

# Synthesis and characterization of 2,5-diphenyl-3,4-di(2-pyridyl)cyclopentadienone by thermal dehydration of 2,5-diphenyl-3,4-di(2-pyridyl)cyclopentandiolone in the presence of silica gel

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## Abstract

The compound, 2,5-diphenyl-3,4-di(2-pyridyl)cyclopentadienone (**2**), has been synthesized by thermal dehydration of 2,5-diphenyl-3,4-di(2-pyridyl)cyclopentandiolone (**1**) over silica gel under N<sub>2</sub> atmosphere at 200°C. The product (**2**), has been characterized by elemental analysis, IR, UV–VIS, and <sup>1</sup>H NMR spectroscopy. Thermal dehydration of (**1**) over silica gel has also been studied by TGA, DTG, and DSC. The effective kinetic and thermodynamic parameters of dehydration have been estimated, and a mechanism of dehydration from Brönsted sites on silica gel has been proposed. Comparative dehydration experiments using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ZnO, and NiSO<sub>4</sub> proved silica gel to be superior in converting compound (**1**) to (**2**). © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Catalytic dehydration; Silica gel; Diol; Diene; IR; UV–VIS; <sup>1</sup>H NMR; TG; DSC; Kinetics; Mechanism

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## 1. Introduction

Thermal dehydration of various compounds in high boiling solvents such as DMSO [1], ethylene glycol [2], and toluene [3], are usually accompanied by the difficulties of isolation and purification of the products. Newkom et al. [2] have synthesized the red diene (**2**) from the white diol (**1**) by carrying out the dehydration in refluxing ethylene glycol. Isolation and

purification of compound (**2**) from ethylene glycol is tedious and time consuming, although not impossible. This may be one of the reasons why spectral data on (**2**) are also limited.

Catalytic dehydration of alcohols by solid acids has received considerable attention in the past [4], and it has been pointed out that the basic properties of some solid acids play an important role in dehydration reaction [5]. The type and the number of acid sites on the catalyst are of key importance in determining the rate and the mechanism of dehydration process [6–9,19].

In this paper, we report the synthesis of the diene (**2**) by solid state thermal dehydration of the diol (**1**) over

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silica gel and the results of our TGA and DSC studies. The solid state dehydration, has the advantage of quick extraction and purification of the product, and the convenient use of (2) as a complexing agent for transition metal ions. Thermal dehydration of (1) over ZnO and NiSO<sub>4</sub> is very fast while in the case of Al<sub>2</sub>O<sub>3</sub> it is slow. The affinity of Zn<sup>2+</sup> and Ni<sup>2+</sup> to co-ordinate to the dehydration product (2), limits the possibility of using ZnO and NiSO<sub>4</sub> for this purpose. A dehydration mechanism involving Brønsted acid sites and formation of oxonium ion and carbonium ion intermediates is proposed. The spectral data on the product are also reported and discussed.

## 2. Experimental

### 2.1. Materials

The white diol (1), was prepared using a literature procedure [10]. Calculated (%) elemental composition for C<sub>27</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> were C, 76.76; H, 5.25; N, 6.63%. Found: C, 76.70; H, 5.22; N, 6.59%.

Silica gel 60 (70–230 mesh, Merck) was used for dehydration. All other reagents and solvents used were purchased from Fluka and Aldrich and used as received.

### 2.2. Physical measurements

UV–VIS absorption spectra were recorded on a HP 8450 diode-array spectrophotometer. Infrared spectra were recorded in KBr pellets with a Perkin–Elmer Paragon 1000 FT-IR instrument. <sup>1</sup>H NMR spectra were obtained using a Bruker AC-P 200 MHz spectrometer. Elemental analyses were performed by using a Heraeus CHN-O-RAPID elemental analyzer.

TGA and DSC were performed using a Mettler TA 4000 thermal analyzer (TG 50, DSC 25). The thermal analyzer was equipped with data acquisition and handling system (Mettler Graphware TA 72 PS.5). Experiments were carried out in a dynamic atmosphere (20 cm<sup>3</sup> min<sup>-1</sup>) of nitrogen. TG curves were recorded by heating to 300°C at six different heating rates ( $\theta=5, 10, 12, 15, 18, 20$  K min<sup>-1</sup>) using equivalent weights (ca. 10–13 mg) of a homogenized mixture of the diol (1), and silica gel (1:2 ratio). DSC curves were recorded by heating similar samples (ca.

20 mg) to 400°C, and the enthalpy of dehydration was determined from the peak area. Indium was used as reference to calibrate the temperature and heat flow.

### 2.3. Preparation of the red diene (2)

A homogenized mixture of 84.5 mg (0.2 mmol) of the white diol (1), and 850 mg of silica gel, was heated at 200°C in a furnace equipped with nitrogen gas inlet for 20 min. The reaction mixture was then cooled to room temperature and the product was extracted using 60 cm<sup>3</sup> of diethyl ether. Slow evaporation of the solvent under vacuum gave 66.5 mg of red fine crystals of (2). Yield: 86%. Calculated elemental analysis for C<sub>27</sub>H<sub>18</sub>N<sub>2</sub>O were C, 83.90; H, 4.70; N, 7.25%. Found: C, 84.1; H, 4.65; N, 7.20%.

## 3. Results and discussion

### 3.1. Spectroscopic studies

Thermal dehydration of the white diol (1), was accompanied by remarkable changes in the IR spectrum, most notably in the 3500–1400 cm<sup>-1</sup> region (Fig. 1). The broad band due to the OH stretching vibration disappeared upon dehydration. The shift in C=O stretching frequency from 1735 cm<sup>-1</sup> in the white diol to 1715 cm<sup>-1</sup> in the red diene (2), indicate that C=O group was involved in a delocalized conjugated system. The IR spectrum of white diol shows bands due to the stretching vibrations of C=N at 1592 cm<sup>-1</sup> and C=C at 1450 cm<sup>-1</sup> which are shifted in the red diene to 1581 and 1440 cm<sup>-1</sup>, respectively, indicating increase in conjugation.

Fig. 2 shows the UV–VIS spectrum of the dehydration product (2). Compound (1) was a white solid with absorption bands at 262 nm (log  $\epsilon=3.891$ ) and 212 nm (log  $\epsilon=4.186$ ) in acetonitrile, whereas the dehydration product was a deep red solid with (in acetonitrile) a strong absorption band at 492 nm (log  $\epsilon=3.067$ ) in addition to the bands at 324 nm (log  $\epsilon=3.700$ ), 258 nm (log  $\epsilon=4.303$ ), and 210 nm (log  $\epsilon=4.228$ ). These absorption maxima are red shifted and their molar absorption coefficients ( $\epsilon$ ), are increased by adding acid to the solution. The observed changes are in accord with the increase in the delocalization of the  $\pi$ -electron system upon protonation of the pyridine moieties.

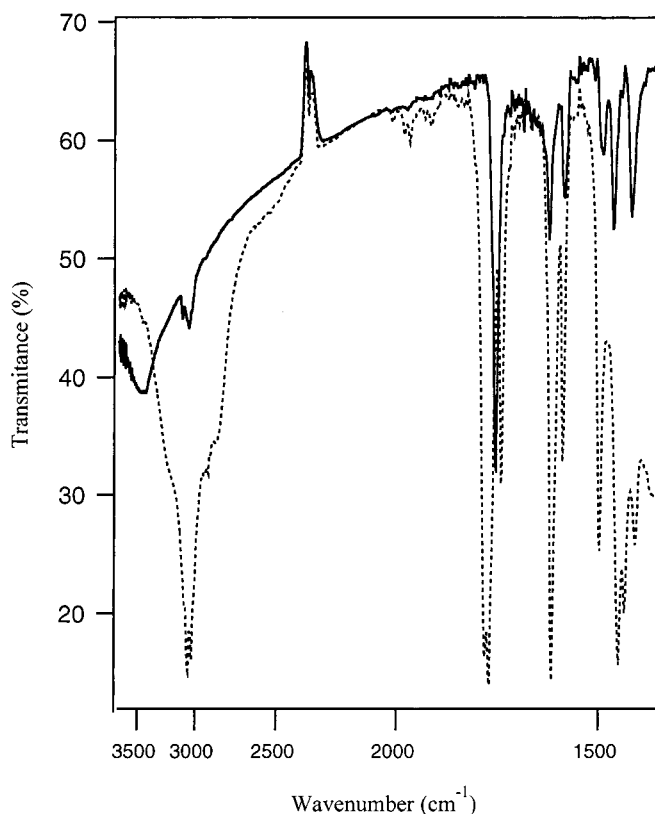
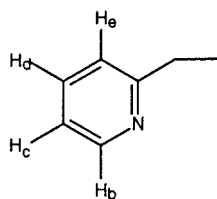


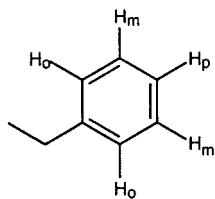
Fig. 1. Infrared spectra of diol (1), - - - - and diene (2), — in the 4000–1500  $\text{cm}^{-1}$  region.

Room temperature  $^1\text{H}$  NMR spectrum of the diol (1), and dehydration product (2) are consistent with expectations. Three types of protons are characterized in the spectrum of the starting diol (1). The two protons on the five-membered ring, appearing as a singlet at 5.05 ppm ( $2\text{H}_a$ , Scheme 1), the protons of the two phenyl rings, which appear as a multiplet at 7.1–7.3 ppm, and the protons belonging to the pyridine rings, showing a doublet at 8.45 ppm ( $2\text{H}_b$ ), a triplet at 7.72 ppm ( $2\text{H}_d$ ), a doublet at

7.42 ppm ( $2\text{H}_c$ ), and a triplet at about 7.2 ppm ( $2\text{H}_e$ ), which have some overlap with the phenyl protons. The most remarkable change that takes place in the  $^1\text{H}$  NMR spectrum upon dehydration is the disappearance of the singlet at 5.05 ppm due to the elimination of the  $\text{H}_a$  atoms on the five-membered ring in the dehydration process (Scheme 1). In addition, there is some shift to higher fields of the pyridine protons due to the increase in the degree of conjugation which results in more shielding of these protons. As a result, some overlapping of the signals from pyridine and those from phenyl protons is observed in the  $^1\text{H}$  NMR spectrum of the diene. In fact, only one doublet at 8.32 ppm ( $2\text{H}_b$ ) and one triplet at 7.57 ppm ( $2\text{H}_d$ ), of the pyridine protons are well resolved. Other pyridine protons along with those from the phenyl rings appear at 7.1–7.3 ppm. The complexity in the  $^1\text{H}$  NMR spectrum of the diene can be resolved by adding a few drops of DCl to the NMR solution. In fact in the NMR spectrum



py



ph

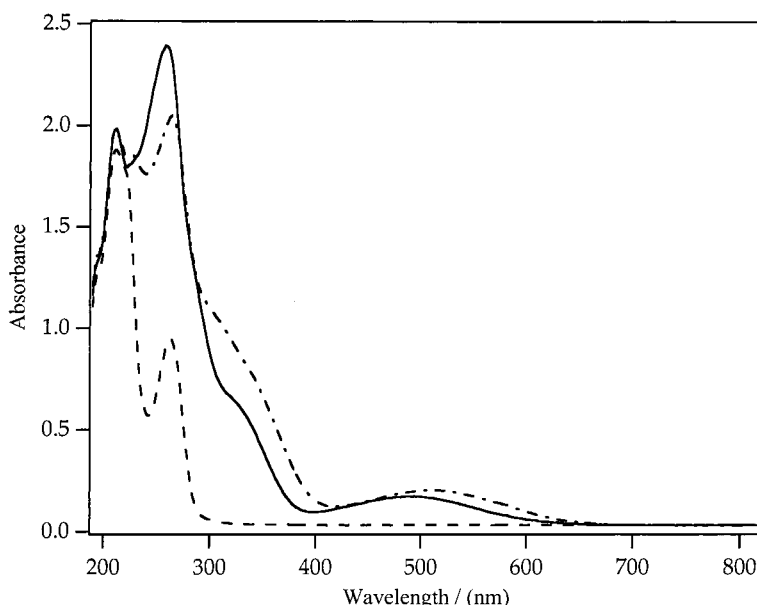


Fig. 2. UV-VIS spectra of diol (1), - - - -; diene (2), —; and the perchlorate salt of (2), - · - · - · in acetonitrile.

of the perchlorate salt of compound (2), pyridine protons appear at 8.62 ppm ( $2H_b$ , d), 8.45 ppm ( $2H_d$ , t), 7.99 ppm ( $2H_c$ , t), and 7.68 ppm ( $2H_e$ , d). The protons of phenyl rings appear at 7.45 ppm ( $4H_o$ , d), 7.40 ppm ( $2H_p$ , t), and 7.22 ppm ( $4H_m$ , t).

### 3.2. TA studies

Fig. 3 displays the TG, DTG, and DSC curves of the reaction mixture obtained at heating rate  $\theta=20 \text{ K min}^{-1}$ , under  $N_2$  atmosphere. Similar curves were obtained for other heating rates. The TG curve displays three steps. The first, between 40 and  $120^\circ\text{C}$ , belongs to the loss of water from meso-

pores of silica gel [11], which correlates well with the blank, Fig. 4. The second step between 150 and  $250^\circ\text{C}$ , is associated with 2.87% mass loss which is attributed to the dehydration of the diol ( $-2H_2O \cong 2.84\%$ ), Scheme 1. The third step beginning at about  $250^\circ\text{C}$  belongs to the decomposition of the red product.

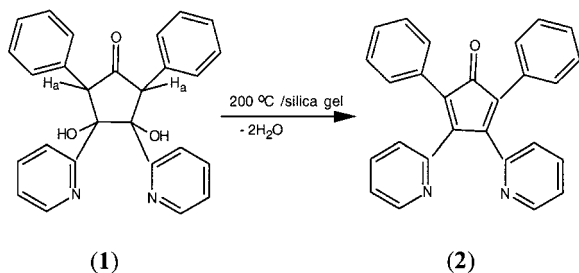
In order to estimate the activation energy of the dehydration process, the temperatures ( $T_m$ ) at maximum weight loss (TG) in the dehydration process were determined as a function of heating rate ( $\theta$ ) applied from the thermoanalytical curves. The effective activation energy ( $E_a=176 \text{ kJ mol}^{-1}$ ) was directly estimated [12] from the slope of the graph of  $\log \theta$  against  $1/T_m$  (Fig. 5) according to Eq. (1)

$$E_a = -2.303 R \left[ \frac{d(\log \theta)}{d(1/T_m)} \right] \quad (1)$$

Assuming a first order kinetic [13], and using Eq. (2)

$$\log \left[ \frac{-\log(1-\alpha)}{T_m^2} \right] = \log \frac{AR}{\theta E_a} - \frac{E_a}{2.3RT_m} \quad (2)$$

the pre-exponential factor was calculated,  $\log A=25$ , where  $\alpha$  is the degree of conversion for dehydration



Scheme 1.

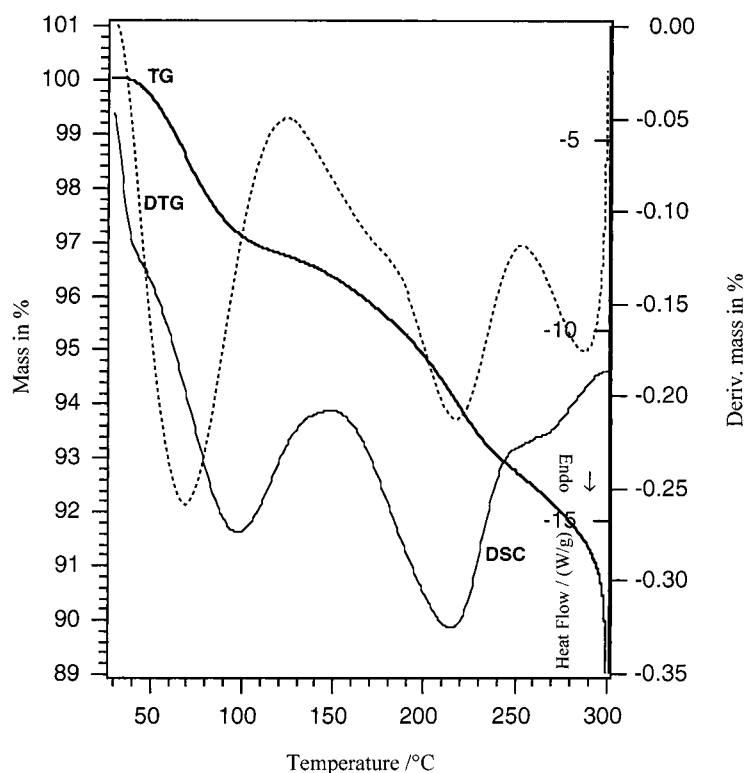


Fig. 3. TG, DTG, and DSC curves of the dehydration of diol (**1**), at a heating rate of  $10^{\circ}\text{C min}^{-1}$  under a dynamic atmosphere ( $20\text{ ml min}^{-1}$ ) of  $\text{N}_2$ .

and  $R$  the gas constant ( $8.314\text{ J mol}^{-1}\text{ K}^{-1}$ ). The global activation energy of dehydration of diol (**1**) is lower, by about  $50\text{ kJ mol}^{-1}$ , than that [8,19] for the conversion of two moles of 2-propanol or *t*-butanol to the corresponding alkene (176 versus  $2 \times 113\text{ kJ}$ ). Assuming that the release of two water molecules from diol (**1**), in dehydration reaction is a concerted process within the time scale of TG and DSC analysis, this difference can be attributed to a negative contribution to  $E_a$  from the resonance energy of the conjugated product. A relatively high effective dehydration rate,  $k=2.14 \times 10^6\text{ s}^{-1}$  calculated from Arrhenius equation,  $k = Ae^{-E_a/RT}$ , is also in accord with the expectation.

The DSC curve consist of two well defined endothermic reaction steps, Fig. 3. The first is due to the release of water from the mesopores of silica gel, and the second corresponds to the dehydration of diol (**1**). From the peak area of the DSC curve, the effective enthalpy change,  $\Delta H$ , is equal to

$76.8\text{ kJ mol}^{-1}$ . This value is less positive than those for similar cases such as dehydration of *t*-butanol [14]. Using equation  $C_p = \Delta H / \Delta T$  [14],  $C_p$  was calculated to be  $825.5\text{ J mol}^{-1}\text{ K}^{-1}$ . The global entropy of dehydration,  $\Delta S = 161.7\text{ J mol}^{-1}\text{ K}^{-1}$ , was calculated from equation  $\Delta S = 2.303 C_p \log(T_2/T_1)$  [15]. This value is in accord with the expectation for a less ordered product comparing to the starting material, and loss of water in the reaction.

### 3.3. Mechanism of dehydration

The reaction mechanism is discussed in the light of the observed activity of the dehydration catalysts. The following two are well known mechanisms of olefin formation from alcohols ( $\text{R-CHOH-CH}_3$ , for example); one consists of oxonium ion and carbonium ion as reaction intermediates [16] represented by Eq. (3), and the other is an acid-base concerted reaction [17], represented by Eq. (4).

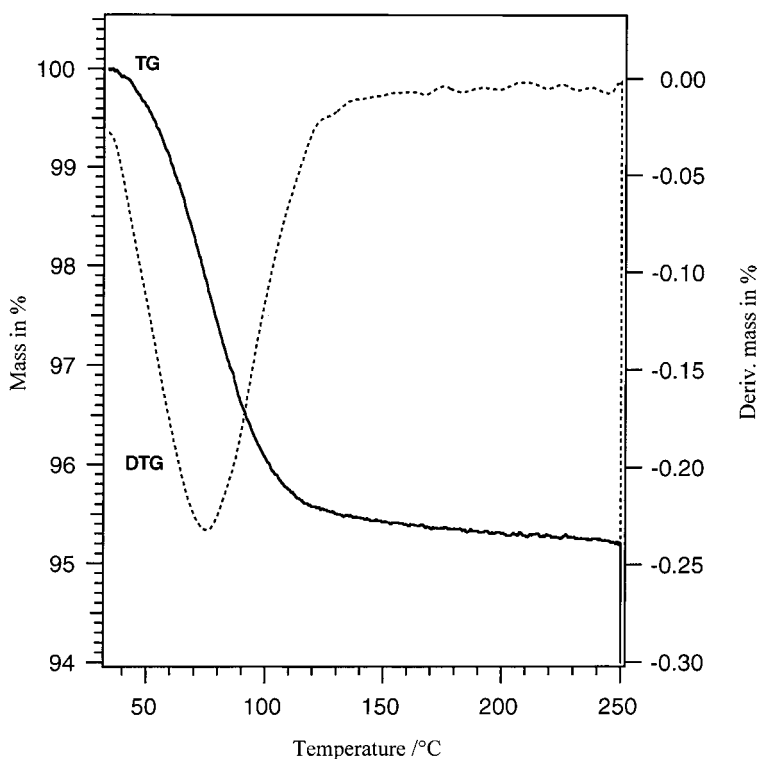
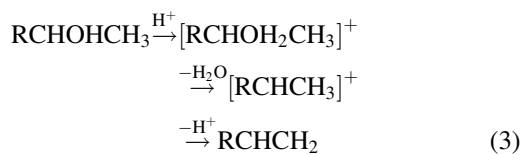


Fig. 4. TG and DTG curves of silica gel at a heating rate of  $10^{\circ}\text{C min}^{-1}$  under a dynamic atmosphere ( $20\text{ ml min}^{-1}$ ) of  $\text{N}_2$ .



Eq. (3) includes an alkoxonium ion  $[\text{RCHOH}_2\text{CH}_3]^+$  and a carbonium ion  $[\text{RCHCH}_3]^+$ , and the reaction is catalyzed by a Brönsted acid. In Eq. (4) the C–O and C–H bonds of alcohol break simultaneously to eliminate a hydroxy ion and a proton. The latter is effectively catalyzed by solid catalysts such as  $\text{Al}_2\text{O}_3$  which has both Lewis acidity and basicity. A third reaction path can also be speculated, consisting of adsorption of alcohol on Lewis acid sites, elimination of  $\text{OH}^-$  to form a carbonium ion, and formation of olefin by elimination of a proton.

The alkoxonium-carbonium ion mechanism in Eq. (3) represents a reaction catalyzed by Brönsted acid.

The dehydration of secondary alcohols over  $\text{SiO}_2$  proceeds by this path. The concerted mechanism represented by Eq. (4), and the third mechanism, in which a carbonium ion is initially formed by abstraction of  $\text{OH}^-$  followed by elimination of a proton, are more probable when the Lewis acidity is strong. The dehydration of alcohols over  $\text{Al}_2\text{O}_3$  proceed via either of the last two mechanisms due to the concerted action of Lewis acid sites and basic sites. In the case of  $\text{Al}_2\text{O}_3$ , an alternative mechanism of dehydration with an alkoxide intermediate from an alcohol molecule and an aluminum atom on the surface has also been reported [4].

The acid strength and the type of acid sites in silica gel,  $\text{ZnO}$ ,  $\text{NiSO}_4$ , and  $\text{Al}_2\text{O}_3$ , which we have used as dehydration catalysts, are different [17], therefore showing different catalytic activities. The fact that silica gel,  $\text{ZnO}$ , and  $\text{NiSO}_4$  act much more effectively in the conversion of the diol (**1**), to the diene (**2**), than  $\text{Al}_2\text{O}_3$ , indicates that the Brönsted acid sites are active in the dehydration reaction. The pyridine rings of (**1**)

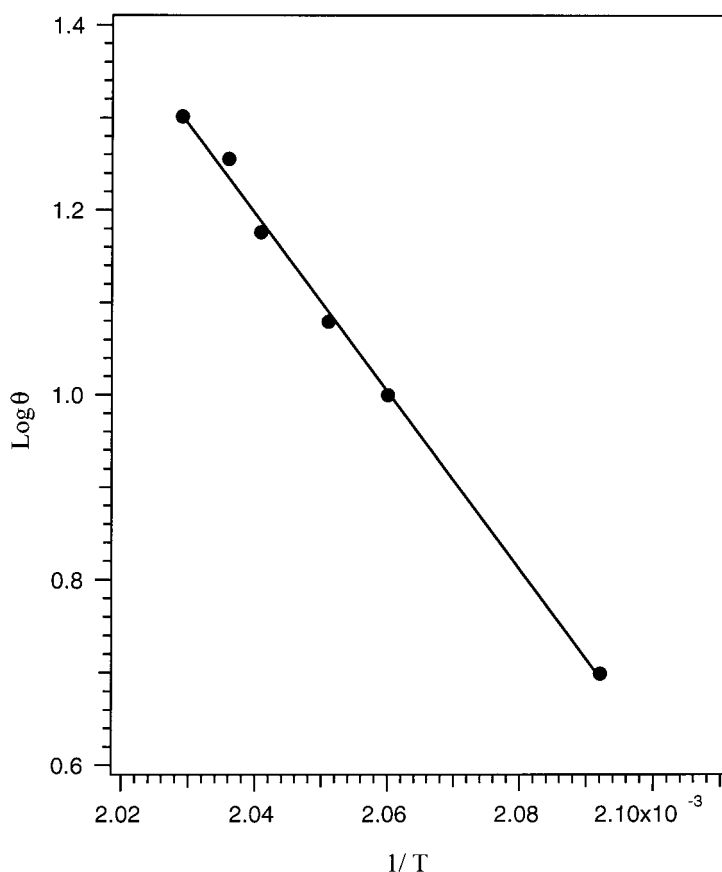


Fig. 5. Log  $\theta$  versus  $1/T$  plot for thermal dehydration of diol (1).

which have a more prominent poisoning effect on the Brønsted acid sites of  $\gamma$ - $\text{Al}_2\text{O}_3$  [18], play a retarding role on the dehydration by  $\text{Al}_2\text{O}_3$ , while the chelate effect in forming a co-ordination compound between the product (2), and  $\text{M}^{2+}$  metal ion, has an accelerating effect for  $\text{ZnO}$  and  $\text{NiSO}_4$ . The ease of dehydration by  $\text{ZnO}$ , and  $\text{NiSO}_4$  is, however, overwhelmed by the difficulties of releasing the diene (2), from  $[\text{Zn}(\text{2})_2]^{2+}$ , or  $[\text{Ni}(\text{2})\text{O}_2\text{SO}_2]$  complexes. Therefore, silica gel, with a remarkable performance in the dehydration process, is the catalyst of choice for the conversion of (1) to (2).

#### 4. Conclusions

A new method has been developed for the synthesis of 2,5-diphenyl-3,4-di(2-pyridyl)cyclopentadienone

with high efficiency, (86%), based on the solid state dehydration of its diol precursor over silica gel at  $200^\circ\text{C}$  under nitrogen atmosphere. The ease of extraction and purification of the product has made it possible to measure its spectroscopic properties. Considering the active role of Brønsted acid sites on silica gel in the dehydration process, a reaction mechanism consisting of an alkoxonium ion and a carbonium ion is proposed.

The TG and DSC analysis of dehydration process indicates that efficient conversion of the diol (1) to diene (2) takes place between  $170$  and  $235^\circ\text{C}$  without any risk of decomposition of the product. The mass loss for this endothermic process is in accordance with the expectation of  $-2\text{H}_2\text{O}$ . The low activation energy for diol dehydration indicates a significant contribution to the activated complex from the delocalized  $\pi$  system.

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