

Synthesis of indole, benzofuran and benzothiophene by reaction of 2-anilinoethanol, 2-phenoxyethanol and 2-(phenylthio)ethanol on AlPO_4 and Pd/AlPO_4 catalysts

Jean Afxantidis ^{a,*}, Naima Bouchry ^b, Jean-Pierre Aune ^a

^a *Laboratoire de Synthèse Organique Industrielle, ENSSPICAM Université d'Aix-Marseille III 13397 Marseille, France*

^b *Département de Chimie, Faculté des Sciences d' El Jadida, Morocco*

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Abstract

The synthesis of indole, benzofuran and benzothiophene is possible from compounds of the general formula: $\Phi\text{-X-CH}_2\text{-CH}_2\text{-OH}$ ($\text{X} = \text{NH, O, S}$). The reaction of 2-anilinoethanol, 2-phenoxyethanol and 2-(phenylthio)ethanol on aluminium orthophosphate and palladium supported by aluminium orthophosphate catalysts was studied. The synthesis of benzothiophene over AlPO_4 was optimized by the response surface methodology. A possible mechanistic pathway involving an acid media cyclization is discussed.

Keywords: Aluminium orthophosphate; Anilinoethanol; Benzofuran; Benzothiophene; Indole; Palladium; Phenoxyethanol; Phenylthioethanol

1. Introduction

The synthesis of indole, benzofuran and benzothiophene has been intensively studied. These products can be obtained as depicted in Fig. 1 [1–3].

We have tried the synthesis of indole, benzofuran and benzothiophene by pyrolysis of 2-anilinoethanol, phenoxyethanol and 2-(phenylthio)ethanol, respectively. The heterocycles were obtained with low yields (5% of indole at 800°C, 2% of benzofuran at 950°C and 4% of benzothiophene at 850°C). In order to improve these results, we tried the heterogeneous catalysis by using AlPO_4 and Pd/AlPO_4 .

Aluminium orthophosphate catalysts (AlPO_4), have been used in a great number of reactions (isomerizations, polymerizations, oxidations, alcohol dehydrations and dehydrogenations and olefin alkylations) [4]. The syntheses of alkylindoles [5], benzofuran [6] and benzothiophene [7] have been studied in gas phase on aluminium orthophosphate, taking advantage of the great specific area, high acidity and oxidizing properties.

Aluminium orthophosphate, AlPO_4 , has also been studied as Ni [8], Pd [9,10], Pt [11] or Rh [12] support and applied to the catalysis of various reactions with excellent results.

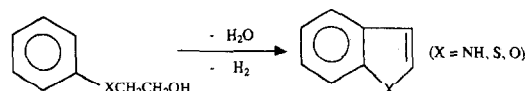


Fig. 1.

* Corresponding author.

On the other hand, the Pd supported catalyst (Pd/C) [13,14] was used in the synthesis of indole, and the best yield in indole from 2-anilinoethanol (75.3%) was obtained by gas phase reaction at 325°C.

2. Experimental

2.1. Chemicals

2-Anilinoethanol (bp 125°C/3 mmHg), 2-phenoxyethanol (bp 100°C/2 mmHg) and 2-(phenylthio)ethanol (bp 107°C/2 mmHg) are commercial products (Aldrich), used after distillation under reduced pressure.

Aluminium orthophosphate was obtained from a mixture of 116 g aluminium chloride hexahydrate, 32 ml 85% phosphoric acid and 180 ml distilled water. The catalyst was precipitated as a gel upon addition of ammonium hydroxide to pH 9. The mixture was left to stand for 12 h, then filtered and washed with isopropanol. The gel was left for 24 h in a drying oven at 120°C and calcined at 650°C for 3 h and the solid sieved. The particle diameter was $\leq 40 \mu\text{m}$.

Palladium supported by aluminium orthophosphate was obtained from a mixture of 1.1 g palladium chloride in 4 ml concentrated hydrogen chloride, 60 ml DMF and 20 g AlPO_4 . The resulting paste was placed in a drying oven at 120°C for 24 h. 2 g $\text{Pd}^{2+}/\text{AlPO}_4$ were treated for 1 h in 20 ml of refluxing cyclohexene. The mixture was filtered and the solid dried on vacuum.

The chemical analyses of Pd, P, Al and Cl were carried out at 'Service d'Analyse CNRS –Solaize –France'

The catalyst surface acidity and basicity were determined by UV spectrophotometric titration by using irreversible adsorption of cyclohexylamine ($\text{p}K_a = 10.6$; $\lambda \text{ max} = 220 \text{ nm}$) and benzoic acid ($\text{p}K_a = 4.19$; $\lambda \text{ max} = 275 \text{ nm}$) at room temperature [15,16] (Table 1). According to results of Marinas et al. [10], the number of acidic sites (as measured with cyclohexylamine) decreases when the metallic phase is incorporated onto the support. In addition it was reported [10] that the number of basic sites (as measured with *m*-nitrobenzoic acid) increased when Pd was incorporated onto $\text{AlPO}_4\text{-SiO}_2$, catalyst which gave the same results as AlPO_4 with regards to the decrease in acidity.

The textural properties of Pd/AlPO_4 and AlPO_4 were determined from the nitrogen adsorption-desorption at 77 K. Experimental data are collected in Table 1.

The metal surface area ($10 \text{ m}^2 \text{ g}^{-1} \text{ Pd}$, dispersion = 2%) of Pd supported catalyst was determined by hydrogen chemisorption performed at room temperature by using classical volumetric material; the solid was desorbed at 473 K before measurement by use of Benson's method [17].

2.2. Apparatus

The reactions were carried out in a stainless steel tubular reactor (length 270 mm, inner diameter 10 mm, volume 15.7 ml) placed in an oven and in which the catalyst in powder form and

Table 1
Textural properties of AlPO_4 and Pd/AlPO_4 catalysts

Catalyst	Al/P (mol)	S_{BET}^a ($\text{m}^2 \text{ g}^{-1}$)	S_t^b ($\text{m}^2 \text{ g}^{-1}$)	V_p^c ($\text{cm}^3 \text{ g}^{-1}$)	r_p^d (nm)	Basicity (mmol g^{-1})	Acidity (mmol g^{-1})	Pd (wt%)	Cl (wt%)
AlPO_4	1.1	178	155	0.935	10.5	0.45	0.71	–	0.056
Pd/AlPO_4	1.1	165	159	0.85	10.3	–	0.28	3	<0.2

^a Specific surface area (BET equation).

^b Determined by Boer's *t* curve.

^c Pore volume.

^d Mean pore radius ($r_p = 2V_p/S$) [18].

pieces of quartz were introduced. The starting materials were introduced with a peristaltic pump, nitrogen being used as carrier gas. The products were recovered in a flask cooled by a mixture of acetone and liquid nitrogen. The products of the gas phase were recovered in a bladder.

2.3. Analysis

The separation of the reaction mixture was performed by gas phase chromatography. We used a chromatograph equipped with a FID (250°C) and a 30 m DB1 capillary column with He (0.5 bar) as carrier gas. The injector temperature was 250°C and the selected temperature programs and gradients were 80°C–10 min, 6°C/min, 260°C–15 min. The analysis of benzonitrile and aniline was performed in the same conditions on a 30 m CP WAX capillary column. The identification of the reaction products was performed by coupling gas phase chromatography and mass spectrometry. The quantity of water produced by the reaction was determined by the Karl–Fischer method. Gaseous products were analyzed by gas phase chromatography on packed columns (carrier gas helium 1 bar, temperature program 50°C–5 min, 130°C–10 min, detector thermal conductivity 180°C, injector 80°C) for methane, carbon dioxide, acetylene, ethylene, ethane, ammonia (Porapak Q 2.5 m) and hydrogen sulfide (Porapak N 2 m) and on molecular sieves 3 m (carrier gas helium 1 bar, temperature program 40°C–5 min, 150°C–10 min, detector of thermal conductivity 180°C, injector 80°C) for oxygen, nitrogen and carbon monoxide.

3. Results

The response studied is the yield in benzoheterocycles Y .

$$Y = \frac{\text{Moles of benzoheterocycle obtained}}{\text{Moles of starting material injected}} \times 100$$

This yield is function of the selectivity S^1 and of the recovery efficiency R .

$$S = \frac{\text{Mass of benzoheterocycle obtained}}{\text{Mass of products recovered (liquid phase)}} \times 100$$

$$R = \frac{\text{Mass of products recovered}}{\text{Mass of starting material injected (liquid phase)}} \times 100$$

The factors influencing the results are the temperature, the nitrogen flow and the starting material flow. In order to vary the ratio mass of catalyst to mass of injected starting material ($M_{\text{cat}}/M_{\text{p}}$), we introduced a fixed quantity of catalyst (M_{cat}) in the reactor and varied the starting material flow, each reaction lasting 15 min.

Then we chose these three factors as experimental variables: T for temperature; N for nitrogen flow; D for starting material flow.

3.1. Heterocyclization over Pd/AlPO₄

The synthesis of indole and benzofuran were carried out over Pd/AlPO₄, and the results were compared with those obtained without catalyst. Since sulphur derivatives are a poison for palladium catalysts, the supported metal catalyst was not used in the cyclization of 2-(phenylthio)ethanol. Yields and selectivities in indole and benzofuran are collected in Table 2. The composition of reaction mixture is as follows:

Substrate	Products	
	Liquid phase	Gas phase
2-anilinoethanol	indole, aniline, toluene, styrene, benzonitrile, water, benzene	ammonia, carbon monoxide, carbon dioxide, methane, ethane, acetylene, ethylene
2-phenoxyethanol	phenol, benzofuran,	carbon monoxide, ethylene,

¹ Determined by GPC.

toluene, water, benzene, styrene	carbon dioxide, methane, ethane, acetylene
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Aniline (40–42%), ammonia and ethylene were the major products obtained from 2-anilinoethanol and phenol (47–45%) and ethylene were the major products obtained from 2-phenoxyethanol.

Those results show that the presence of supported catalyst does not improve yields and selectivities. In view of this, we shifted from Pd/AlPO₄ to AlPO₄.

3.2. Indole synthesis over AlPO₄

The reaction mixture of 2-anilinoethanol, at 750°C with a nitrogen flow of 3 l/h and a substrate flow of 52 g/h, over 1 g of AlPO₄ is as follows:

Liquid phase		Gaseous phase	
Products	Yield (%)	Products	Yield
benzene	10	carbon monoxide	traces
toluene	2	carbon dioxide	traces
styrene	3	methane	
benzotrile	5	ethane	
aniline	55	ethylene	major product
indole	2	acetylene	
water	5	ammonia	major product

The results in indole on aluminium orthophosphate are given in Table 3.

3.3. Benzofuran synthesis on AlPO₄

At 650°C, with a nitrogen flow of 8.25 l/h and a 2-phenoxyethanol flow of 51 g/h, on 0.7 g of AlPO₄, the reaction mixture holds the following products:

Liquid phase		Gaseous phase	
Products	Yield (%)	Products	Yield
benzene	7	carbon monoxide	traces
toluene	1	carbon dioxide	traces
styrene	3	methane	
phenol	50	ethane	
benzofuran	6	ethylene	major product
water	8	acetylene	

The results in benzofuran on aluminium orthophosphate are given in Table 4. By using AlPO₄ catalyst, the maximum yield in benzofuran (11%) is twice as high as that obtained without catalyst in the same conditions ($T=683^{\circ}\text{C}$, $N=6.5$ l/h, $D=73$ g/h, on 0.5 g of catalyst ($M_{\text{cat}}/M_{\text{p}}=0.04$)).

3.4. Benzothiophene synthesis

The reaction mixture of 2-(phenylthio)ethanol at 650°C, with a nitrogen flow of 8.25 l/h and a substrate flow of 130 g/h, on 0.5 g of AlPO₄ gives the following products:

Liquid phase		Gaseous phase	
Products	Yield (%)	Products	Yield
benzene	8	carbon monoxide	traces
toluene	2	carbon dioxide	traces
styrene	4	methane	
thiophenol	20	ethane	
benzothiophene	33	ethylene	major product
water	4	acetylene hydrogen sulfide	

Table 2
2-Anilinoethanol and 2-phenoxyethanol cyclization without catalyst and on Pd/AlPO₄

Substrate	Catalyst	<i>T</i> (°C)	<i>N</i> (l/h)	<i>D</i> (g/h)	<i>M</i> _{cat} (g)	<i>M</i> _{cat} / <i>M</i> _p	<i>Y</i> (%)	<i>S</i> (%)	<i>R</i> (%)
2-anilinoethanol	–	650	6.50	52	–	–	5	6	76
	Pd/AlPO ₄	650	8.25	14	0.50	0.14	4	4	73
	Pd/AlPO ₄	650	6.50	89	0.50	0.02	3	3	98
2-phenoxyethanol	–	683	6.50	73	–	–	5	6	74
	Pd/AlPO ₄	650	6.50	98	0.50	0.20	4	5	73
	Pd/AlPO ₄	550	8.25	53	0.50	0.04	3	3	98

Table 3
2-Anilinoethanol cyclization on AlPO₄, results in indole

<i>T</i> (°C)	<i>N</i> (l/h)	<i>D</i> (g/h)	<i>M</i> _{cat} (g)	<i>M</i> _{cat} / <i>M</i> _p	<i>Y</i> (%)	<i>S</i> (%)	<i>R</i> (%)
750	3.00	52	1.00	0.08	2	2	70
650	4.75	53	1.00	0.08	2	2	78
650	8.25	53	1.00	0.08	3	2	87
550	10.00	54	1.00	0.08	–	traces	87

Table 4
2-Phenoxyethanol cyclization on AlPO₄, results in benzofuran

<i>T</i> (°C)	<i>N</i> (l/h)	<i>D</i> (g/h)	<i>M</i> _{cat} (g)	<i>M</i> _{cat} / <i>M</i> _p	<i>Y</i> (%)	<i>S</i> (%)	<i>R</i> (%)
650	3.00	52	1.00	0.08	8	9	85
550	4.75	53	1.00	0.08	6	7	84
750	8.25	53	1.00	0.08	4	5	44
717	10.00	54	1.00	0.16	5	7	40
683	6.50	73	0.50	0.04	11	12	80
683	6.50	83	0.25	0.02	10	10	80

Table 5
Correspondence between the levels of the coded variables *X* and the values of the real variables *U*

levels of <i>X</i> ₁	–1	–0.5	0	0.5	1		
<i>U</i> ₁ = <i>N</i> (l/h)	4.75	6.50	8.25	10.00	11.75		
levels of <i>X</i> ₂	–0.866	–0.5774	–0.2887	0	0.2887	0.5774	0.866
<i>U</i> ₂ = <i>T</i> (°C)	550	583	617	650	683	717	750
levels of <i>X</i> ₃		–0.8165	0	0.8165			
<i>U</i> ₃ = <i>D</i> (g/h)		50	130	210			

The cyclization of 2-(phenylthio)ethanol gives benzothiophene with 33% yield, which is better than those observed in the syntheses of indole and benzofuran. This led us to study the 2-(phenylthio)ethanol cyclization by the surface response methodology using Doehlert's plans [18]. Doehlert's nettings present a uniform space distribution of the experimental points, all these points are equidistant and they are particularly useful when one wants either to study an experimental domain as a whole or to interpolate a response.

The region of interest has the following limits: 550°C ≤ *T* ≤ 750°C; 4.75 l/h ≤ *N* ≤ 11.75 l/h; 50 g/h ≤ *D* ≤ 210 g/h.

An interesting quality of those plans is the distinct number of levels occupied by the different variables. In this case, the first variable (*X*₁) occupies five levels, the second (*X*₂) seven and the last (*X*₃) three. The experimental constraints can lead to assign the fewest possible levels to one or several variables.

The precision of the measure is good for the temperature (less than 1% of measure error), but it is not so good for the nitrogen flow (2–3%) and for the substrate flow (3–4%). Thus we decided to attribute seven levels to the temperature (*X*₂), five to the nitrogen flow (*X*₁), three to the starting material flow (*X*₃).

The different values taken by the variables corresponding to the different levels of the plan are given in Table 5. The real variables *U* correspond to the variables *X* coded within –1 and +1.

As indicated previously, an invariable mass of catalyst (0.5 g) was introduced in the reactor,

Table 6
2-(Phenylthio)ethanol cyclization on AlPO_4 , results in benzothiophene

Exp. no.	T (°C)	N (l/h)	D (g/h)	M_{cat} (g)	M_{cat}/M_p	Y (%)	S (%)	R (%)
1	650	8.25	130	0.5	0.015	27	33	72
2	650	11.75	130	0.5	0.015	20	26	68
3	650	4.75	130	0.5	0.015	26	30	75
4	750	10.00	130	0.5	0.015	9	15	51
5	550	6.50	130	0.5	0.015	15	14	90
6	550	10.00	130	0.5	0.015	15	15	85
7	750	6.50	130	0.5	0.015	10	17	50
8	683	10.00	210	0.5	0.010	20	27	65
9	617	6.50	50	0.5	0.040	31	34	80
10	617	10.00	50	0.5	0.040	28	32	75
11	717	8.25	50	0.5	0.040	20	31	56
12	683	6.50	210	0.5	0.010	25	31	70
13	583	8.25	210	0.5	0.010	12	12	84

which allowed us to vary the ratio M_{cat}/M_p between 0.01 and 0.04. The repetition of the experience at the centre of the experimental domain gave the following results: $Y=28\%$, 26% , 28% ; $S=34\%$, 33% , 33% ; $R=74\%$, 72% , 75% .

The results in benzothiophene on aluminium orthophosphate are given in Table 6.

The calculations carried out using the NEM-ROD Logiciel [19] led to a theoretical maximum yield of 32.4% ($S=37\%$, $R=76.5\%$). This result was verified and we obtained an experimental yield of 31% ($S=35\%$, $R=75\%$) for the following conditions:

$X_1 = -0.234$, $U_1 = N = 7.4$ l/h; $X_2 = -0.276$, $U_2 = T = 618^\circ\text{C}$; $X_3 = -1$, $U_3 = D = 32$ g/h; over 0.5 g of catalyst.

The surface responses are presented in Fig. 2 and Fig. 3.

The total material balance of this reaction (including coke, liquid phase products and gases) is presented in Table 7.

3.5. Study of the catalytic activity evolution with time

In order to verify if there is no deactivation of the AlPO_4 catalyst during the synthesis of benzothiophene, a series of experiments was carried out with different reaction times under the optimal conditions. Experimental data are shown in Table 8.

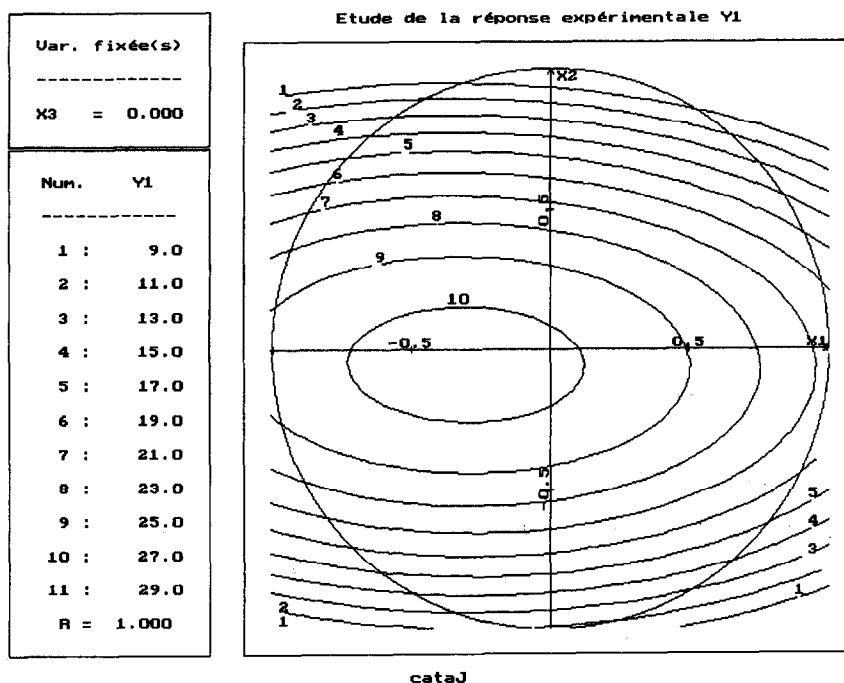


Fig. 2. Evolution of the benzothiophene yield (Y_1) in function of the temperature (X_2 in ordinate) and of the nitrogen flow (X_1 in abscissa) for a fixed starting material flow ($X_3=0.000$).

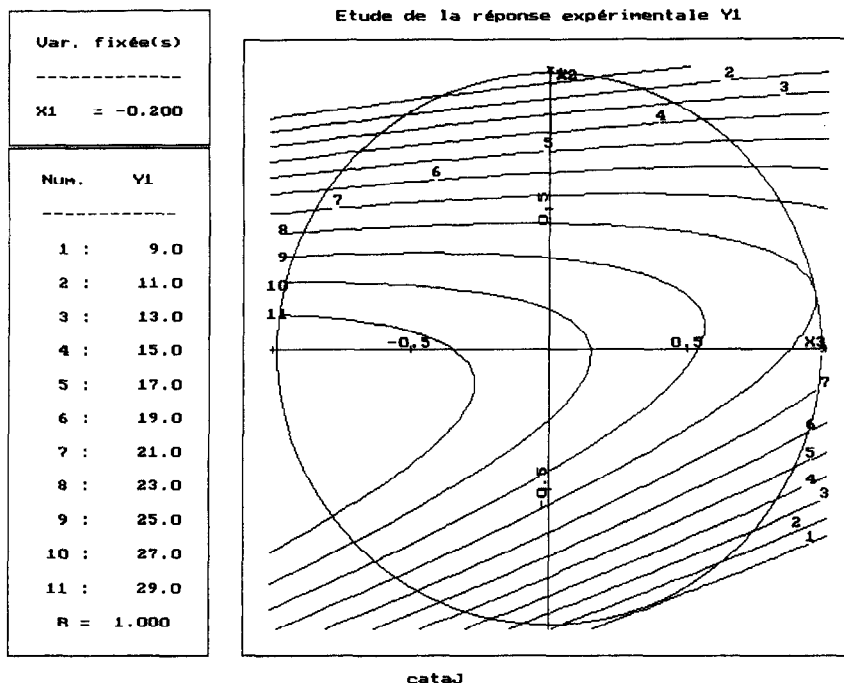


Fig. 3. Evolution of the benzothiophene yield (Y_1) in function of the temperature (X_2 in ordinate) and of the starting material flow (X_3 in abscissa) for a fixed nitrogen flow ($X_1 = -0.200$).

Table 7

2-(Phenylthio)ethanol cyclization over AlPO_4 , total material balance of the optimal reaction

Material	%
coke	4
benzene	7
toluene	1
styrene	2
thiophenol	16
benzothiophene	28
water	1
gases	16
heavy products and polymers	25

Table 8

Catalytic activity, evolution with time

Time (min)	R (%)
10	29
15	31
20	28
25	24
30	18

We notice that whereas the yields remain constant when the time reaction does not exceed 20

min, they rapidly decrease for longer reaction times. Esteban determined that there is no poisoning of the catalyst with aniline during the formation of indole derivatives [5]. Thus we can expect that this yield decrease is due to the coating of the catalyst surface by coke and no vaporizable heavy products and not to the saturation of the acid sites by basic heteroatomic species.

4. Discussion

Aluminium orthophosphate catalysts have often been used as acid catalysts [20–31]. Esteban [5,6] postulated that aluminium orthophosphate catalysts intervene by their Lewis acid sites during the formation of benzofuran from orthoalkylphenols and of indoles from aniline and carbonyl derivatives. The existence of oxidizing sites on the surface of the catalyst improves the yields in indolic compounds. On the other hand, aluminium orthophosphate catalysts have been used in alcohol dehydration [4,31].

Thus, according to these observations, we suggest an acid type mechanism which can proceed

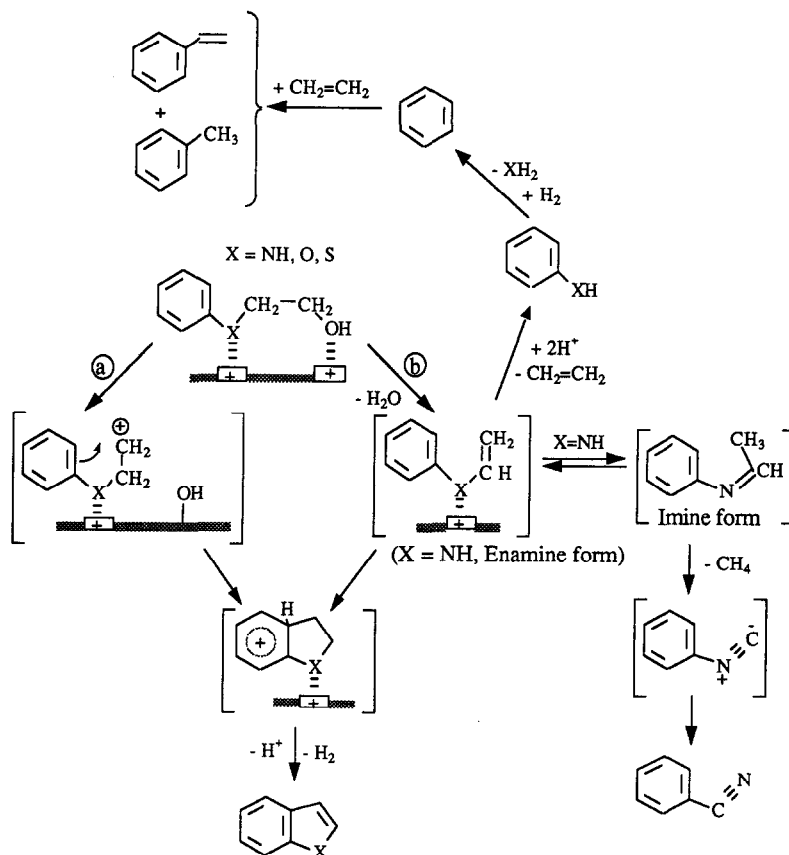


Fig. 4. Mechanistic path of the cyclization reaction.

on the Lewis acid sites either by direct formation of carbocation intermediate (pathway a), or by previous dehydration of the alcohol function into olefin (pathway b) (Fig. 4). In the reaction sequence, we can also consider the participation of the protons of the surface hydroxyl groups which are still present up to 800°C [20,22]. An alternative cause of the presence of the protons is the participation of the basic sites which can involve an abstraction of an H^+ from an adsorbed species (substrate or intermediates) during the reaction [27].

Pathway b can be compared to the mechanism proposed by Onikubo [32], who suggested that the oxidizing properties of the platinum-phthalocyanine catalyst were responsible for the formation of indole from *N*-ethyl aniline. Similarly, because AlPO_4 catalyst has not only acid sites, but also oxidizing sites on its surface [5], we can suggest that the enamine form gives indole after

dehydrogenation and the imine form gives a benzonitrile intermediate, which rearranges easily into benzonitrile at high temperature [33]. The absence of acetaldehyde and thioacetaldehyde in the mixtures resulting of 2-phenoxyethanol and 2-(phenylthio)ethanol can be explained by the fact that the presence of an intermediate comparable to the imine form is impossible in the case of the oxygenated or sulphurated products.

The gaseous products formation (ammonia, hydrogen sulfide and ethylene) can be attributed to the acidity of the catalyst, which has been successfully employed in cracking reactions [6,23].

The cyclization products yield difference can be explained by the capacity of the different heteroatoms to react with the acid sites of the catalyst. In the case of 2-anilinoethanol, the nitrogen atom has a more basic character than the oxygen atom of the alcohol group and so, it is likely to be more strongly adsorbed on the catalyst surface, which

induces the formation of aniline as main product. When the nitrogen atom is replaced by a sulphur atom (2-(phenylthio)ethanol) which is the least basic of the three heteroatoms and which is likely to be weakly adsorbed on the active sites, the yield in cyclization product increases. 2-Phenoxyethanol shows an intermediate behaviour.

Over Pd/AlPO₄ catalyst the yields and selectivities in heterocycles products were smaller than those observed over AlPO₄. This result could be attributed to the total acid site concentration² of Pd/AlPO₄, smaller than that of AlPO₄ only.

5. Conclusion

The catalytic activity of aluminium orthophosphate in the cyclization of the studied alcohols by formation of a carbon–aromatic carbon bond allows us to sensibly improve the yields in benzothiophene compared with those obtained without catalyst and to slightly improve those in benzofuran. On the other hand, the reaction of 2-anilinoethanol on this catalyst gives only low quantities of indole, the major product being aniline.

The use of Pd supported AlPO₄ catalyst does not improve these results. Indeed, it has a lower catalytic activity than solely the support, perhaps due to the decrease in its acidity.

We believe that the cyclization mechanism is of the Friedel–Crafts type. The difference in yield obtained for the three products can be explained by the difference in heteroatom basicity (N > O > S). The sulphur atom being the least basic, the alcohol function reacts preferentially and leads to quite a good yield in cyclization product.

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² Titration by using cyclohexylamine allows the total acid concentration to be determined but does not allow comparison of the strength of acidic sites.

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