The solutions were electrolysed during three hours, at room temperature with current densities about 0.03 $A.cm^{-2}$. After precipitation of the remaining lignin the oxidation products were extracted by diethyl eter. The extracted products were identified by GC-MS coupling and quantified by GC (Fig.1).The percentages of the extracted products are reported on **Table 3**. The resulting reaction mixtures show slight differences.

	Ni (%)	PbO_2 (%)	DSA (%)
Guaiacol	16	12	8
Hydroxymethoxyphenyl ethanone	12	11	15
Hydroxybenzaldehyde	4	2	2
Vanillin	56	64	63
Vanillic acid	5	4	1
Hydroxymethoxybenzene acetic acid	5	5	8

Table 3. Electrooxidation of lignin in alkaline medium: effect of electrode material on the product distribution.

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ELECTROSYNTHESIS OF STILBENE - EFFECT OF EXPERIMENTAL PARAMETERS ON THE REACTION YIELD AND STEREOCHEMISTRY

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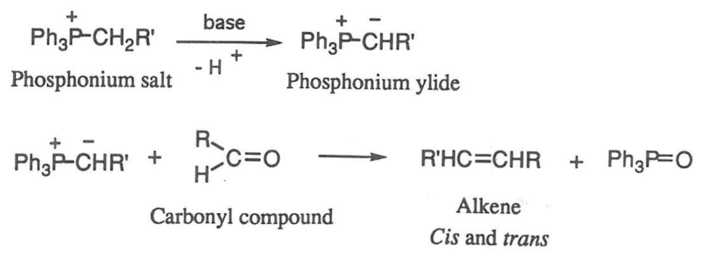
ABSTRACT

The influence of experimental parameters on the yields and stereochemistry of Wittig reaction was studied. The synthesis of stilbene initiated by different electrogenerated bases was used as a model reaction. Preparative electrolyses were carried out in different conditions including constant potential or constant current with different electrode materials and using solvents of different polarity. Both the yield and the stereochemistry of the reaction are affected by the electrolysis experimental conditions. Hence, the proper selection of experimental conditions in Wittig reactions allows the choice of the stereosselectivity of the reactions and the optimization of yields.

Keywords: Electrogenerated bases, Wittig reactions, Electrosynthesis

INTRODUCTION

The synthesis of unsaturated compounds is commonly carried out by Wittig reactions [1,2]. This reaction involves the condensation of a phosphorous ylide and a carbonyl compound, according to scheme 1:



Scheme 1 - Wittig reaction.

Different techniques have been employed to deprotonate the phosphonium salt and generate the ylide [1,2]. The technique described here is based on the deprotonation by electrogenerated bases (EGB). Electrogenerated bases are formed *in situ* by cathodic reduction of organic precursors denominated probases (PB) [3].

The feasibility, yields and stereochemistry of Wittig reactions can be influenced by a variety of experimental conditions that may be applied to the reaction [1,2]. These conditions include the choice of base to generate the ylide, the solvent, the presence of certain cations, the temperature, the reactant ratios, etc. In an attempt to study the influence of experimental parameters on the yields and stereochemistry of this reaction, the synthesis of stilbene from benzaldehyde (PhCHO) and benzyltriphenylphosphonium salt ($Ph_3P^+CH_2Ph$, Br^-) initiated by several electrogenerated bases, was used as a model reaction.

EXPERIMENTAL

Azobenzene was recrystalized in hot ethanol and dried under vacuum before use; the fuchsone was prepared by photochemical coupling of benzophenone and 2,6-di-*tert*-butylphenol [4]; the dicyano(fluoren-9-ylidene)methane was synthesised by Knoevenagel condensation from fluorenone and malononitrile [5]. The phosphonium salt, $Ph_3P^+CH_2Ph$, Br^- was prepared by reaction between triphenylphosphine and benzyl bromide [6]. The benzaldehyde was distilled at reduced pressure under nitrogen before use.

The lithium chloride and lithium perchlorate used as supporting electrolytes were dried under vacuum at 40 °C before use. The tetrabutylammonium tetrafluoroborate was prepared from solutions of sodium tetrafluoroborate and tetrabutylammonium hydrogensulphate, recrystalized and dried.

The solvents N,N-dimethylformamide, dimethylsulfoxide, tetrahydrofurane, dichloromethane and toluene were dried with molecular sieves 4 Å for 24 hours. The solutions of supporting electrolyte in the solvent were passed through a column filled with neutral alumina before the electrolysis were performed.

The preparative electrolyses were carried out in a divided cell on mercury pool, platinum gauze or vitreous carbon cathodes. A saturated calomel electrode was used as reference electrode, in controlled potential electrolyses.

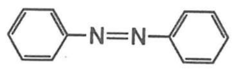
Preparative electrolyses were performed using a potentiostat, Hi-Tek model DT2101 and a digital integrator, Hi-Tek model DIB S2, allowed the coulometric measurements.

The progress of the reaction and the analyses of the products of the electrolyses were made by high performance liquid chromatography (HPLC) and gas chromatography (GC). The HPLC system was equipped with a RP-18 column and the GC was equipped with a packed column 10% OV-101. Stilbene yields and *cis/trans* ratios were determined by GC (using biphenyl as internal standard).

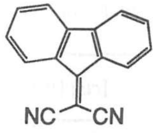
RESULTS AND DISCUSSION

To obtain a systematic study of the influence of experimental parameters on the yield and stereochemistry of stilbene electrosynthesis by Wittig reaction, preparative electrolyses of solutions containing the probase, the phosphonium salt and benzaldehyde were performed in batch cells. The electrolyses were carried out at different experimental conditions, such as constant current / constant potential in different electrode materials with several probases and solvents of different polarity.

Three different probases, azobenzene (1), dicyano(fluorenil-9-ylidene)methane (2) and fuchsone (3) were used in this work. Both the reduction mechanism and the species acting as bases are different.



(1)



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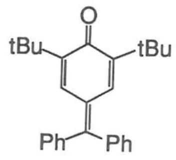

(3)

The study was initiated by comparing the results obtained when the electrolyses were carried out at constant current with those of the electrolyses performed at constant potential. The results of these electrolyses are presented in table 1.

It seems that stilbene yield and cis/trans ratios are similar in both types of electrolyses, although the yield obtained at constant current in dimethylsulfoxide is slightly higher.

Table 1 - Results of preparative electrolyses carried out to prepare stilbene using azobenzene ($5x10^{-3}$ mol dm^{-3}) as probase, $Ph_3P^+CH_2Ph$, Br^- ($1x10^{-2}$ mol dm^{-3}) and benzaldehyde ($1x10^{-2}$ mol dm^{-3}). The electrolyses were performed in a divided cell at a platinum gauze cathode, using Bu_4NBF_4 (0.1 mol dm^{-3}) as supporting electrolyte in two different solvents.

Type of electrolyses	Solvent	Yield / %	[*cis*]:[*trans*]
Constant current	Dimethylsulfoxide	96 ± 4	2.0
Constant potential	Dimethylsulfoxide	79 ± 2	1.9
Constant current	N,N-dimethylformamide	78 ± 2	2.0
Constant potential	N,N-dimetilformamida	79 ± 1	2.0

There are several references in the literature to electrosynthetic reactions whose yields and products are affected by the electrode material [7]. Thus, to study the influence of the cathode material on stilbene synthesis, preparative electrolyses at vitreous carbon, platinum gauze and mercury pool electrodes were performed. The results obtained are presented in table 2. The yield of the reaction is not affected by electrode material; however, the proportion of *trans*-stilbene is higher at mercury pool cathodes.

Table 2 - Results of preparative electrolyses carried out to prepare stilbene, at constant potential, using azobenzene (5×10^{-3} mol dm^{-3}) as probase, $Ph_3P^+CH_2Ph$, Br^- (1×10^{-2} mol dm^{-3}) and benzaldehyde (1×10^{-2} mol dm^{-3}). The electrolyses were performed in a divided cell at different cathodes, using Bu_4NBF_4 (0.1 mol dm^{-3}) as supporting electrolyte in N,N-dimethylformamide.

Cathode material	Yield / %	[*cis*]:[*trans*]
Vitreous carbon	79 ± 1	2.0
Platinum gauze	80 ± 2	2.0
Mercury pool	80	1.4

Electrolyses were carried out with three probases to study the influence of the probase on the electrosynthesis of stilbene and the results obtained are presented in table 3. It seems that both the yield and the proportion of isomers formed are affected by the base used to deprotonate the phosphonium salt.

Table 3 - Results of preparative electrolyses carried out to prepare stilbene, at constant potential, using different probases, $Ph_3P^+CH_2Ph$, Br^- (1×10^{-2} mol dm^{-3}) and benzaldehyde (1×10^{-2} mol dm^{-3}). The electrolyses were performed in a divided cell at a vitreous carbon cathode, using Bu_4NBF_4 (0.1 mol dm^{-3}) as supporting electrolyte in N,N-dimethylformamide.

Probase	[Probase] / mol dm^{-3}	Yield / %	[*cis*]:[*trans*]
azobenzene	5×10^{-3}	79 ± 1	2.0
dicyano(fluoren-9-ylidene)methane	1×10^{-2}	80 ± 3	1.6
dicyano(fluoren-9-ylidene)methane	2×10^{-2}	74 ± 3	1.3
fuchsone	1×10^{-2}	58 ± 2	1.7

The influence of the solvent in the Wittig reaction has been the subject of much apparently contradictory work during the last years [1,8-10]. Preparative electrolyses using azobenzene as probase were carried out in solvents or mixtures of solvents of different polarity. Electrolyses were performed at constant current to allow the use of low dielectric constant solvents as tetrahydrofurane and toluene. The results of these electrolyses are presented in table 4.

Table 4 - Results of preparative electrolyses carried out to prepare stilbene, at constant current ($j = 0.7$ mA cm^{-2}), using azobenzene (5×10^{-3} mol dm^{-3}) as probase, $Ph_3P^+CH_2Ph$, Br^- (1×10^{-2} mol dm^{-3}) and benzaldehyde (1×10^{-2} mol dm^{-3}). The electrolyses were performed in a divided cell at a platinum gauze cathode, using Bu_4NBF_4 (0.1 mol dm^{-3}) as supporting electrolyte in different solvents.

Solvent	ε (*)	Yield / %	[*cis*]:[*trans*]
Dimethylsulfoxide	46.6	96 ± 4	2.0
N,N-dimethylformamide	36.7	78 ± 2	2.0
Toluene / N,N-dimethylformamide (70/30)	12.7	77 ± 3	1.6
Toluene / N,N-dimethylformamide (80/20)	9.2	60 ± 1	1.2
Dichloromethane	9.1	72 ± 2	1.0
Toluene / N,N-dimethylformamide (85/15)	7.5	61 ± 6	0.9
Tetrahydrofurane	7.4	28 ± 5	0.8

(*) The values of the dielectric constants of the solvents were taken from reference [11]. The dielectric constants used for the mixed solvents are the weighted average of the dielectric constants of the components of the mixture [12].

The reaction is strongly dependent on the solvent used and there is a trend in decreasing stilbene yield as the polarity of the solvent diminishes. The solvent has also a marked influence on the reaction stereochemistry; it is possible to observe an increase in the proportion of *trans*-stilbene with a decrease in the dielectric constant of the solvent.

Both the yield and the stereochemistry of Wittig reactions are affected by the electrolyses experimental conditions. Hence, the proper selection of experimental conditions in Wittig reactions allows the choice of the stereoselectivity of the reactions and the optimization of yields.

Acknowledgments: We thank Professor J.H.P. Utley for the gift of a fuchsone sample.

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ELECTROCATALYTIC BEHAVIOUR OF DOPED TIN DIOXIDE FILM

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Abstract

Sb doped tin dioxide films were prepared by thermal decomposition of $SnCl_4.5H_2O$ and $SbCl_3$ mixtures applied on pretreated Ti surfaces. Precursor solutions containing 20 % p/v $SnCl_4.5H_2O$ and 0.1, 0.2 or 0.3% p/v $SbCl_3$ were used. The influence of Sb on film morphology and on electrochemical activity were assessed by SEM and cyclic voltammetry in solutions containing ferri-ferrocyanide couple, respectively. In general the films were quite adherent to the substrate, with mud like cracked appearance when observed by SEM. Their conductivity increased with the $SbCl_3$ content in the mixture. Organic oxidation at the SnO_2-Sb_2O_5 interface was found to be in the same potential domain to that observed on Pt polycrystalline electrodes suggesting a common mechanism. Electrocatalytic performance was evaluated regarding the electroconversion of 3,4-dimetoxibenzoic and 3,4-dihidroxibenzoic acids, for an specific electrolysis condition.

Key Words: Tin dioxide, eletrocatalysis, organic conversion, aromatic compounds

Introdução

Entre os materiais estudados (grafite, PbO_2, IrO_2, RuO_2, etc.) com vista à sua aplicação em tecnologias electrolíticas de tratamento de efluentes orgânicos, os eléctrodos de titânio recobertos por filmes de dióxido de estanho são os que têm apresentado melhores características [1-3]. Os eléctrodos SnO_2/Ti têm revelado maior estabilidade química e electroquímica, valor de sobrepotencial de evolução de oxigénio mais elevado e maior eficiência, quando usados como ânodos, na conversão dos compostos orgânicos aromáticos em soluções aquosas, com uma menor produção de produtos intermédios, e ainda possibilitando a sua remoção por oxidação completa em CO_2 e H_2O [4 - 7].

O dióxido de estanho é um semicondutor tipo n de 3.5 eV de hiato de banda directa quando puro. A dopagem com antimónio permite aumentar a condutividade do SnO_2 favorecendo os mecanismos de oxidação de espécies adsorvidas à superfície. Para compostos aromáticos tem sido observado aumento de eficiência de oxidação e conversão completa até CO_2 [2]. O mecanismo operante é associado a uma maior produção de espécies reactivas, como sejam os radicais hidroxilos ou o ozono resultantes da descarga anódica da água [8,9].

Várias técnicas têm sido utilizadas na preparação de filmes de dióxido de estanho sobre diferentes tipos de substratos [10]. O método de decomposição térmica é bastante usado na produção de filmes tipo DSA, a partir de soluções precursoras contendo sais dos metais do óxido pretendido. As características físicas e electrónicas dos eléctrodos são influenciadas pelo substrato e seu pré-tratamento, pela composição da solução precursora, técnica de aplicação, temperaturas de evaporação do solvente e de formação do óxido.

No caso dos filmes SnO_2 dopados com antimónio as soluções utilizadas contêm basicamente $SnCl_4.5H_2O$ e pequenas percentagens de $SbCl_3$ [11,12]. A formação do óxido ocorre a temperaturas entre 400 e 500°C, sendo admissível a presença do Sb na matrix do SnO_2 na forma de Sb_2O_5[2].

Neste trabalho foi estudado o comportamento electrocatalítico de ânodos de SnO_2 dopados com Sb_2O_5, preparados por decomposição térmica sobre substratos de Ti. A voltametria cíclica foi