S was passed in a slow stream through the filtrate to remove traces of copper salts as CuS which was filtered off. Evaporation of the solvent gave 4,4'-biphenyl-bis-phosphonic acid (0.6 g; 74% yield), m.p. > 300°C (lit. > 300°C [11]); λ_{\max} 263 nm; ν_{\max} 1389 cm⁻¹ (P–C stretch); Found: C, 45.1; H, 3.6; P, 20.9. Calc. for C₁₂H₁₂O₆P₂: C, 45.8; H, 3.8; P, 19.8%.

2.3.11. Diethyl 4-iodobenzenephosphonate

A mixture of 4-iodobenzenephosphonic acid (3.0 g) and triethyl formate (60 ml) was treated with a few drops of HBF₄ in Et₂O (54% w/v) and then refluxed for 18 h with stirring. Excess of triethyl formate and ethanol were evaporated off under vacuum to give residual diethyl 4-iodobenzenephosphonate (2.94 g; 83% yield), b.p. 131°C/0.31 mm Hg (lit. 105°C/0.15 mm Hg [12a,12b]); ¹H-NMR, δ (DMSO): 7.4 (2H, m), 7.75 (2H, m).

2.3.12. 4-Iodobenzenephosphonic acid [14]

Phosphanilic acid (5 g) was dissolved in HCl (5 M; 75 ml) and was diazotized at 0–5°C by addition of sodium nitrite (2 g) in water (15 ml) [13]. The resulting solution was reacted with KI (6 g) in water (30 ml). When the reaction had subsided, the mixture was heated to 95°C for 30 min, decolorized with aqueous sodium bisulphite and concentrated to 50 ml. On cooling the resulting solution, crude 4-iodobenzenephosphonic acid crystallized out (3.2 g) and was purified by redissolving it in aqueous sodium hydroxide and reprecipitating it with conc. HCl. The resulting solid was washed well with distilled water and dried over P₂O₅.

2.3.13. 4,4'-Biphenyl-bis-monophosphate

A solution of 4,4'-dihydroxybiphenyl (1.86 g) in pyridine (8 ml) was added slowly dropwise to a stirred ice-cold solution of POCl₃ (3 ml) in pyridine (30 ml). After stirring the mixture at room temperature for 30 min, the pyridine was

distilled off in vacuo and, after cooling, the residue was added to ice-water (40 ml). The solution was filtered and the filtrate was evaporated to dryness to give 4,4'-biphenyl-bis-monophosphate as a colourless solid (2.68 g; 77% yield) which was recrystallized from water, m.p. 300°C; ν_{\max} 1496 cm⁻¹ (P–O–C stretch); Found: C, 41.6; H, 3.4; P, 17.9. C₁₂H₁₂O₈P₂ requires C, 41.6 H, 3.4; P, 17.9%.

2.3.14. 4,4'-Dimethylbiphenyl- α,α' -bis-phosphonic acid

A mixture of α,α' -dibromo-4,4'-dimethylbiphenyl (1.7 g) and triisopropylphosphite (2.08 g) was heated at 150°C for 4 h during which isopropyl bromide steadily distilled out. The reaction mixture was then distilled (0.3 mm Hg) to remove excess of triisopropyl phosphite and the residue was hydrolysed by refluxing it for 18 h with conc. HCl (30 ml). The excess of HCl was distilled off to give a solid which was washed several times with distilled water and dried in vacuo (50°C, 1 mm Hg); 4,4'-dimethylbiphenyl- α,α' -bis-phosphonic acid was obtained by recrystallization from methanol, m.p. > 300°C. Found: C, 48.9; H, 4.6; P, 17.9. C₁₄H₁₆O₆P₂ requires C, 49.1; H, 4.6; P, 18.1%.

2.3.15. α,α' -Dibromo-4,4'-dimethylbiphenyl

A mixture of 4,4'-dimethylbiphenyl (1.3 g), *N*-bromosuccinimide (2.8 g) and benzoyl peroxide (50 mg) in CCl₄ (25 ml) was refluxed for 12 h. The hot mixture was filtered, the residue washed with CCl₄ and the filtrate was evaporated to give the required dibromo compound as a colourless solid (1.8 g; 76% yield) which was recrystallized from CCl₄, m.p. 141°C; ¹H-NMR δ (CCl₄): 4.6 (4H, s), 7.55 (8H, m).

2.3.16. 4,4'-Dimethylbiphenyl

A mixture of 4-iodotoluene (4.25 g) and copper powder (9.95 g) was heated at 240°C for 4 h under argon. The resulting solid was triturated with CH₂Cl₂ and filtered through Celite. Evaporation of the solvent from the filtrate gave crude 4,4'-dimethylbiphenyl (1.45 g; 82% yield),

m.p. 121°C (lit., 125°C [7]), $^1\text{H-NMR}$, $\delta(\text{DMSO})$: 2.35 (6H, s), 7.25 (4H, d), 7.52 (4H, d). Found: C, 92.2; H, 7.7. Calc. for $\text{C}_{14}\text{H}_{14}$: C, 92.3 H, 7.7%.

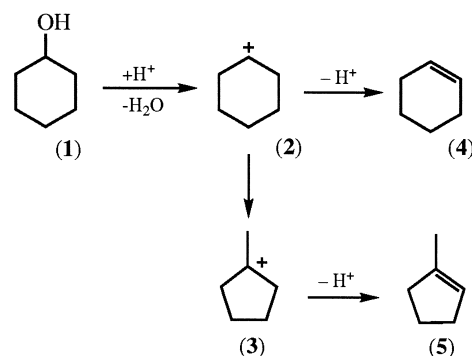
3. Results and discussion

3.1. Characterization of catalysts

The physical properties of the catalysts are summarised in Table 1. As might be expected for lamellar compounds, interlayer spacings as measured by powder X-ray diffraction analysis are considerably greater for the organically-substituted and pillared materials than they are for the purely inorganic phosphates. However, the apparent spacing for the bis-vinyl substituted phosphate seems to be greater than those of the pillared ones. Surface areas vary widely, possibly in relation to degree of crystallinity but the substituted and cavitated organically-substituted materials have considerably the largest values. Acidity measurements reveal amorphous zirconium phosphate as the most acidic and, as this also has a large surface area, it might be expected to be the most effective for acid-catalysed reactions although not necessarily selective. The γ -alumina was a commercial specimen (Spence type-H) and was used as a typical 'oxide' catalyst having basic and acidic sites with little or no shape selectivity towards dehydration.

3.2. Dehydration of cyclohexanol

This is the simplest reaction studied, having limited possibility of rearrangement of any intermediate carbocations produced by action of acid. Catalysed dehydration of cyclohexanol over zeolites gives cyclohexene as the only alkene and is frequently accompanied by significant dehydrogenation to cyclohexanone [13]. In the experiments described here, no cyclohexanone was observed to be formed and, sometimes, dehydration to cyclohexene was accom-



panied by rearrangement to methylcyclopentene. Amorphous zirconium phosphate (ZrPA) and the mixed zirconium 4,4'-biphenyl-bisphosphonate/bis-monohydrogen phosphate (ZrBP/PA) were the most efficient at converting cyclohexanol (1) into cyclohexene (4) and methylcyclopentene (5; Scheme 1). As can be seen from Table 2, without formal acidic sites, the organo-substituted phosphates and phosphonates (ZrVPC, ZrBP/BOPA) are much less efficient at converting cyclohexanol into alkene than are the ones containing only phosphate (ZrPA) or mixed phosphonate/phosphate (ZrBP/PA) or alumina itself, despite their larger surface areas. Interestingly, with the very crystalline zirconium phosphate (ZrP[126:11]), there is only a modest conversion into alkene compared with the amorphous variety (ZrPA), presumably again due to the smaller number of acidic sites per gramme of the former (and

Table 2
Products of dehydration of cyclohexanol^a

Catalyst ^b	Conversion of alcohol (%)	Proportion of alkene (%)	
		cyclohexene	methylcyclopentene
ZrP (126:11)	65	100	0
ZrPA	100	86	14
ZrVPC	13	100	0
ZrBP/BOPA	49	100	0
ZrBP/PA	100	98	2
Alumina	95	100	0

^aAt a flow rate of 0.2 l/min of N_2 .

^bThe full names and abbreviations for the catalysts appear in Section 2.

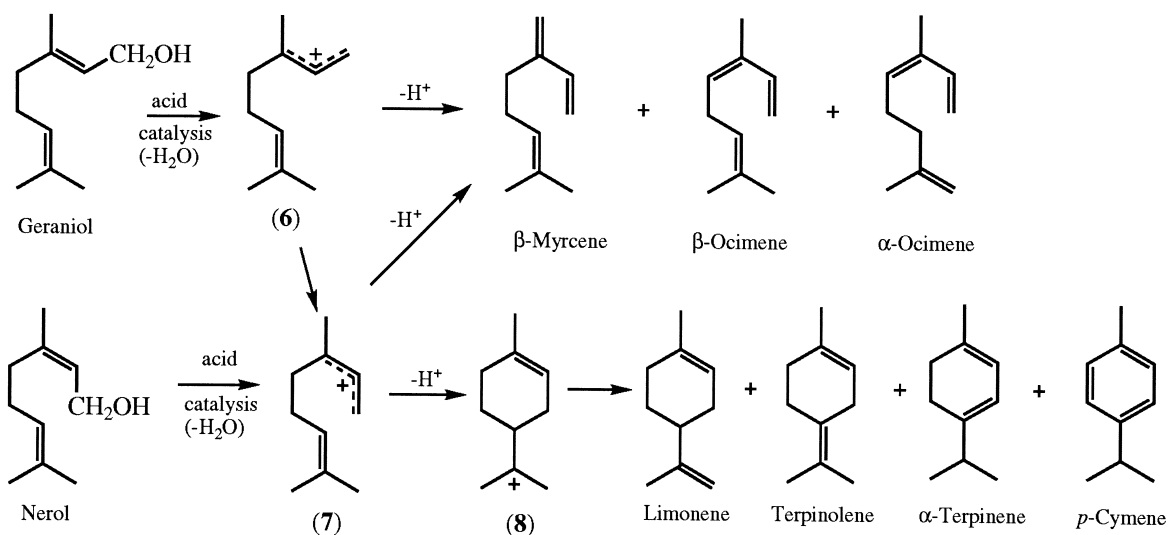
smaller surface area). The acidity of the catalyst appears to be the most important factor for the dehydration of a simple alcohol like cyclohexanol. As can be seen from Table 2, the most efficient conversion catalysts lead to greater formation of methylcyclopentene (ZrPA and ZrBP/PA). This reaction requires rearrangement of an initially formed cyclohexyl carbocation (**2**; Scheme 1) into a methylcyclopentyl carbocation (**3**). For the very acidic catalysts, the results suggest they are able to form definite carbocation species (**2**, **3**) on the surface. For the less efficient catalysts which show no evidence for rearrangement, dehydration probably simply involves a bimolecular elimination without formation of a formal carbocation, as in a solution phase E_2 reaction. An explanation of the observed difference based on different carbocation lifetimes on the catalyst surface seems unlikely as the cyclohexyl carbocation is known to undergo ring contraction very readily in solution [15].

3.3. Dehydration of geraniol and nerol

Geraniol and nerol are isomeric about the allylic double bond which is *E* for geraniol and *Z* for nerol (Scheme 2). Consequently, reactions

of geraniol derivatives in solution favour formation of acyclic products whereas reactions of nerol derivatives prefer to form monocyclic products [16a,16b]. The formation of such monocyclic products results from interaction of an allylic cation of correct orientation with respect to the other terminal trisubstituted bond (structure **7**). For steric reasons, this sort of interaction is not possible in the corresponding cation (**6**) formed from geraniol in which the allylic cation is orientated away from the other terminal double bond.

The catalysed gas phase dehydration of nerol and geraniol might be expected to be less selective than is the case for solvolysis because, at the higher temperatures involved, rotation and vibration in the allylic cations (**6**, **7**) will be more pronounced unless there is strong electronic interaction at the catalyst surface. The lack of steric differentiation between geraniol and nerol is apparent with dehydration carried out over alumina. Rotation of the neryl ion occurs to give the less hindered, and therefore more stable, geranyl ion. Thus, the dehydration product compositions are almost identical for both alcohols (Table 3). The ratio of acyclic to cyclic products for geraniol is 90:10 whilst for nerol it is similar at 86:13.



Scheme 2.

Table 3

Percentage proportions of products from the action of catalysts on geraniol and nerol

Monoterpene alcohol	Catalyst ^a	T ^b (°C)	Conversion of alcohol (%)	Composition of reaction products (% molar proportions) ^c									
				A	B	C	D	Total (A–D)	E	F	G	H	Total (E–H)
Geraniol	ZrP (126:11)	250	59	47	24	14	7	92	7	0	1	0	8
	ZrPA	150	97	41	19	25	2	87	7	3	3	0	13
	ZrBP/PA	250	97	48	16	21	2	87	8	0	5	0	13
	ZrDP/PA	250	77	51	16	21	5	93	6	0	1	0	7
	Alumina	250	91	55	13	19	3	90	8	0	2	0	10
Nerol	Zr (126:11)	250	48	33	4	16	4	57	31	2	8	0	41
	ZrPA	150	100	20	4	6	0	30	30	18	13	9	70
	ZrBP/PA	250	98	30	5	13	0	48	30	9	12	1	52
	ZrDP/PA	250	73	36	4	17	0	57	33	3	7	0	43
	Alumina	250	86	63	5	16	2	86	12	0	1	0	13

^aThe full names and abbreviations are given in Section 2.^bTemperature of main reactor tube (see Section 3); flow rate of N₂ was 0.5 l/min.^cA–D are acyclic products; E–H are monocyclic. A = β -myrcene, B = β -ocimene, C = α -ocimene, D = linalool, E = limonene, F = α -terpinene, G = terpinolene, H = *p*-cymen. And see Scheme 2. Any percentages not exactly adding to 100% are due to small rounding of errors.

When zirconium phosphates are used as catalysts, greater selectivity is observed. Thus, for geraniol, the ratio of acyclic to cyclic products averages about 90:10, identical to the result found with alumina but, for nerol, this ratio becomes about 50:50, very different from that found with alumina (Table 3). The selectivity of formation of individual products is similar over all of the zirconium catalysts for either geraniol (90:10) or nerol (50:50). This strongly indicates that the selectivity arises from geraniol or nerol being held at the catalyst surface in their ground-state conformations (*viz.*, little rotation occurs on the surface), perhaps because each of the substrates has two isolated double bonds and is bonded to the catalyst surface through *both* of them and not just through the allylic one. In this fashion, selectivity would be maintained, the preponderance of monocyclic products found for nerol compared with geraniol then being due to an allylic cation in close proximity to a second double bond in the molecule (7, Scheme 2).

The overall product compositions for dehydration of geraniol and nerol are shown in Scheme 2. For geraniol, there are no significant variations in the relative amounts of the prod-

ucts A–H for either the zirconium catalysts or for alumina (Table 3). The conversion is worst for the crystalline ZrP (126:11) but this is probably a reflection of its significantly smaller specific surface area compared with the other catalysts. Conversion of geraniol into products is high even at 150°C for the amorphous ZrPA with its large specific surface area and significant proportion of strongly acidic sites (Table 1). In contrast, ZrDP/PA, a cavitated material with acid sites expected from its method of preparation to be located mainly internally, gave much worse conversions than ZrPA even at the higher temperature of 250°C (Table 3). This adverse cavitation effect on the percentage conversion of geraniol is off-set in cavitated ZrBP/PA probably because of its very large surface area (Table 3). As in the simpler dehydration of cyclohexanol discussed in Section 3.2, the results indicate the importance of the method of preparation of the zirconium catalysts on their *efficiency* in converting geraniol into products but that there is little difference amongst them with regard to selectivity towards product composition, nor between them and alumina.

In contrast, the dehydration of nerol over the

Table 4
Percentage proportions of products from action of catalysts on α -pinene^a

Catalyst ^b	Conversion of α -pinene (%)	Composition of reaction products (%) ^c									
		M	N	O	P	Q	R	S	T	U	V
ZrP (126:11)	37	0	5	30	3	35	8	0	14	0	5
ZrPA	94	3	6	14	3	31	3	11	4	11	14
ZrVPC	24	0	8	29	8	42	0	4	0	8	0
ZrBP/BOPA	57	0	5	32	2	30	11	5	12	4	0
ZrBP/PA	94	14	3	26	1	15	16	7	8	6	3

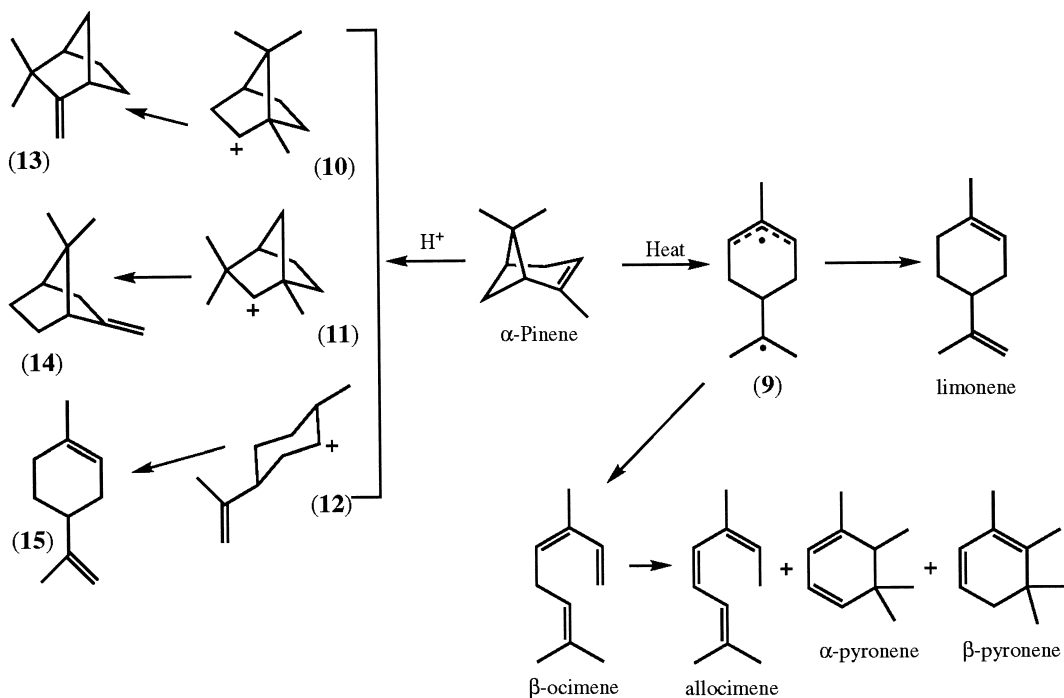
^a Reactor temperature, 300°C; flow rate of N₂ was 0.5 l/min.

^b The full names and abbreviations for the catalysts are given in Section 2.

^c The M = α -fenchene (skeleton **14**; Scheme 3); N = camphene; O = α -pyronene, P = β -pyronene (Scheme 2); Q = limonene, R = α -terpinene, S = γ -terpinene, T = terpinolene; U = isoterpinolene (from skeleton **15**; Scheme 2); V = *p*-cymene.

zirconium catalysts shows more variation in the product compositions which are also very different from those observed over alumina. Again, as for geraniol and cyclohexanol, conversion efficiencies are lowest for crystalline ZrP(126:11) and best for the more acidic amorphous material, ZrPA. Comparing nerol with geraniol, it seems clear that the acidity and surface areas of the catalysts govern efficiencies of conversion into dehydration products via a

carbocation mechanism as with cyclohexanol since the catalyst efficiencies (percentage conversions at equal flow rates and temperature) are very similar for both alcohols. However, it seems also clear that, on the surfaces of the zirconium catalysts, nerol and geraniol maintain a considerable degree of their steric integrity even at temperatures of 250°C when rotational and vibrational excitation could have been expected to have led to a common equilibrated



Scheme 3.

intermediate state. In marked contrast, over alumina there is no such differentiation, indicating that nerol must be able to rotate to an intermediate more like that formed from the thermochemically more stable geraniol. Such an effect is more likely if the other terminal trisubstituted double bond in nerol and geraniol is held strongly to a zirconium catalyst surface but not to alumina.

3.4. Rearrangement of α -pinene

The gas phase isomerization of α -pinene is complex (Table 4) and has been discussed earlier [4]. In the absence of a catalyst, the reaction proceeds through a diradical species (**9**; Scheme 3), yielding ocimene which then cyclises to the pyrenenes and limonene. In contrast, in the presence of an acid catalyst, α -pinene yields camphene (**13**) through intermediate (**10**; Scheme 3), fenchene (**14**) through intermediate (**11**; Scheme 3) and monocyclic terpenes such as limonene (**15**) via intermediate (**12**; Scheme 3).

It has been shown previously [4] that zirconium phosphate type catalysts show evidence for both radical and carbocation reactions, behaving as a 'surface' in the first and as an acid in the second. As might be expected, amorphous zirconium phosphate, being very acidic and having a large surface area, favours acid-catalysed reactions whereas the organo-substituted, formally non-acidic phosphates promote radical reactions. Precise analysis is not possible without further research because both radical and acid-catalysed routes give a common major product, limonene. The formation of α -fenchene over the cavitated ZrBP/PA is unexpected. In almost all cases of acid catalysed ring-expansion of α -pinene, formation of the camphene skeletal structure (**13**) proceeds through initial shift of the *gem*-dimethyl bridge to give cation (**10**) rather than a shift of the methylene bridge to yield a precursor (**11**) of the fenchene skeletal structure (**14**) (Table 4). This is in keeping with the greater electron donating effect of the *gem*-

dimethyl bridge compared with the methylene bridge. Of all the catalysts examined, including a series of zirconium, titanium and tin phosphates [17], cavitated ZrBP/PA is the only one to produce this effect and this is probably an example of the course of a reaction being influenced by the topography of the catalyst.

4. Conclusions

The results show that organo-substituted zirconium phosphates can produce effects that go beyond those expected from simple variations in acidity and/or surface area. It is likely that the conformation of the surface of ZrBP/PA or the existence cavities, affects the rate of rearrangement by controlling the orientation of the substrate or an intermediate or transition state. Since zirconium phosphates are easily and reproducibly modified by organo-substitution, they offer the possibility for 'tailoring' particular reactions.

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