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ABSTRACTS

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The application of the metallic salts of tartaric acid derivates for the resolution of P-chiral compounds

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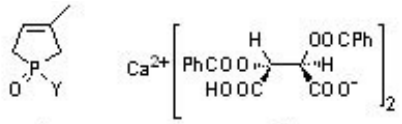
The P-chiral compounds are widely used in organic syntheses. Especially the chiral phosphines are very important, as they can be ligands in transition metal complexes and they can be applied in homogeneous catalytic processes. Since the P-chiral compounds cannot be found in enantiomeric forms in the natural pool of chirality, the primary source of these compounds is asymmetric synthesis and resolution.

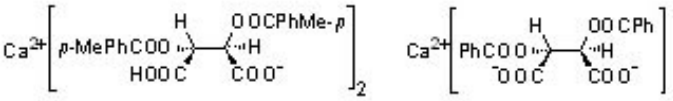
During the last few years numerous experiments had been achieved to resolve the 1-substitued-3-methyl-3-phospholene 1-oxides (**1**) using different resolving agents. The synthetic importance of these compounds can be summarized by the fact that they can be starting materials in the preparation of five-, six-, seven- and eight membered P-heterocycles, and they can be the precursors of the corresponding phosphines. Recently, an efficient method has been elaborated to resolve phospholene oxides (**1**) via molecular complex formation, using TADDOL derivates [1]. We have also achieved good results using calcium hydrogen *O*,*O*'-dibenzoyl-(2*R*,3*R*)-tartrate (**2**) or calcium hydrogen *O*,*O*'-di-*p*-toluyl-(2R,3R)-tartrate (**3**) to form diastereomeric coordination complexes with the enantiomers of phospholene oxides [2] (**1**).

In the next stage we tried to resolve **1** using calcium *O*,*O*'-dibenzoyl-(2*R*,3*R*)-tartrate (**4**), in addition Mg^{2+}, Zn^{2+}, Cu^{2+}salts of *O*,*O*'-dibenzoyl-(2*R*,3*R*)-tartaric acid and the Ca^{2+} salts of other resolving agents.



1 2

Y = aryl, alkyl, alkoxy



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O-alkylation of phenol derivatives under microwave conditions

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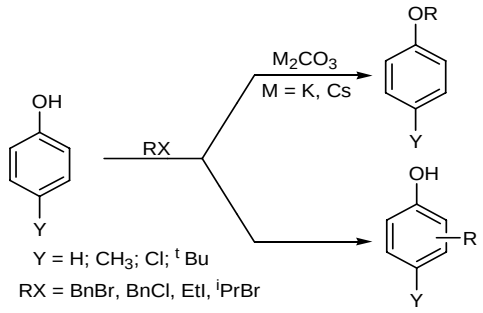
The use of microwave technique is spreading more and more in synthetic organic chemistry. There is already some application in industrial scale, however, the real breakthrough is expected in next years. Phase transfer catalysis has become also a good tool in environmentally friendly chemistry.

Alkylation of different CH-acid compounds under microwave conditions were studied earlier in our research group.

During my research work we have studied O-alkylation of various phenol derivatives under microwave conditions. Our aim was to examine what will happen if the phase transfer catalytic and the microwave techniques are combined. Will there be any synergism? Control experiments were carried out under conventional heating. Besides, our aim was to find the optimum conditions of these reactions and to identify the products.



We have evaluated the dependence of the course of alkylations on the presence or absence of the base and catalyst, and we have explored the optimum reaction conditions.

Resolution of *trans*-1,2-cyclohexanediol via supercritical carbon dioxide extraction

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Preparation of optically pure forms of chiral compounds is a highly important task in several areas of today's chemical industry. Synthesis and circulation of these compounds is extremely large-scale, and as such mitigating their environmental impact is a prominent topic within green chemistry.

I investigated the resolution of *trans*-1,2-cyclohexanediol (CHD), using – based on screenings – L-(+)-tartaric acid, according to the modified Pope-Peachy method: the resolving agent was added to the racemic compound in half-equivalent quantity, forming a stable complex with CHD in ethanol. Supercritical carbon dioxide extraction at 20 MPa and 33 °C was used to recover an enantiomer mixture enriched in *S*,*S*-CHD. The raffinate was decomposed via addition of Na_2CO_3.

The method described above is very favorable for green chemistry: carbon dioxide is inexpensive, available in great purity and is non-flammable, the product is free from solvent residue and the carbon-dioxide can be easily reused. Tartaric acid is naturally occurring, making it environmentally friendly, and can also be reused. A problem is posed, however, by the chemical raffinate decomposition, which causes significant material loss, and the solvents involved (methanol and chloroform) cause great environmental stress. Therefore, I investigated the in situ decomposition of the raffinate: the diastereomer can be decomposed by raising the extraction temperature and/or pressure, allowing the extraction of an enantiomer mixture enriched in *R*,*R*-CHD. This decomposition method is significant because it enables the regeneration of tartaric acid, while the resolution process (with the exception of the sample preparation) becomes solvent-free.

The other area of my work was studying the effect of the tartaric acid : CHD molar ratio in the range of 0 to 2. Unexpectedly, 50% of the racemic compound was recovered in the first extraction step at molar ratios over 0.5. Enantiomeric excess values increased at higher molar ratios: over 1.5 they exceeded 80% in both the extract and raffinate, with yields nearing 50-50% of the racemic compound. Powder X-ray diffraction analysis confirmed the existence of a stable complex formed between *R*, *R*-CHD and *R*, *R*-tartaric acid, while indicating the absence of a complex for *S*, *S*-CHD. The *S*, *S*-CHD – *R*, *R*-tartaric acid complex could not be prepared from any solvent. Single crystals of the *R*, *R*- CHD – *R*, *R*-tartaric acid complex were grown successfully from n-hexane – acetone solvent mixture, from these the structure of the complex was determined using single crystal diffractometry.

Permeability assay in the early phase of drug discovery

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Discovery of potent drug compounds are one of the most expensive and longest action of drug discovery. In the last two decades appeared high-throughput (HT) *in vitro* assays to reduce expenses and measurement times. The data from HT *in vitro* methods show correspondence of structure - influence and facilitate the choice of potent drugs.

Prediction of orally used drug absorption is a very important exercise in the early phase of drug discovery. Based on this statement the majority of orally administered drugs are described to be passive transported across the lipophilic cell membranes. Parallel Artificial-Membrane Permeability Assay (PAMPA), as a passive-permeability screen with focus on the simulation of transcellular processes, is a helpful stand-in for cellular models [the first PAMPA publication by Kansy et al. in 1998]. This method has been developed and has been used in original drug research in Gedeon Richter Plc. from 2005. We use two PAMPA methods. One of them can predict the potent drug absorption from gastrointestinal (GI) tract (PAMPA-GI), and the other one can predict the blood-brain barrier (BBB) penetration of potent drug (PAMPA-BBB).

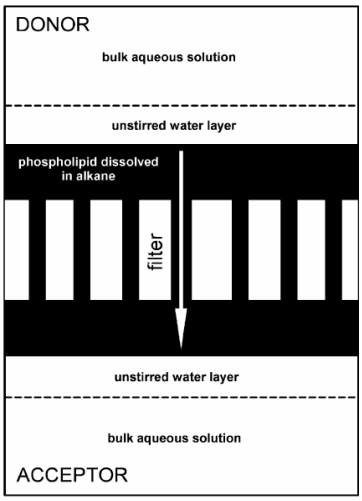

Fig. 1. Transport mechanism of PAMPA (Avdeef, A. et al. Eur. J. Pharm. Sci., Volume 22, Issue 1, 2004, Pages 33-41)

Synthesis and use of P-heterocycles in Pt(II)-complexes

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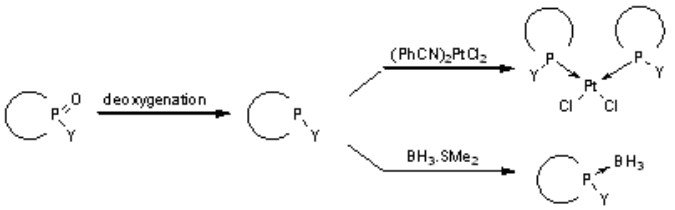
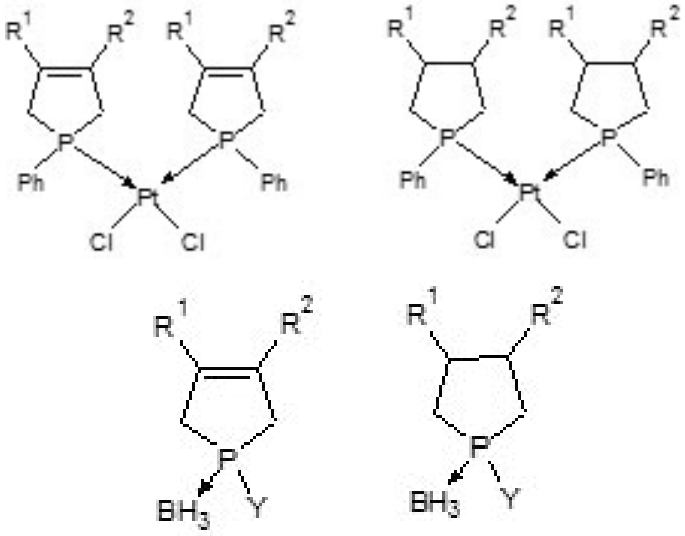
Over the last few decades the dramatically increased importance of asymmetric transformations catalyzed by transition metal complexes has been paralleled by the growing desire for chiral ligands. Among these, the P(III)-compounds are especially significant as the phosphine-metal complexes have proven to be versatile modifiers and can function as stereospecific catalysts. An impressive number of applications have been reported where almost enantiopure products were obtained in high chemical yield. Furthermore, these Rh-, Ru-, Pd- and Pt-complexes are frequently used catalysts in hydroformylations and hydrogenations.

My research work comprised the synthesis of five- and six-membered phosphorous heterocycles, their borane and platinum(II) complexes illustrated by the following scheme.



After deoxygenation, the 3-methyl- and 3,4-dimethyl-1-phenyl-3-phospholene oxides and their saturated derivatives were reacted with dichlorodibenzonitrileplatinum and dimethylsulfide borane. Thus, the compounds shown below were obtained.



Our future plan is to test these platinum(II) complexes in homogenous catalysed reactions.

Synthesis of new biologically active vindoline derivatives

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Vindoline (1), catharanthine (2) and their derivatives are the major components of important bis-indole alkaloids, from which vinblastine and vincristine have been used in anticancer therapy.

In spite of the fact that the chemistry of vinblastine and vincristine represents one of the most exciting fields of research of alkaloids, about simple aromatic electrophilic substitutions (nitration, halogenation, *etc*.) accomplished on A ring of the monomer alkaloid vindoline only few data can be found in the literature.

In the course of investigations of the S_EAr reactions of the aromatic ring A of vindoline (1), nitration and halogenation reactions were studied. Nitration of the 10-bromovindoline resulted in 12-bromo-10-nitro derivative, due to *Reverdin*-rearrangement. 12-Amino-10-chlorovindoline was also prepared.

Moreover, the ester function of vindoline in the position 16 was transformed into amides by reacting it with D-amino acid esters. Experiments were also carried out to connect amino acids to the amino group of the aromatic ring A.

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Both species specific and evolutionarily conserved structural elements are affecting the catalytic activity of *Mycobacterium tuberculosis* dUTPase

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Tuberculosis is the most dangerous infectious disease causing the death of 2 million people per year, according to recent data from WHO. Some of the mycobacterial strains have become resistant to currently used antituberculotics, therefore development of new drugs is needed from basic research initiatives.

dUTPase, which has long been studied in our laboratory, plays a crucial role in preserving DNA integrity. It catalyzes the cleavage of dUTP into dUMP and inorganic pyrophosphate, and thereby determines the intracellular dUTP/dTTP ratio. The enzyme dUTPase is likely essential for *Mycobacterium tuberculosis* because in mycobacteria, the dUTPase-catalyzed reaction is the only *de novo* biosynthetic route leading to dUMP, the obligatory precursor for dTTP biosynthesis. Experimental data suggest that in the absence of dUTPase thymine-less cell death occurs, therefore dUTPase is a potential drug-target.

To explore the difference between human and *Mycobacterium tuberculosis* dUTPases and to find out what amino acids are responsible for dUTP binding, several mutations were created site-specifically on the C-terminal arm of *Mycobacterium tuberculosis* dUTPase. The mutant proteins were expressed in *Escherichia coli* cells and were purified using affinity chromatography. Activity was measured via radioactive dUTP hydrolysis assay and also by measuring the release of protons with phenol red pH indicator in a spectrophotometer. The dissociation constant of the enzyme-substrate complex was determined by fluorimetric titration via a previously incorporated tryptophan amino acid.

Our data suggest that the C-terminal arm of *Mycobacterium tuberculosis* dUTPase accelerates but is not essential for dUTP hydrolysis. 3-200-fold decrease in enzyme activity was detected in the case of the various mutants. The dissociation constants showed one order of magnitude increase compared to the wild type enzyme, which means weaker interactions between the enzyme and its substrate. We also found, that a mycobacterium-specific loop in dUTPase affects enzymatic activity, which will serve as a basis for species-specific drug-design.

Statistical Analyses of Length Growth Patterns in Fission Yeast

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In the first half of the 20th century yeasts have become model organisms in different fields of cell biology. Since the late '50s *Schizosaccharomyces pombe* (also known as fission yeast) has been spotlighted through its favourable physiological features, for example, its symmetrical division enables good synchronisation techniques, which are necessary for cell cycle studies. The cylindrically shaped fission yeast cells grow exclusively at their tips almost from birth to division by maintaining a constant diameter, therefore cell length is approximately proportional to cell volume. As a consequence, cell length is an easily measurable parameter, which characterizes cell age, i.e., progression through the cell cycle. Length growth patterns may therefore

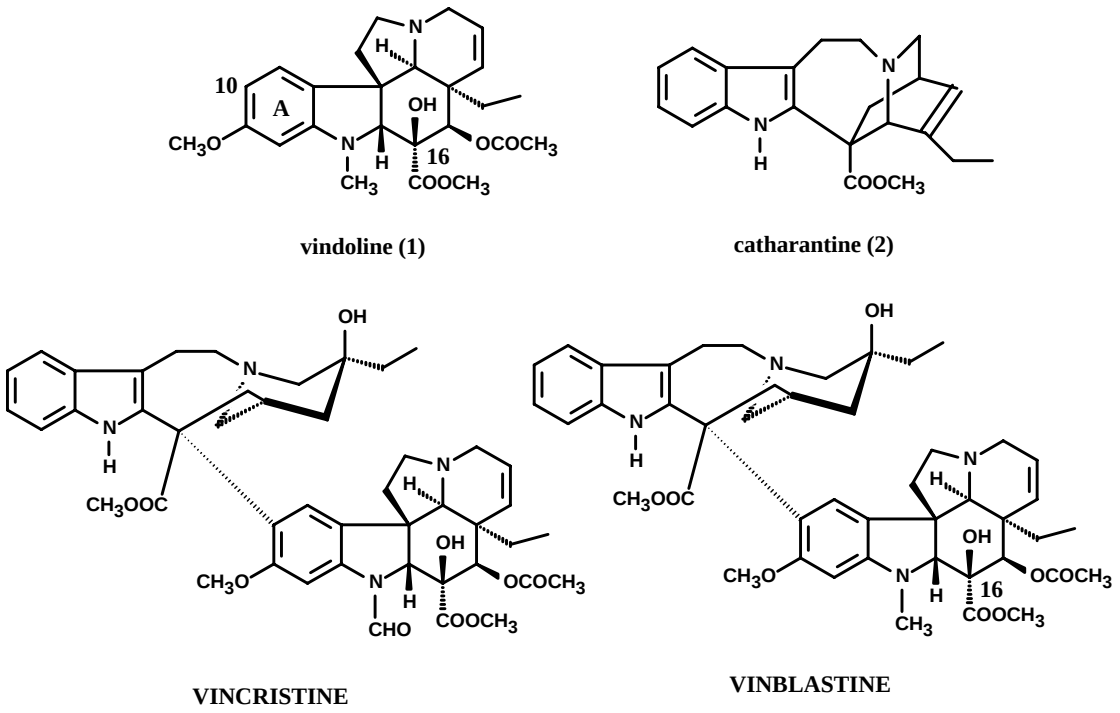

Fig. 2.

indicate connections between volume changes and cell cycle events. The classical method to study the growth of individual cells is time-lapse microphotography; cells are growing on the surface of an agar pad in a thermostated photomicroscope, and later on we can study the growth pattern of cell length simply by a projector.

In different cell types, there is considerable controversy concerning the exact growth profile of size parameters during the cell cycle. Linear, exponential and bilinear (i.e., two linear segments with a rate change point) models are commonly considered, and the same model may not apply for all species. Selection of the most adequate model to describe a given data-set requires the use of quantitative model selection criteria, which are suitable for comparing differently parameterised models. Length increase data from two individual fission yeast cells (one wild-type and one *wee1*Δ mutant), measured on time-lapse films have been reanalysed using these model selection criteria. To fit the data, a recently introduced linearised biexponential model was developed, which makes possible a smooth, continuously differentiable transition between two linear segments. (This function might be even more realistic than using two linear segments with a breakpoint.) Essentially all the quantitative selection criteria considered here indicated that the bilinear model was somewhat more adequate than the exponential one for fitting these two fission yeast cell data. Although the bilinear model seems more adequate, especially in the case of the *wee1*Δ cell, the statistical evidence is not strong enough to favour one model clearly over the other.

Later, this method was extended for 122 newly measured fission yeast cells, 60 wild type and 62 *wee1*Δ mutants. The above mentioned model selection criteria were used for discriminating among linear, exponential and bilinear models and selecting the most adequate one in the case of these cells' length growth patterns. Although relatively small differences were found in several cases, essentially all the quantitative selection criteria considered here indicated that the bilinear model was generally more adequate than either the exponential or the linear ones. "Average cells" were also constructed from both the wild type and the *wee1*Δ mutant individual cells' data, whose patterns were definitely found to be bilinear by any criterion used. For further evidence, this method is also planned to be applied for some more cell cycle mutants of fission yeast.

Stability and stabilizability of six-membered ring carbenes and silylenes

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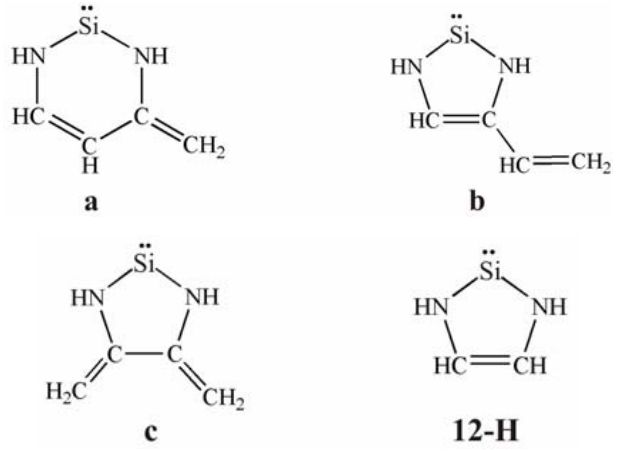
The stability of the recently synthetised six-membered ring silylene (**a**) and its nine isomers were investigated by quantum chemical methods. The three most stable isomers were compared to the well-known stable Denk-sylilene (**12-H**). The related analogous carbenes and germylenes were also studied.

All calculations were performed using the B3LYP method at cc-pVTZ or 6-311++G** level. The most imortant results are the following.

1 The global minimum of the potential energy hypersurface corresponds to structure **b**, which has not been synthetised yet. The synthetised structure **a** was only the second most stable

isomer. An other five-membered ring izomer, **c** was only 3.4 kcal/mol less stable than **a**. The global minimum of the potential energy hypersurface of the analogue carbenes was a tetravalent silene isomer.



2 The stucture and energy order of the molecular orbitals show that **a** is less reactive than the certainly inactive **12-H** in both nucleophilic and electrophilic reactions. The conjugation at the butadiene part of **b** did not remain, the endocyclic double bond probably becomes the part of an aromatic system. The remaining conjugation at the butadiene part of **a** and **c** suggests no conjugation at the ring.

3 The isodesmic reaction energies indicates that the ring strain is not considerable in **a** and **c** isomers, thats why these structures could be almost as stable as the Denk-sylilene. The similar aromatic stabilization was found in **b** and in **12-H**. The aromaticity of **b** was supported by the geometry data, bond indexes and NICS calculations. There is a good hope that the aromatic **b** is a sythetisable compound.

4 According to the 1,2*H*-migration reaction energies and activation barriers instead of the carbene analogue of **a** a tetravalent structure is more likely to be synthetised.

5 Changing the γ-substituents of **a** (counted from the divalent centrum) has only a little effect on the stability. None of the substituted molecules were aromatic, so aromaticity has no important role in the stability of the six membered ring silylene (**a**).

This work will be continued with the investigation of dimerisation and 1,2*H*-migration reactions of all the three isomers.

Synthesis of Novel 5-HT$_6$ Receptor Ligands

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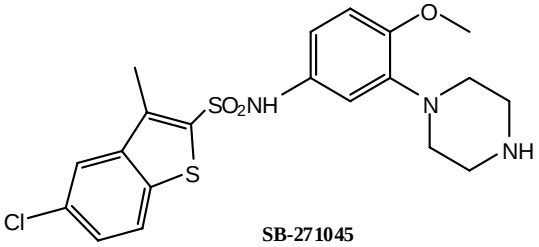
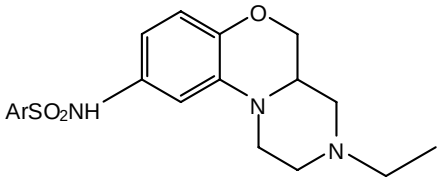
Owing to its unique distribution, occurring exclusively in the central nervous system, the recently discovered 5-HT$_6$ serotonin receptor is a promising novel target for the development of medicaments against diseases of the central nervous system. Antagonization of the receptor increases colinergic and glutaminergic neurotransmission and improves cognitive functions. Selective, potent 5-HT$_6$ antagonists could play an important role in the future treatment of diseases of the CNS like dementia associated with Alzheimer's disease, depression or obesity.

Over the course of my research in cooperation with ESTEVE, Spain, four tricyclic analogs of a selective 5-HT$_6$ antagonist (SB-271045, GlaxoSmithKline) containing a phenylpiperazine structure were synthetized (1a-d).



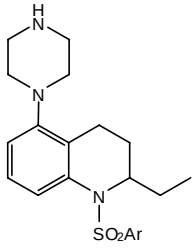
SB-271045



1a - d

Ar
1a : 1-naphthyl
1b : phenyl
1c : 4-methylphenyl
1d : 2,5-dimethoxyphenyl

As the second part of the research, an investigation of the possibilities for the synthesis of the 2-ethyltetrahydroquinoline compounds having the general formula **2** was carried out. The common intermediate of the compounds **2** was accessed *via* several routes and the synthesis of the first analogue was completed.



2

Synthesis of novel optically active crown ethers containing an alkyl diarylphosphinate or a proton-ionizable diarylphosphinicacid unit and their achiral analogues

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Proton-ionizable crown ethers have received a great deal of attention, because at pH values higher than their pK_a, they are mostly ionized to ligand anions, which increase the cation–ligand complex stability with enhancement of selectivity, and avoid the need for a counter anion in cation transport through various membrane systems or in solvent extraction. The latter feature is very advantageous especially in the case of practical separations where the transport of hydrophilic aqueous phase anions, such as chloride, nitrate and sulfate should be avoided. Acidic proton-ionizable macrocycles can be used to transport some heavy metal cations and organic primary ammonium ions from a source phase of relatively low pH value. Bradshaw and coworkers prepared racemic proton-ionizable ligands, containing a fairly acidic dialkylhydrogenphosphate unit [1]. These lipophilic ionophores showed a reasonable transport of alkali and some heavy metal cations in an aqueous source phase–dichloromethane bulk membrane–aqueous receiving phase system [2]. In order to find crown ether type host molecules possessing enhanced selectivity for both the enantiomers of protonated primary amines and metal cations in binding, solvent extraction, membrane transport and other studies, we prepared novel enantiopure macrocycles (*R*,*R*)-**9**, (*R*,*R*)-**10** and their achiral parent compounds **7**, **8** by hydrolysis of the latter esters (*R*,*R*)-**12** and **11** containing the acidic diarylphosphinic acid moiety. Novel proton-ionizable ligands (*R*,*R*)-**12** and **11** seem to have several advantageous features compared to the reported crown ethers possessing the dialkylhydrogenphosphate unit. The two aromatic rings make the pseudo-18-crown-6 framework more rigid conferring higher selectivity in the molecular recognition process. Ligands (*R*,*R*)-**12** and **11** are more resistant to both acids and bases so their applications can be wider. The aromatic rings of macrocycles (*R*,*R*)-**12** and **11** readily undergo electrophilic substitution and by introducing appropriate substituents into them the acidity of the OH proton, the lipophilicity, the complexation properties and the photophysical behaviour of the latter macrocycles can favourably be altered.

The enantiopure ligand (*R*,*R*)-**9** and (*R*,*R*)-**10** was prepared from methyl (**1**) and ethyl (**2**) bis(2-hydroxyphenyl)phosphinate and enantiopure dimethyl-substituted tetraethylene glycol ditosylate (*S*,*S*)-**6** at 50°C in DMF using K_2CO_3 as a base. The achiral analogues **7** and **8** were also prepared by Williamson ether synthesis under the same conditions, mentioned above, although in this case the macrocyclization was carried out with tetraethylene glycol derivatives containing three different leaving groups, such as tosylate (**3**), chloride (**4**) and iodide (**5**). Enantiopure proton-ionizable ligand (*R*,*R*)-**12** and the achiral analogue **11** containing the diarylphosphinic acid moiety was prepared from the corresponding phosphinic acid esters (*R*,*R*)-**9**, (*R*,*R*)-**10**, **7** and **8**, respectively, by acidic hydrolysis at elevated temperature using a dioxane–10% aqueous HCl (1:1) mixture. This work was supported by the Hungarian Scientific Research Fund (OTKA K62654, PD71910).

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Monitoring and optimization reactions of oxo-compounds with *in situ* Fourier transform IR spectroscopy

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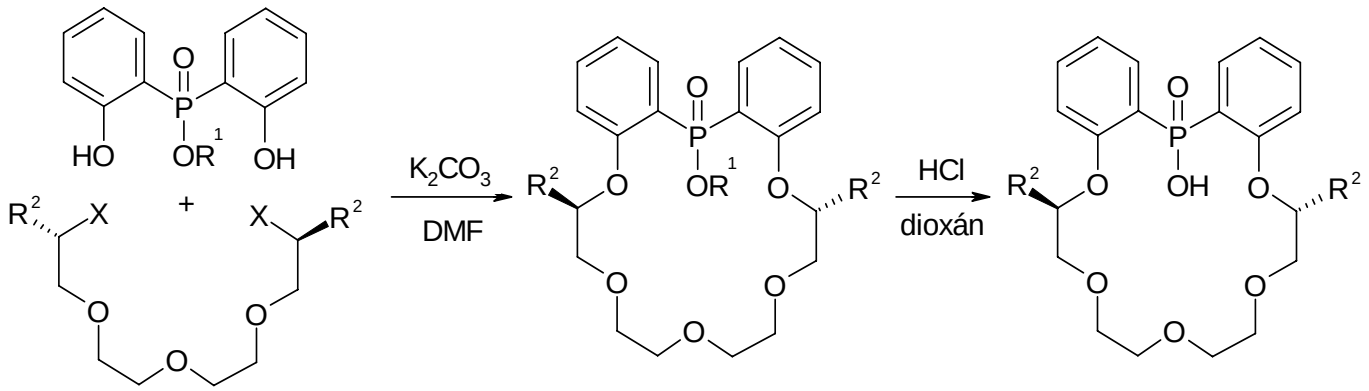
The Fourier transform IR spectroscopy becomes more and more important in synthetic organic, pharmaceutical and plastic industry, since it gives the possibility of online monitoring of reactions and observing intermediates. This information is appropriate not only to optimize reactions, but also to modify the technologies from environmental point of view. The aim of the research was to study the possibilities given by the *in situ* Fourier transform IR spectroscopy.

In the first part of the research the oximation of different aldehydes and ketones was studied. Acetone, ethyl-methyl-ketone and benzaldehyde were used as the oxo-compound (1). The effect of the pH on the two-step oximations was studied and the reactions were optimized. The solubility of ethyl-methyl-ketone and benzaldehyde is poor in water, hence heterogenous reactions had to be studied. The experiments were carried out in an environmental way, without organic solvents. The reactions were studied in heterogeneous phase with changing the reaction-parameters. It is a great step forward that heterogeneous liquid-



	R^1
1	Me
2	Et

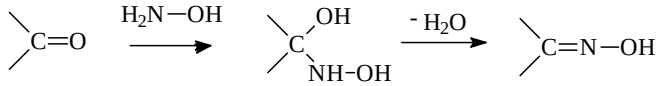
	R^2	X
3	H	OTs
4	H	Cl
5	H	I
(*S*,*S*)-**6**	Me	OTs

	R^1	R^2
7	Et	H
8	Me	H
(*R*,*R*)-**9**	Et	Me
(*R*,*R*)-**10**	Me	Me

	R^2
11	H
(*R*,*R*)-**12**	Me

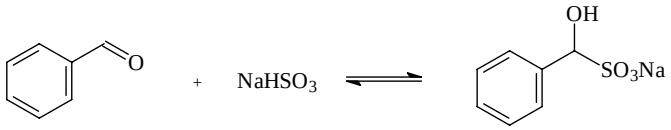
Fig. 3.

liquid phase reactions could be monitored and optimized.



(1) (2) (3)

At the second part of the research, the aim was to optimize and monitor reactions which lead to equilibrium. In chemical industry these kind of reactions are not rare, therefore the easy and environmental way of optimizing this reactions is important. The model chosen was the addition reaction of benzaldehyde and sodium-bisulfite. The equilibrium constants of the reaction were determined from the experiments carried out at room-temperature and at 60 ˚C.



(4) (5) (6)

Correlation between the additive package and the hydrolytic stability of high density polyethylene pipes

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Polyethylene (PE) is widely used in the construction industry for gas and water pipes. These pipes have to resist different impacts: heat, oxygen, UV radiation, aqueous media, etc. In order to achieve the expected life time, even 50 years, the PE pipes have to be stabilized adequately. Besides the chemical effectiveness of the antioxidants their interactions, migration and dissolution into water have to be also considered.

My research is focused on the study of the characteristics of polyethylene pipes stabilized with different combinations of a primary (hindered phenol) and a secondary (sulphur-containing and hindered amine) antioxidant. The aim of research is to determine the correlation between the composition and the effectiveness of additive packages during processing of pipes and soaking them in water. Phillips type Tipelin PS 380 grade polyethylene was for the experiments. The polymer was homogenized with the additives and pelletized at TVK then pipes of 32 mm nominal external diameter were extruded at Pannonpipe. The pipes were aged in water at 80 ˚C for 0, 3, 5, 7 and 12 months at TVK.

The chemical characteristics of the polymer (methyl, unsaturated and carbonyl groups) are studied by infrared spectroscopy (FT-IR). The discoloration of pipes is characterized by the yellow index (YI) and the optical L parameter. The rheological properties are investigated by melt flow index (MFI) and the residual thermo-oxidative stability of the polymer by oxidation induction time (OIT) measurements. The physical structure of pipes is characterized by the density and the fusion properties. The mechanical strength of the polymer is measured by tensile tests. To determine the strength of pipes the rate of crack propagation is investigated according to the ISO 13480:1997 standard (Cone-test).

The change in the characteristics of pipes stabilized with combinations of two phenolic and five secondary antioxidants is described in my paper. The results show that the various additive packages influence the processing and hydrolytic stability

of the polymer differently. The properties of the polymer are controlled mainly by the chemical reactions taken place during the processing, while the consumption of stabilizers and the discoloration of polymer are determined by the soaking time. Correlation can be established between the chemical structure of the polymer and the strength of the pipes.

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Characterization of *Trichoderma reesei* Rut C30 cellulase enzyme production on various carbon sources

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Nowadays, ethanol is the most important renewable fuel in terms of volume and market value. Currently it is produced from sugar- and starch-based materials such as sugarcane and corn. But these agricultural products are going to get more expensive, thus second generation ethanol derived from lignocellulosic materials come to the fore.

The main components of lignocelluloses are cellulose, hemicelluloses and lignin. Lignocellulosic materials have very complex structure, hence requiring pretreatment to loosen up this intact polysaccharide network. In the bioconversion of lignocellulosic materials cellulase enzyme complex has important role. This complex consists of three types of enzymes that act synergistically in cellulose hydrolysis. Endoglucanases randomly attack cellulose chains and release cello-oligosaccharides, exoglucanases cleave cellobiose units from the end of cellulose chains and β-glucosidase converts the resulting cellobiose to glucose. Hemicelluloses are more heterogeneous polymers and several enzymes are needed to their degradation.

In the course of my TDK work I dealt with the fermentation and characterization of cellulase and hemicellulase enzymes produced by *Trichoderma reesei* Rut C30 in shake flask cultivations on steam pretreated corn stover, lactose and delignified spruce pulp (Solka Floc), as a reference. Corn stover is an agricultural, lactose a dairy industrial residue, which are available in huge volume at low-price. The oxygen-demand of the fungus was ensured by shaking the flasks. Fermentations were followed by pH and reducing sugar measurements. The produced enzymes were characterized by protein and various enzyme activity measurements (filter paper, β-glucosidase, xylanase and xyloglucanase activities). An attempt was made to test the hydrolytic potential of the produced enzyme complexes in subsequent hydrolysis. The aim of my future work is to characterize wide spectra of enzymes produced by *Trichoderma reesei* Rut C30, and to evaluate possible substrates suitable for both enzyme fermentation and hydrolysis.