

tion of organic pollutants, due to its excellent properties (inexpensiveness, non-toxic nature, high photosensitivity and at the same resistant to photo-corrosion) [7].

The aim of this work was the application of hydrothermal activation to the ZnO precipitates to obtain powders, observing the effect on the photocatalytic efficiency for azo dye discoloration.

EXPERIMENTAL DETAILS

1. Materials synthesis

All chemicals were commercial analytical grade of purity reagents without any further purification. In a typical experiment, the Zn^{2+} precursor ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) solution was prepared by dissolving of 2 g Zn acetate in 200 ml deionized water. Sodium hydroxide (2,4 g) was dissolved into 15 ml water. The precipitant sodium solution was added slowly into zinc acetate solution until reaching $\text{pH} = 13$. The pH of the solution was checked by means of color-fixed indicator strips (Machery-Nagel, Germany). The resulting suspension was magnetically stirred for 2h and then transferred into a Teflon-lined autoclave. The autoclave was heated at 140°C for 12 h, after that the autoclave was cooled down naturally. The white powder was collected and washed with distilled water and ethanol several times. Then the resulting powder was dried at 80°C for 10 hours. The so prepared ZnO material was denoted by (B).

In order to estimate the activities of these materials additional photocatalytic experiment with ZnO referent samples was conducted. Activated ZnO powder (A) was obtained by procedures, described in Bulgarian Patent [8]. The preparation procedure includes dissolution of commercial ZnO in nitric acid, followed by the addition of NH_4OH solution leading to precipitation of $\text{Zn}(\text{OH})\text{CO}_3$ in the course of CO_2 bubbling (barbotage) and finally thermal decomposition at 450°C 2 h.

2 Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D2 Phaser diffractometer in the range of 2θ values between 25° and 75° using Cu K_α radiation ($\lambda = 0.154056 \text{ nm}$) at 40 kV and 35 mA. The samples were scanned at a step of 0.05° and signal collection time 1 second per step. The observed patterns were cross-matched with those available in the JCPDS database.

The IRS investigations were carried out on a Bruker FT-IR Tensor-37 spectrometer in the 400 – 4000 cm^{-1} spectral region using a KBr technique. The measurements were performed at 2 cm^{-1} resolution, accumulating 32 scans.

The express BET method has been applied to measure the specific surface area, based on low-temperature adsorption of nitrogen – i.e. at the boiling temperature of liquid nitrogen 77K. The relative error of the method amounts to about 8%. The specific surface area measurement and the pore size distribution were accomplished on an automated apparatus NOVA Win/ Nova Win – CFR Quantachrom – Gas Sorption System. The calculation of the specific surface area was done using the BET equation, whereupon the pore size distribution, as well as the average pore diameter were evaluated by Density Functional Theory (DFT) assuming a cylindrical model of the pores. The total pore volume was estimated in accordance with the rule of Gurvich at relative pressure $P/P_0 = 0.96$.

The UV–Vis absorption spectra were recorded by a spectrophotometer UV-1600PC using wavelength range from 200 to 800 nm.

3 Photocatalytic activity tests

The model azo dye Reactive Black 5 (RB5) aqueous solution with concentration of 20 ppm was used for the tests. The suspensions were prepared by addition of 150 mg ZnO into the solution in a magnetically stirred glass beaker. Prior to switching on the illumination, the suspension had been kept in the dark for half an hour to achieve adsorption-desorption equilibrium. Then the solution was illuminated with polychromatic UV-A lamp illumination (18 W giving 0.66 mW/cm^2 illumination intensity) with maximum emission at wavelength 365 nm under continuous stirring at room temperature. The absorbance of RB5 solution is measured at 599 nm, corresponding to the azo bond. The course of the photocatalytic oxidation reaction was followed by taking aliquot samples of the solution at regular time intervals and calculating the residual concentration, based on calibration, using spectrophotometer UV-1600PC in the wavelength range from 200 to 800 nm.

RESULTS AND DISCUSSION

Figure 1 shows an XRD spectrum of a ZnO activated (a) and hydrothermal (b) powders. The results show that all the ZnO samples possess a wurtzite structure (space group P63mc), and the diffraction peaks can be

indexed to hexagonal ZnO (JCPDS no. 36 – 1451) [9]. The samples possess high degree of crystallization, which is obvious from the narrow width of the peaks. No other crystallographic phases were registered.

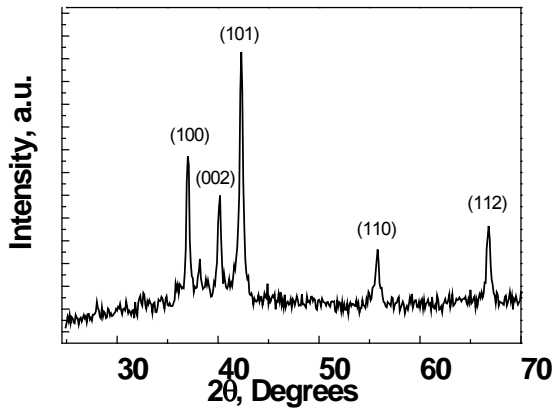


Figure 1-a. XRD pattern of activated ZnO powders (sample A)

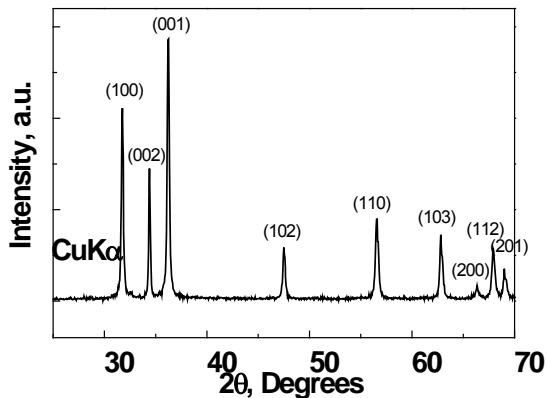


Figure 1-b. XRD pattern of hydrothermally obtained ZnO powders (sample B)

Figure 2 represents the IR spectrum of hydrothermally activated ZnO powders with characteristic bands at 422, 471 and 575 with a shoulder at 534 cm^{-1} .

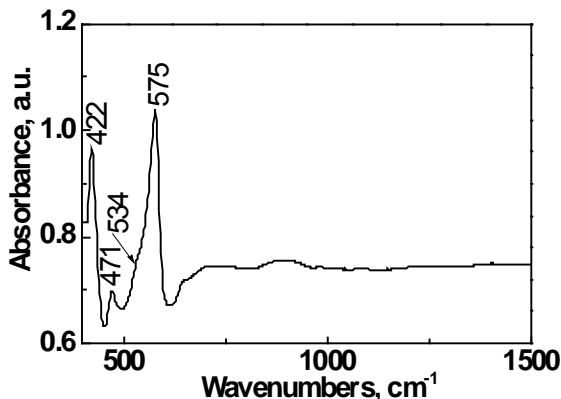


Figure 2. IR spectrum of hydrothermally obtained ZnO sample

The ZnO powders IRS spectra show characteristic bands at 422, 471 and 575 with a shoulder at 534 cm^{-1} . These bands of ZnO are somewhat different from the ones, observed at 487 and 517 cm^{-1} by Hariharan [10]. In several other works the respective bands are observed at 539 cm^{-1} , close to the shoulder, observed also at 539 cm^{-1} in the present work [11] and the one at 419 cm^{-1} [12]. All the bands were assigned to the Zn-O bonding without specifying the type of vibrations at 422 cm^{-1} indicative of Zn-O bonding [11], the 539 cm^{-1} and 419 cm^{-1} bands were also ascribed to Zn-O bonding, for ZnO flowers-like crystals [12].

The desorption isotherm of hydrothermally treated precipitate B belongs to the type IV of isotherms probably with a hysteresis loop H3, following the nomenclature of IUPAC, representative of the presence of cylindrical pores. Similar BET behavior was displayed by the ZnO particles [13]. The adsorption-desorption isotherm of the sample A is similar. Taking into account the pore size distribution it can be concluded that the hydrothermally obtained powders contain both micropores (2 – 10 nm) and mesopores in the range 10 – 22 nm. The average pore diameters for B sample is 8.4 nm and total pore volume is $2.1 \times 10^{-2} \text{cm}^3/\text{g}$. The surface area of the sample A ($19 \text{m}^2/\text{g}$) is larger than that of the sample B ($10 \text{m}^2/\text{g}$).

Figure 3 represents the results from the testing of the photocatalytic activity of the sample B, compared with referent ZnO sample A, prepared by activation.

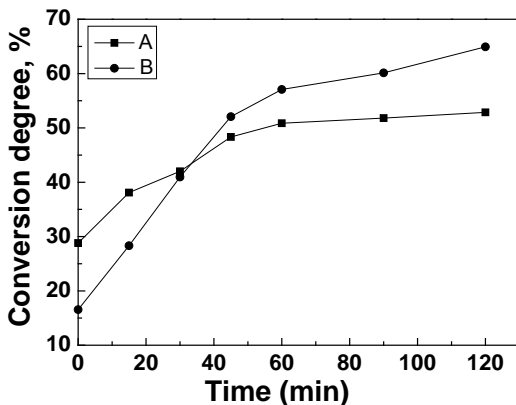


Figure 3. Conversion degree as a function of the time of illumination of hydrothermally prepared sample B and referent sample A

The conversion degree of the dye degradation was evaluated using the following equation:

$$D, \% = (C_0 - C / C_0) \times 100 \quad (1)$$

Where C_0 is the initial absorbance of the dye solution, C is the absorbance of the decolorized solution after 120 minutes. The presented values of the degradation were measured with 150 mg of photocatalyst in 150 ml of the solution.

The sample A is more active (30% adsorptive discoloration in the dark) due to its higher specific surface area, respectively larger adsorption capacity. However the advantage of mesoporous hydrothermally obtained sample becomes obvious after the 40th minute of UV illumination, which is understandable in view of the large size of the dye molecule of Reactive Black 5 and probable diffusion retardation effect. It is well-known that the photocatalytic activities are strongly dependent on the specific surface areas of the photocatalyst samples as the reactant molecules are adsorbed on their surfaces. The presence of mesopores in sample B porous structure provides a larger number of active sites for the photocatalytic reactions. In

addition to this, the mesoporous channels also facilitated the diffusion of reactant molecules thereby increasing the quantum efficiency of photocatalytic material [14].

CONCLUSIONS

Two types of ZnO photocatalyst samples have been prepared by: 1) precipitation method (sample A), 2) hydrothermal treatment (sample B). The photocatalytic activity test revealed that sample B is more active than A, due to the prevailing mesopores in the porous structure. The photocatalytic activity is a counterplay between two factors: adsorption capacity, which is higher at greater specific surface area (sample A), on one side. The second factor is the facilitated diffusion in mesopores (sample B), whose advantage is revealed only after longer time intervals of irradiation making the entire internal surface area available to the adsorbate molecules. The low-cost hydrothermal synthesis procedure enables obtaining well crystallized wurtzite phase ZnO powders, having great potential for photocatalytic applications.

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НАСОЧЕН СИНТЕЗ И РЕГИОСЕЛЕКТИВНИ ЦИКЛИЗАЦИИ НА 4-ХИДРОКСИ-1,3,4-ТРИФЕНИЛАЛЕНИЛ ФОСФОНАТ И ФОСФИН ОКСИД

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ABSTRACT

The paper describes a convenient and efficient method for regioselective synthesis of 4-hydroxy-1,3,4-triphenylallenyl phosphonate and phosphine oxide using an atom economical [2,3]-sigmatropic rearrangement of intermediate propargyl phosphites or phosphinites. These can be readily prepared via reaction of protected alkynol with dimethyl chlorophosphite or chlorodiphenyl phosphine respectively in the presence of a base. Reactions of the prepared 3-hydroxymethyl-substituted allenephosphonate and allenyl phosphine oxide with protected and unprotected hydroxyl group with different electrophilic reagents such as sulfonyl chloride, bromine, benzenesulfonyl and benzeneselenanyl chlorides takes place with 5-endo-trig cyclization or 2,3-addition reaction depending on the kind of the substituents in phosphoryl group. Cycloisomerization reactions of 3-hydroxymethyl-substituted allenephosphonate and allenyl phosphine oxide with the so called coin metals ions such as Ag^+ , Au^+ , Cu^+ etc. leads to formation of the 2-phosphorylated-2,5-dihydrofurans.

Key words: *Synthesis, hydroxy group protection, phosphorylated 4-hydroxyallenes, electrophilic cyclization, 2,5-dihydro-1,2-oxaphospholes, 2,5-dihydrofuranes.*

ВЪВЕДЕНИЕ

През последните десетилетия изследванията в областта на органичната химия се характеризират с бързото развитие на химията на аленовите съединения [1]. Особено интересни субстрати за изследване на реакциите на електрофилно присъединяване са функционализираните алени. В литературата са описани редица методи за получаване на фосфорилираните алени (фосфонати [2] и фосфин оксиди [3]). За разлика от аленовите въглеводороди, наличието на фосфорна функционална група, свързана с аленовата система, съществено променя хода на реакциите с електрофилни реагенти, като литературните данни [4] показват, че в повечето случаи протича петчленна хетероциклизация.

В продължение на нашите изследвания върху реакциите на циклизация на функционализираните алени ние си поставихме следните цели и задачи в настоящата работа, а именно: 1) Създаване на удобни и високоселективни методи за синтез на 3-хидроксиметил-аленфосфонати и аленил фосфин оксиди с възможности за вариране на заместителите както в аленовата система, така и във фосфорната и хидроксиметилната функция; и 2) Изследване на реакциите на електрофилна циклизация и циклоизомеризация на получените 3-хидроксиметил-аленфосфонати и аленил фосфин оксиди при взаимодействие с електрофилни реагенти и йони на т. нар. монетни метали (Ag, Au и Cu) с оглед проучване на възможностите и ограниченията на протичащата циклизация с конкурентното участие на едната и/или другата функция, свързани с аленовата система.

ИЗЛОЖЕНИЕ

Ние създадохме и използвахме един нов *региоселективен* метод (Схема 1) за получаване на фосфорилирани 3-хидроксиалени, който се състои във взаимодействие на етилмагнезиев бромид, получен *in situ* от етил бромид и магнезий, с фенилацетилен **1** с междинно образуване на съответния етинил магнезиев бромид **A**. Последният след нуклеофилно присъединяване към карбонилната група на бензоина **2**, на който предварително беше защитена хидроксилната група с помощ-

та на DHP (3,4-дихидро-2*H*-пиран), води до получаване на 1-(тетрахидро-2*H*-пиран-2-илокси)-заместения 3-бутин-2-ол **4**.

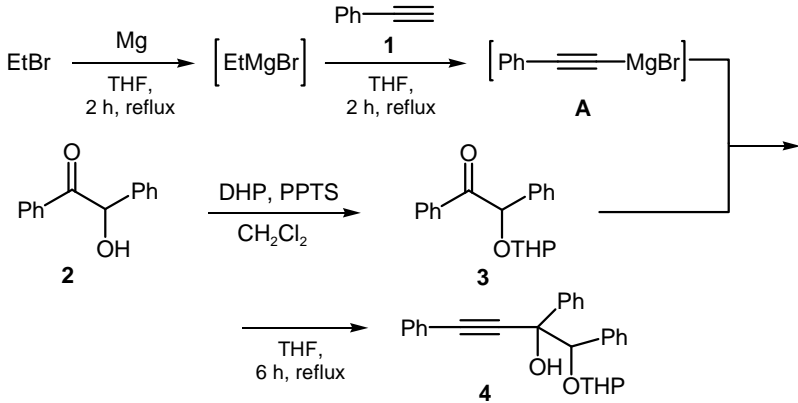


Схема 1

Така синтезираният от нас алкинол **4** използвахме като изходен субстрат за получаването на фосфорилирани 3-хидроксиалени със защитена и незащитена хидроксилна група.

Взаимодействието на алкохола **4** с диметилхлорофосфит в присъствие на триетиламин протича с междинно образуване на съответния пропаргил фосфит **B**, който търпи [2,3]-сигматропна прегрупировка и получаване на 4-(тетрахидро-2*H*-пиран-2-илокси)-бута-1,2-диенфосфоната **5** (Схема 2):

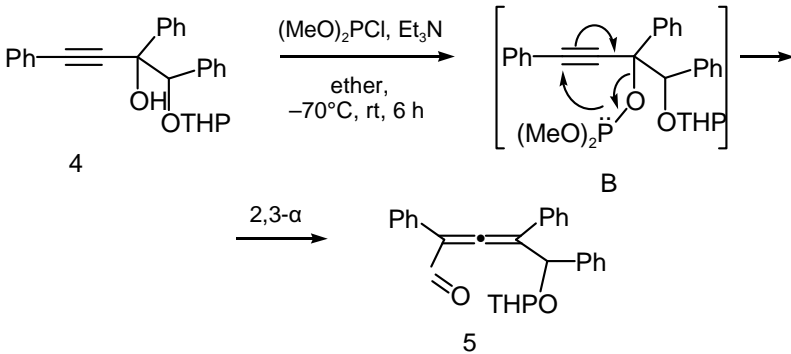


Схема 2

От друга страна, взаимодействието на дифенилхлорофосфин със заместения алкохол **4** в присъствие на база протича с междинно образуване на съответния пропаргил фосфинит **C**, който лесно при стайна температура търпи [2,3]-сигматропна прегрупировка и води до получаване на 2-(4-дифенилфосфиноил-бута-2,3-диенилокси)-тетрахидро-2*H*-пирана **6** (Схема 3):

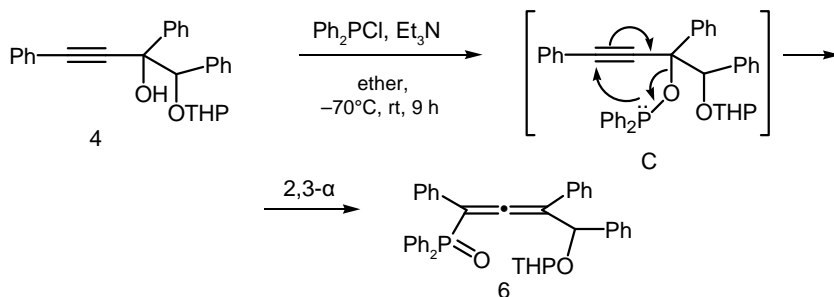


Схема 3

Така получените фосфорилирани алени **5** и **6** по предложението метод използвахме като субстрати за по-нататъшно изследване на реакциите на електрофилна циклизация.

Нашите изследвания показаха, че бромването на аленфосфоната **5** протича с 5-*endo-trig* циклизация с анхимерното съдействие като вътрешен нуклеофил само на фосфонатната група и с получаване на 2,5-дихидро-1,2-оксафосфола **7** (Схема 4):

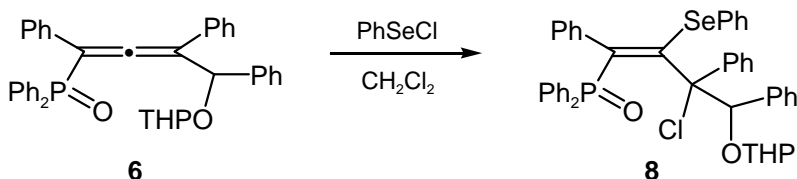
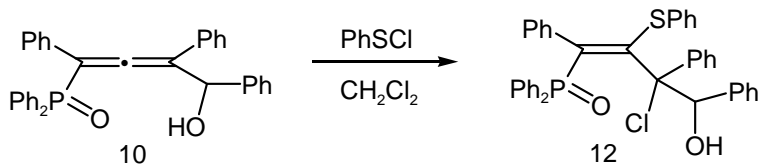


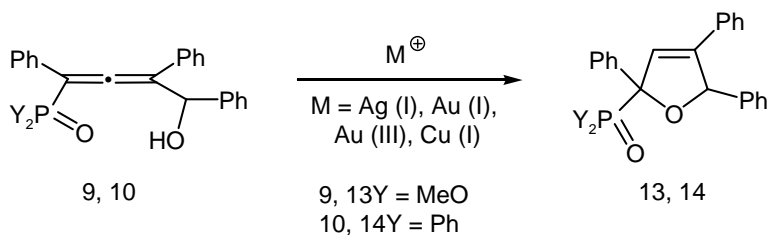
Схема 4

Взаимодействието на аленил фосфин оксида **6** с бензенселанил хлорид протича *региоселективно* с присъединяване на реагента по 2,3-двойната връзка на аленовата система с получаването на ациклическия – бут-(1*E*)-ен-1-ил фосфин оксид **8** (Схема 5):

Реакцията на аленил фосфин оксида **10** с бензенсулфанил хлорид води до получаване на 4-(дифенилфосфиноил)-3-бутен-1-ола **12** (Схема 8):



Изследвахме и реакциите на 3-хидроксиметил-заместените аленил-фосфонат **9** и аленил фосфин оксид **10** с йони на т. нар. монетни метали, като установихме, че се извършва реакция на петчленна циклоизомеризация с участието на хидроксилната група и получаване на 2-фосфорил-заместените 2,5-дихидро-фурани **13** и **14** (Схема 9):



В експериментално отношение ходът на всички реакции е проследяван тънкослойно хроматографски и ИЧ-спектрално, получените продукти са изолирани и пречистени чрез колонна хроматография, а структурата на синтезираните съединения е установена чрез ИЧ-, ^1H -, ^{13}C - и ^{31}P -ЯМР-спектроскопия.

ЗАКЛЮЧЕНИЕ

Създаден е метод за синтез на 4-хидрокси-1,3,4-трифенилаленил фосфонат и фосфин оксид, който е високо *регио*селективен и дава възможност за вариране на заместителите както в аленовата система, така и във функционалната група. Изследвани са реакциите на получените аленилфосфонати и аленил фосфин оксиди със защитена и незащитена хидроксилна група с електрофилни реагенти, като е установено, че протичат с получаване на разнообразни хетероциклени и ненаситени съединения. Установено е, че реакциите на циклоизомеризация проти-

чат с участието на хидроксилната група в циклизация с получаване на 2-фосфорил-заместени 2,5-дихидро-фурани.

БЛАГОДАРНОСТИ

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