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*Research paper*

## Catalytic Debenzylation of 2,4,6,8,10,12-Hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.0.<sup>3,11</sup>0<sup>5,9</sup>] Dodecane with Pd(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> in a Batch Suspension Reactor and Optimization of the Reaction Parameters *via* the Taguchi Method

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**Abstract:** In this paper, the Taguchi method was used for the optimization of the reaction parameters for the synthesis of 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazatetracyclo[5,5,0,0<sup>3,11</sup>,0<sup>5,9</sup>]dodecane in the presence of Pd(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst in a batch suspension reactor. In order to achieve optimal conditions for this reaction, the experimental studies were conducted under varying reaction parameters, such as temperature, pressure, catalyst to substrate weight ratio, reaction time, and co-catalyst amount. The setting of the reaction parameters was determined in Qualitek-4 (Nutek<sup>®</sup>) software using the Taguchi experimental design method. Identification of the significant factors and their attributed levels in the Taguchi method were statistically performed *via* the analysis of variance (ANOVA) technique.

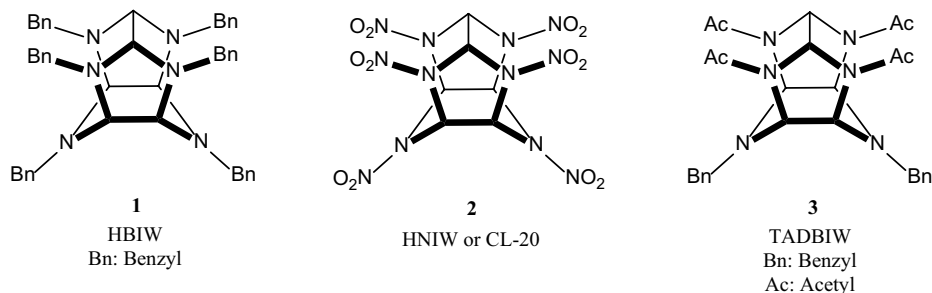
**Keywords:** Taguchi approach, debenzylation, synthesis, Pd(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, analysis of variance, TADBIW

## Nomenclature

- T* Temperature [°C]  
*P* Pressure [bar]  
*R* Catalyst to HBIW weight ratio  
*T<sub>i</sub>* Time [h]  
*C* Co-catalyst amount [mL]

## 1 Introduction

Notwithstanding the fact that the synthesis of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0.3,110<sup>5,9</sup>]dodecane (hexabenzylhexaazaisowurtzitane, HBIW, **1** in Scheme 1) as a precursor for the synthesis of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0.3,110<sup>5,9</sup>]dodecane (hexanitrohexaazaisowurtzitane, HNIW, CL-20, **2** in Scheme 1) is a unique approach for the first step of HNIW synthesis, conversion of HBIW to HNIW in the subsequent steps through different precursors and procedures has remained a challenge. Various intermediate compounds have been suggested as precursors for HNIW [1-5]. 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0.3,110<sup>5,9</sup>]dodecane (tetraacetyldibenzylhexaazaisowurtzitane, TADBIW, **3** in Scheme 1) is an important intermediate for obtaining the final product (CL-20), and will be discussed in this project [6, 7]. Due to the importance of this step, the debenzylation of HBIW in conjunction with acetylation under a wide variety of hydrogenation conditions with palladium catalysts has been investigated to obtain TADBIW [6, 7].



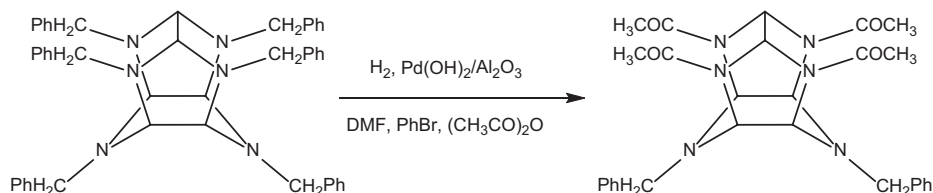
**Scheme 1.** The structures of HBIW (**1**), HNIW (**2**), and TADBIW (**3**)

Palladium-based catalysts are widely used for the selective hydrogenolysis of C–N bonds. Their crucial advantage in the HBIW debenzylation is the selectivity of the hydrogenolysis of outer  $C_{(\text{aryl})}$ –N bonds, retaining the inner  $C_{(\text{alkyl})}$ –N bonds [8, 10]. Recently, various supported palladium catalysts have been investigated for the above mentioned reaction [11–18]. The low stability and poisoning of palladium-based catalysts in the debenzylation of HBIW increased the cost of the hydrogenolysis, and thus restricted the utilisation of HNIW. According to the literature [11–18], agglomeration of palladium nanoparticles inside the carbon pores, which leads to faster deactivation of the catalyst during the debenzylation process, is the main drawback of this catalyst type. This aspect motivated our research team to work on the application of  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$ , which is less prone to agglomeration of the palladium nanoparticles.

Taguchi's orthogonal array is based on a mathematical model of factorial designs [19]. Taguchi's orthogonal arrays provide an alternative to the conventional optimization approach. In this respect, the experimental design approach, including the Taguchi method, can reduce the number of experiments while retaining data collection quality [20]. Currently, many engineers are using Taguchi's orthogonal array to design experiments in many fields, such as education, engineering, physics, chemistry, environmental science, *etc.* [21–23].

In a recent example, researchers used Taguchi's techniques to investigate the permanent magnet. The permanent magnet is characterized by high remanence, energy product, and coercivity. These parameters affect the magnetic property [24, 25]. Chan and co-workers investigated the effect of four parameters: catalyst loading, type of catalyst, reaction temperature, and nitrogen gas, on liquid yield (bio-oil) [26].

In continuation and in accord with the explanations mentioned above as part of our ongoing program to develop efficient and robust methods for the synthesis of HNIW [27–34], TADBIW was prepared through a one-pot reaction by debenzylation in conjunction with acetylation over  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$ , as shown in Scheme 2. Also, in this study, the influential factors on the debenzylation of HBIW with  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$  in a batch suspension reactor were investigated using the Taguchi experimental design approach. The aim of this work was to apply Taguchi's experimental design in the optimization of the effective factors and to evaluate the effect of each factor on the yield of TADBIW.



**Scheme 2.** Synthesis of TADBIW through a one-pot debenzylation reaction over  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$  in conjunction with acetylation

## 2 Experimental

### 2.1 Apparatus, materials, and measurements

All chemicals were purchased from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland), and used without further purification. Pd/C (10%) was purchased from Aldrich Chemical Co. The alumina ( $\text{Al}_2\text{O}_3$ ) used in this study was aluminium oxide 90 active neutral (activity stage I) for column chromatography 0.063-0.200 mm (70-230 mesh ASTM), CAS 1344-28-1, molar mass 101.96 g/mol. Purified HBIW was prepared according to a published procedure [4]. The Pd percentage in  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$  was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Perkin Elmer Optima 5300 DV). Melting points were determined on an Electrothermal 9100 apparatus. The Fourier transform infrared spectroscopy (FT-IR) spectra were measured on a Jasco 6300 FT-IR spectrometer (KBr disks).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 250 MHz instrument model WG-300 and the  $\delta$  units were referenced to tetramethylsilane internal standard. Thin-layer chromatography (TLC) was used to monitor the reactions. The structural properties of the catalyst was analyzed by X-ray powder diffraction (XRD) with an X-Pert Philips advanced diffractometer using Cu ( $K\alpha$ ) radiation (wavelength: 1.5406 Å), Pw3040/60, operated at 40 kV and 40 mA and room temperature over the  $2\theta$  range from 20 to 80°.

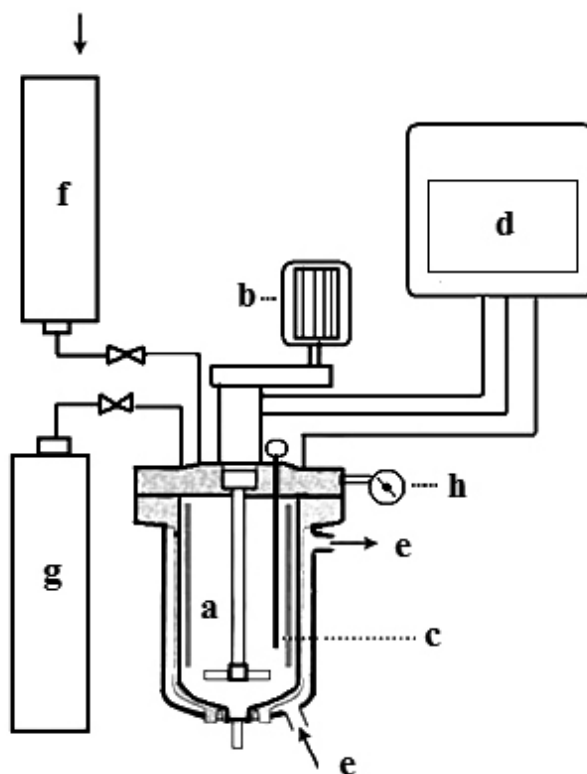
### 2.2 Preparation of $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$

Tetrachloropalladic acid ( $\text{H}_2\text{PdCl}_4$ ) was prepared according to a published procedure [35-38]. A solution of tetrachloropalladic acid ( $\text{H}_2\text{PdCl}_4$ ) was prepared by mixing palladium chloride (0.174 g) into aqueous hydrochloric acid (0.02 M, 25 mL) with stirring (15 min) at room temperature until complete dissolution, and the reaction mixture was concentrated by vacuum distillation.

The aqueous solution of the  $\text{H}_2\text{PdCl}_4$  precursor was added dropwise to a suspension of  $\text{Al}_2\text{O}_3$  (0.56 g) in water (50 mL) and maintained with stirring for 2 h at 70 °C. After the impregnation step,  $\text{PdCl}_4^{2-}$  which had been adsorbed physically onto the surface of the  $\text{Al}_2\text{O}_3$  was precipitated in the form of  $\text{Pd}(\text{OH})_2$  by gradually adding aqueous  $\text{Na}_2\text{CO}_3$  solution (20% w/w). The addition of the sodium carbonate solution was continued until pH 8 was obtained. After complete precipitation, the mixture was left to stir for 3 h at 50 °C. The solid obtained was filtered off and washed with distilled water. Finally, the  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$  was dried at room temperature for 24 h.

### 2.3 Synthesis of TADBIW

After preparation of the  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$ , all participant materials in the synthesis of TADBIW were introduced into a 2-L jacketed stainless steel reactor. The reaction mixture was stirred by a turbine-type impeller, which was connected to the magnetic seal drive to prevent gas leakage. The reaction temperature was measured with a thermocouple placed inside the reactor and was controlled by a circulating oil system. A schematic representation of the experimental setup is shown in Figure 1 [39].



**Figure 1.** Schematic representation of experimental set up: a – impeller; b – motor; c – thermocouple; d – temperature and agitation speed control panel; e – oil circulation; f – hydrogen cylinder; g – nitrogen cylinder; h – pressure gauge

For the synthetic process, the reactor system was first warmed up and then charged with a quantity of HBIW (10 g), DMF (100 mL), and phenyl bromide (co-catalyst). After the addition of these materials, the reactor was purged with

nitrogen to eliminate dissolved oxygen. Acetic anhydride and  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$  catalyst were then added immediately prior to the introduction of hydrogen so that the acetic anhydride did not have time to react with the HBIW to form an acetylated by-product prior to commencement of the desired hydrogenation reaction [39]. The reaction was monitored with time during each trial and at the end of the reaction. The reaction mixture was discharged, and the precipitated TADBIW on  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$  was filtered off from the mixture. The precipitated TADBIW was dissolved in hot acetic acid ( $\sim 60^\circ\text{C}$ ), the catalyst was filtered off and methanol was added to the filtrate solution of TADBIW in acetic acid. After a while, white crystals of TADBIW were starting to precipitate and after 2-3 h the precipitation process of TADBIW crystals was complete. The TADBIW crystals were filtered off and dried. Under these conditions, the reaction yield was 72.5%. Characterization of the product was performed by recording its melting point and TLC. The melting point of the synthesized product was  $319\text{--}321^\circ\text{C}$ .

## 2.4 Experimental design

The prerequisite and important step in designing an experiment is the proper selection of factors and their levels. In this study, five operating factors:

- temperature ( $T$ ),
- pressure ( $P$ ),
- catalyst to HBIW weight ratio ( $R$ ),
- time ( $T_i$ ), and
- co-catalyst amount ( $C$ )

were considered at three levels. These variables are listed in Table 1.

**Table 1.** Selected factors and their level description

Factors description	Unit	Levels		
		1	2	3
$T$	$^\circ\text{C}$	30	40	50
$P$	bar	2	4	6
$R$	–	5	10	15
$T_i$	h	2	4	6
$C$	mL	0.25	0.35	0.45

The factors and their levels were chosen according to a literature review of previous publications on the catalytic hydrodebenzylation of HBIW [40-42]. For the design of an experiment with five factors and three levels for each factor, a standard L18 orthogonal array (OA) was proposed by the

Taguchi method (Table 2). Each row of the table represents one run under the specified conditions.

**Table 2.** Assignment of the factors and levels of the experiments using an  $OA_{18}(3^5)$  matrix and the yields of TADBIW produced as a result

Run no.	Factors and their levels					Yield [%]
	<i>T</i>	<i>P</i>	<i>R</i>	<i>Ti</i>	<i>C</i>	
1	1	1	1	1	1	50
2	1	2	2	2	2	59
3	1	3	3	3	3	57
4	2	1	1	2	2	66.5
5	2	2	2	3	3	62
6	2	3	3	1	1	63
7	3	1	2	1	3	60
8	3	2	3	2	1	62
9	3	3	1	3	2	67
10	1	1	3	3	2	58
11	1	2	1	1	3	52
12	1	3	2	2	1	63
13	2	1	2	3	1	65
14	2	2	3	1	2	55
15	2	3	1	2	3	64
16	3	1	3	2	3	65
17	3	2	1	3	1	72.5
18	3	3	2	1	2	64

### 3 Result and Discussion

#### 3.1 Analysis of variance

The analysis of variance (ANOVA) is a powerful technique in the Taguchi method that explores the percentage contribution of factors affecting the response. This statistical table also screens the significant factors from those with less significance. The strategy of ANOVA is to extract from the results how much variation each factor causes relative to the total variation observed in the result [40, 42]. The statistical analysis of the results was carried out using Qualitek-4 (Nutek<sup>®</sup>) software. Table 3 shows the ANOVA statistical terms for the yield results. There are many statistical terms in the ANOVA table, of which a few are more meaningful.

**Table 3.** ANOVA of yields of the reaction

Variables	DOF <sup>b)</sup>	S <sup>c)</sup>	V <sup>d)</sup>	Pooled <sup>a)</sup>			
				F <sup>e)</sup>	S <sup>f)</sup>	DOF	P <sup>g)</sup>
<i>T</i>	2	233.862	116.931	10.224	210.988	2	40.282
<i>P</i>	2	23.695	11.847	1.035	0.822	2	0.156
<i>R</i>	2	17.445	8.722	–	–	–	0
<i>Ti</i>	2	143.359	74.179	6.468	125.486	2	23.957
<i>C</i>	2	20.359	10.179	–	–	–	0
Other/error	7	80.55	11.436	–	–	11	35.605

a) The insignificant effects pooled while the critical value was at a 90% confidence level.

b) Degrees of Freedom.

c) Sum of squares.

d) Variance.

e) F<sup>2</sup>-ratio.

f) Pure sum of squares.

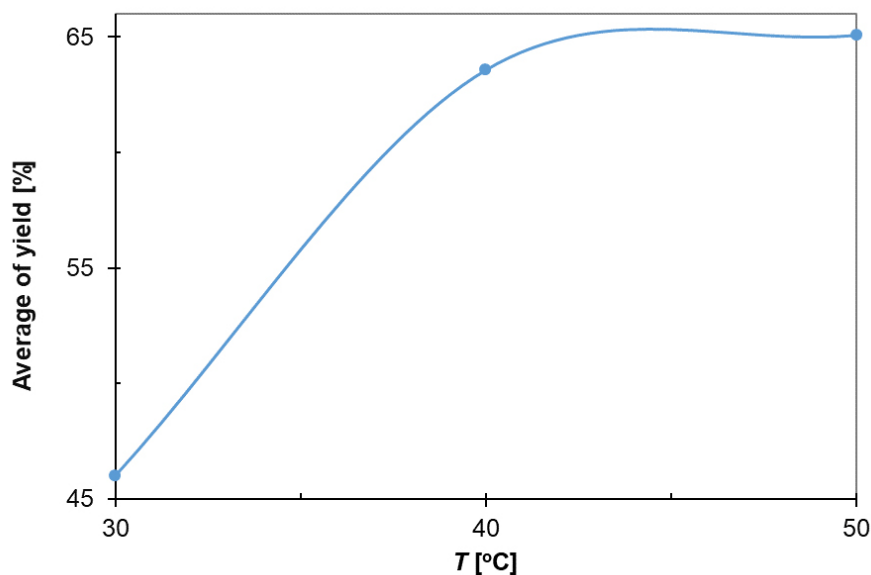
g) Percent (%).

The F<sup>2</sup>-ratio is a criterion for distinguishing the important factors from those with less significance. A low value of the F-ratio for a factor means that the variation of the response with respect to changes of this factor is equal to or smaller than the variation due to errors. If the F<sup>2</sup>-ratio of the controlling factor is greater than about 4 (confidence level of 90%), then that factor has a significant influence on the response. It should be emphasized that the interpretation of the ANOVA table is valid only in the range of levels considered for any factor. If the F-ratio for a factor is less than 4, it does not mean that the factor has no effect on the response absolutely, but only in the range of the selected levels, the variation on the response due to changes in the factor levels has been insignificant compared with errors. That is why the selection of levels is vital in the designed experiments [41, 42]. Table 3 indicates that only the temperature and the time of the reaction are of importance for affecting the result. It is implied from the values in the last column of this table that the temperature has the predominant influence on the yield of the TADBIW synthesis reaction. The bottom row of the ANOVA table contains information about three sources of variability of the results: uncontrollable factors, factors that are not considered in the experiments, and experimental error [20]. Table 3 also indicates that except for the temperature and the time of the reaction, the other selected factors in their range of levels cannot cause a predominant variation in the yield of TADBIW synthesis catalyzed by Pd(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. It can be also found from the F-ratios of the factors of this investigation that pressure can make a contribution to the yield of TADBIW, but its role is not considerable in the range of its levels in this investigation.

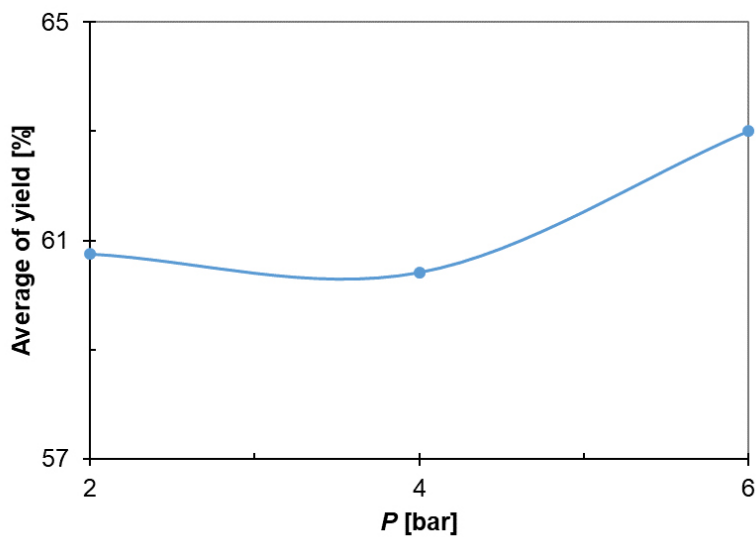


### 3.2 Consideration of the influence of the different factors

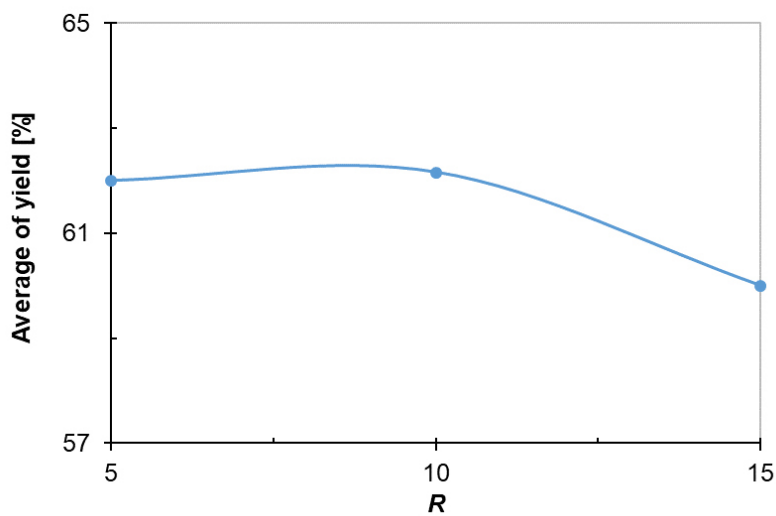
After identification of the individual influence of each factor on the response, the corresponding mean values of the yields for different factors at each level were calculated according to the assignment of the experiment. For this reason, the matching yield values of a factor at a specific level were pooled and then divided by the number of trials in which the considered factor had been set at the specific level [33]. Figures 2-6 show how the average values of the yield will be varied with respect to changing the levels of each factor. Figures 2-6 also show the compliance of the data obtained by analysis of the variance with the results of the experiments. The results of ANOVA are confirmed by Figures 2-6, which are a representation of the degree of the dependence of the yield on the different factors. This truth can be recognized by measuring the mean value of the yield corresponding to each factor at a specific level, and that, as mentioned earlier, the temperature and the time of the reaction are factors that have the greatest contributions in determining the yield of the reaction.



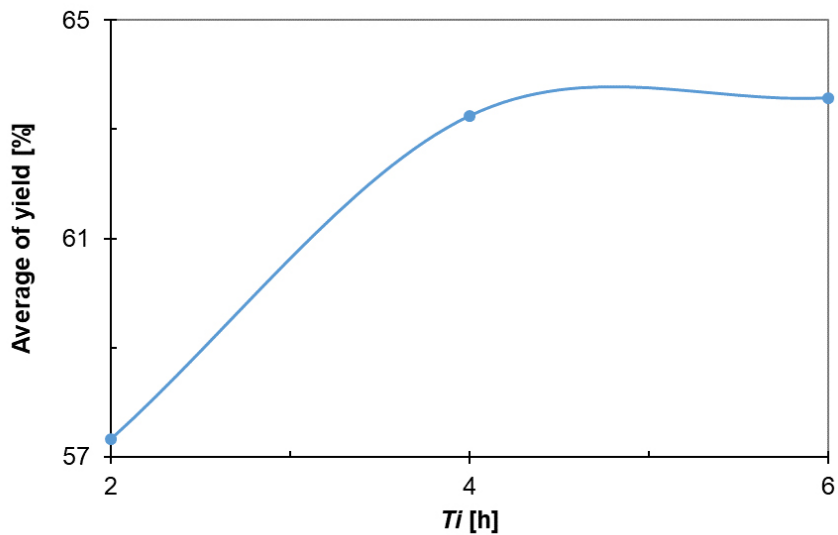
**Figure 2.** Influence of  $T$  on the yield (%) of the TADBIW synthesis



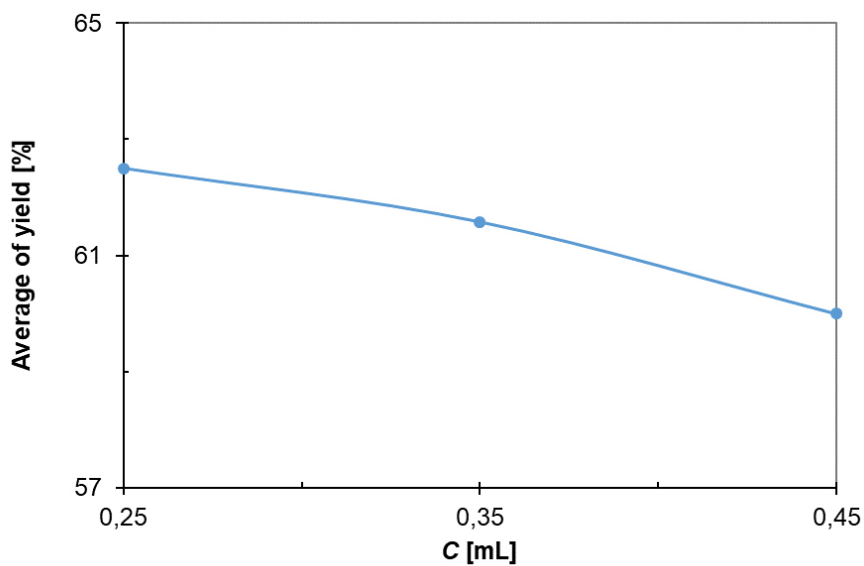
**Figure 3.** Influence of  $P$  on the yield of the TADBIW synthesis



**Figure 4.** Influence of  $R$  on the yield of the TADBIW synthesis



**Figure 5.** Influence of  $T_i$  on the yield of the TADBIW synthesis



**Figure 6.** Influence of  $C$  on the yield of the TADBIW synthesis

### 3.3 Optimum conditions

The optimum conditions for the synthesis of TADBIW with  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$  in a batch suspension reactor, was proposed by ANOVA, subsequent to the determination of the influential factors and their relevant effects (Table 4). For further evaluation of the ANOVA results, TADBIW was synthesized according to the optimal conditions. The reaction yield was ~71% and showed the compliance of the ANOVA results with an actual experiment. The synthesized TADBIW was characterized by its melting point and TLC. The TLC results and the narrow melting point range (315-317 °C) revealed that the synthesized TADBIW was pure. The synthesized TADBIW was then prepared for the  $^1\text{H}$  NMR and FT-IR analysis. The FT-IR and  $^1\text{H}$  NMR spectra completely comply with the spectra which have been reported previously [43-46].

**Table 4.** Optimum conditions and performance

Factors	Level description	Level	Contribution
<i>T</i>	50	3	3.694
<i>P</i>	6	3	1.611
<i>R</i>	10	2	0.777
<i>Ti</i>	6	3	2.194
<i>C</i>	0.25	1	1.194
Total contribution from all factors			9.97
Current grand average of performance			61.388
Expected result from optimum condition			70.858

### 3.4 Comparison of HBIW debenzilation under the same reaction conditions and in the presence of catalysts $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$ and Pd/C

Under similar reaction conditions (as mentioned in the experimental section), the debenzilation reaction of HBIW was also tested using conventional palladium on an activated carbon catalyst (Pd/C). From the results obtained in this reaction and its comparison with the reaction mentioned in the experimental section, the following can be mentioned. When  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$  was used as the catalyst, the product yield was 72.5%, but when the reaction was carried out in the presence of Pd/C as the catalyst, it was 60%. This is when the percentage of palladium in the Pd/C catalyst is 10%, but the percentage of palladium in the  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$  catalyst is 5%, and ICP analysis determined the actual amount of Pd (5%) in the  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$ . When the reaction was carried out in the presence of  $\text{Pd}(\text{OH})_2/\text{Al}_2\text{O}_3$ , the melting point range of the product was 319-321 °C, while the product melting point range when Pd/C was used as the catalyst was 316-318 °C.

## 4 Conclusions

- ◆ TADBIW was synthesized by catalytic debenylation of HBIW with Pd(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. The influences of various operating variables on the yield of this reaction in a batch suspension reactor were statistically analyzed using a Taguchi experimental design.
- ◆ The main conclusion that is valid in the range of levels considered in this study is that of the potential influential factors on the yield of TADBIW with Pd(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, temperature and the time of reaction make the greatest contribution in determining the yield of the reaction. Pressure with an F-ratio of 1.035 has an insignificant variation on the response (yield) of this reaction compared with error, and the catalyst/HBIW ratio and co-catalyst amount make no contribution in determining the yield of this reaction.
- ◆ In this article, the determination of the relative optimum conditions has been illustrated in Table 4. The quality characterization of the yield of TADBIW, from which the optimum conditions and performance can be obtained, is greater, thus the highest possible yield can be predicted by the Taguchi method. According to the optimum conditions from this study, TADBIW could be obtained with 70.858 yield, which is in good agreement with practical experiences.
- ◆ The novelties of this method are the use of Pd(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> as a new catalyst, along with the optimal conditions obtained from Taguchi's statistical approach, which leads to an increase in the yield of the product, up to 72.5%. Furthermore, the preparation of Pd(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, using Al<sub>2</sub>O<sub>3</sub> as a substitute for C, is described in this article.

## Conflict of Interest

The authors declare that they have no conflict of interest.

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