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ABSTRACTS

MODELING THE WARM-UP PHENOMENA OF FLUORESCENT LAMPS

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The aim of the work was to investigate, why the long T5 fluorescent tubes, manufactured by GE-Tungsram at Vác, are characterized by the following transition phenomenon: turning the tube on, the middle remains dark for minutes, while the ends light up rapidly, that causes a disturbing contrast effect. Changes in the technology aiming an improved removal of impurities resulted in regular tubes.

For the deeper investigation of the problem, light intensity measurements were carried out using a self built instrument. The results support that the phenomenon is the following: During the discharge, small time-constant reactions consume the mercury vapour, so the light intensity decreases. Besides this, a large time-constant diffusion transport starts from the mercury depots, located in the ends, and probably an even slower desorption takes place from the walls, too, that rise the mercury concentration until equilibrium, when the final light output is reached. Turning the discharge off, these compounds decompose, the excess of mercury migrates to the cold spot, and also adsorb on the wall-coating. A similar instrument has been built for quality control that is being tested recently, in the factory.

Beside the measurements, quantum chemical computations have been carried out to model the possible reactions. We can conclude that among the contaminants, the water plays a significant role in the phenomenon by the following reaction scheme: $Hg^+ + OH > (HgOH)^+$ [$\Delta E = -39.5$ kcal/mol]; $Hg^+ + H > (HgH)^+$ [$\Delta E = -52.9$ kcal/mol]. All species that are formed in the discharge, react with OH and H radicals by decomposition of water. These species are unstable and decompose to the initial compounds when the discharge ceases.

STUDY ON THE REACTIVITY OF 1-(2,4,6-TRIALKYLPHENYL)PHOSPHOLES

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Phospholes form a representative class of P-heterocycles. We studied the reactivity of phosphole derivatives with a sterically demanding 2,4,6-trialkylphenyl substituent on the phosphorus atom with dienophiles.

Diels-Alder reaction of the phospholes and N-phenylmaleimide at 110 °C gave, surprisingly, a mixture of *endo* and *exo* fused cycloadducts with the P-aryl substituent *anti* to the double-bond. To obtain stable products, the phosphines were oxidized to the corresponding oxides. After the oxidation, we observed that the configuration of the phosphorus atom in the *exo* ring-fused product was inverted under the conditions of the oxidation. The stereochemical conclusions were supported by $^2J_{PC}$ stereospecific couplings.

In certain cases only the *anti* product was formed in the *Diels-Alder* reaction.

In an other experiment, it was proved that the *syn-endo*-cycloadduct was isomerized to the more stable *anti*-derivative.

Furthermore, we studied the reactivity of phosphole-oxides in cycloadditions. As the dienophile, we used N-phenylmaleimide or another molecule of the phosphole-oxide bearing a sterically demanding 2,4,6-trialkylphenyl substituent on the phosphorus atom. In these cases, we obtained the corresponding cycloadducts or the phosphole-oxide dimers, or – in crossed-reactions – the mixture of dimers.

RELATIONSHIP BETWEEN AROMATICITY AND DIELS–ALDER REACTIVITY

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Aromaticity is an old concept in chemistry. Originally it was used as an explanation for the 'peculiar reactivity' of certain compounds. In the recent years many attempts have been made to provide quantitative descriptors for the aromaticity. These were based on physical measurables, like geometrical, magnetic and energetic quantities. In the present work we have demonstrated that the reaction barriers calculated by ab initio methods correlate well with the previously introduced aromaticity measures, thus providing a possibility for the quantitative description of aromaticity in accordance with the original chemical concept. The rection barriers were calculated for $4+2$ Diels–Alder cycloaddition reactions for a large set of five and six membered heterocycles containing one and two heteroatoms. The calculations were carried out at the B3LYP/$6-311+G^{**}$ level of theory. The correlation of the reaction barrier with the Bird index, BDSHRT, NICS(0) and NICS(1) values, ASE and superhomodesmotic reaction energies have been investigated. The correlation for the five membered ring compounds is good, while for the six membered rings it is getting much worse, due to the fact that the aromaticity of the six membered rings shows only a small variance with the change of the heteroatoms.

PHYSICO-CHEMICAL INVESTIGATIONS OF OPTICAL RESOLUTION WITH A DERIVATIVE

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Resolutions via diastereomeric salts can be investigated with the help of ternary and binary phase diagrams. Binary phase diagrams can be determined based on thermoanalytical measurements using the Schroeder–van Laar equation. Thermoanalytical measurements with a DSC (Differential Scanning Calorimeter) need only a few milligrams of sample, and can be performed quickly. This method can be used only for those diastereomeric salts that in solid phase are immiscible, any composition of them is the physical mixture of the diastereomeric crystals, the so-called conglomerates. The phase diagram will show an eutectic point. Efficient resolution can only be expected for compounds showing this type of phase diagrams.

We used the above described technique to investigate resolutions with derivatives. These resolutions are done by preparing the resolving agent to be structurally similar to the compound to be resolved. One enantiomer of the compound to be resolved is reacted with an achiral agent to obtain the resolving agent. The reaction is done in such a way to create a functional group that can interact with the original molecule through acid-base interactions and hydrogen bonding. It has been observed that diastereomeric salts often form very similar crystal structures, with similar acid – base interactions and hydrogen bonds. Since their physico-chemical properties (e.g. melting poins, solubilities) are different the weaker intermolecular interactions must be taken into account. Since optical resolution is based on the different solubilities of the diastereomers it is important to make use of these weaker interactions. When using a derivative as a resolving agent it can be expected that there is a good fit between the acidic and basic molecules.

(R)-phenylethyl amine has been reacted with dicarboxylic acids to form monoamides that have been used for the resolution of phenylethyl amine and 4-methyl phenylethyl amine. It has been observed that the resolutions give good results. The physico-chemical investigations supported this observation.

EXTRACTION OF CORN GERM WITH DIFFERENT SOLVENTS AND THE ANALYTICAL INVESTIGATION OF THE PRODUCTS

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The aim of this study was to investigate the extraction of corn germ and its pressed residual. Experiments were carried out using three processes: laboratory Soxhlet extraction, pilot-plant extraction with four solvents: ethyl alcohol, ethyl acetate, *n*-hexane and isopropyl alcohol and supercritical fluid extraction with carbon dioxide (450 bar, 50 °C). The extraction yields and oil compositions were compared. Higher amount of extract was obtained from the oily corn germ in comparison to the pressed residual. The highest extraction yields were obtained with ethanol from both samples (50.8% and 19.9%) although these extracts became divided into two parts. Increasing the solubility factors (δ) of the solvents the yields also increased.

The extracts were examined by TLC-densitometry, GC and HPLC methods and with standard edible oil analytical tests. The colours of the samples were also determined. The oil samples contain fatty acids (as main compounds linoleic 55%, oleic 28% and palmitic 12% acid), phytosterols (which have been noted for their cholesterol-lowering properties), tocopherols (as main coumpound γ-tocopherol ($\sim$ 750 ppm), α-tocopherol ($\sim$ 200 ppm), α-tocotrienol ($\sim$ 200 ppm), δ-tocopherol ($\sim$ 35 ppm) and β-tocopherol ($\sim$ 10 ppm)) and phosphor.

According to the efficient amount of oily extract and its high quality, SFE is a promising process for food industrial application.

EXAMINATION OF IGNITION AND BURNING PROPERTIES OF HIGH-PRESSURE AUTOMOTIVE DISCHARGE LAMPS

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A new generation of automotive lighting has been recently born. Greater intensity, brightness and efficacy can be achieved in a smaller volume with high-pressure discharge lamps. This leads to better focusability. The most attractive feature of this lamp type is its long lifetime. To enjoy these properties the problems of producing an ignition pulse and operating the unit on the battery voltage (12 V) have to be overcome. This is achieved by an electric device which is called ballast. The specification of automotive industry requires the lamp to reach 80% of its nominal light emission in 4 seconds after turning on. Producing repeated ignition pulses needs time, therefore the number of pulses to ignite the lamp is an important factor to define quality.

In order to determine the ignition probability a test has been developed to count the number of pulses required for ignition. There were 130 ignition trials in the test. The number of impulses followed a quasi geometrical distribution. The best approximation of the ignition probability resulted from the statistical analysis when the first-impulse ignition trials were omitted and only the rest was taken into account. The ignition probability calculated was characteristic for the individual lamps but not for the lamp groups which were manufactured in the same time with the same technology.

By applying alternating current to the lamp the ratio of the maximum value and rms value of the arc voltage was measured. The calculated thermal time constant of the arc was also tested by measurement. We found that it was characteristic both for the individual lamps and for the manufactured series. In our measurements no correlation between the ignition probability and thermal time constant was found. On the other hand, the thermal time constant might be used to measure the pressure of the filling gas in the lamp volume.

DEVELOPMENT OF A NOVEL SEPARATION TECHNIQUE OF FINE PARTICLES USED IN LINEAR FLUORESCENT LAMPS: PRE-STUDIES

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In our studies we used GE halophosphate, barium-aluminate, lanthanum-phosphate and yttrium-oxide phosphors as received.

Relative sedimentation volumes and zeta potential have been measured by using different surfactants as a function of the surfactant concentration and the pH of the solution. From the above experiments cationic surfactants and a specific pH range have been chosen for flotation trials. These trials that have been carried out in a lab scale flotation device showed that electrostatic effects drive the flotation. When one component of solid particles was tried to flotate in the cell and the particles were negatively charged then they attached to the positively charged foam bubbles. When the particles were positively charged the foam has not transported these particles. Upon the above we tried to make a selective separation of two component blends, however, no selectivity has been found.

The possible explanation is that a heterocoagulation occurs between the oppositely charged particles that screens the driving electric effects and/or other forces (such as the inertial and gravitational forces in microflotation and/or some other colloidal force) decrease the selectivity. More work needs to influence the hydrodynamic conditions in the flotation cell and also to avoid the heterocoagulation.

INVESTIGATION OF CERAMIC–METAL BOND IN HIGH-PRESSURE SODIUM LAMPS BY MEANS OF SURFACE ANALYSIS

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The electrical lead-in of high-pressure sodium lamps is usually made of niobium, because its thermal expansion coefficient fits well to that of the arc tube, made of aluminium-oxide ceramic. As a sealing between the niobium and the ceramic body of the lamp serves a special enamel. The quality of the bond between the niobium and this sealing plays a critical role in determining the lifetime of the high-pressure sodium lamps.

Surface analysis methods are adequate means to investigate the above mentioned bond. Model samples were produced by melting the seal to a niobium sheet. The niobium and the seal were separated, and the interface was investigated by SIMS and XPS. We have studied the changes of the concentration of the different elements by means of SIMS depth profiling, and the chemical states by XPS.

We have found that some niobium was dissolved in the seal, and an interfacial layer took place between the niobium and the seal. The composition of this interfacial layer differs from the bulk composition. From the chemical shift of the XPS peaks, we have established, that the dissolved niobium is in the form of niobium(V)-oxide, and there are some differences in the chemical state of the aluminium, too.

RESOLUTION OF α-PHENYLETHYLAMINE AND ITS DERIVATIVES BY α-PHENYLETHYLAMINE ENANTIOMERIC DERIVATIVES

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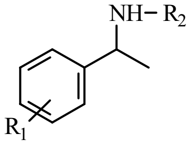
Nowadays, the most frequently applied process to produce optical isomers is the separation of the diastereomeric salts, made from the initial racemic compound. The literature recommends a number of resolving agents to separate the racemic compounds, for example: tartaric acid and its derivatives, phenylethylamine, or phenylisopropylamine and its derivatives, etc. Nevertheless, we often have to use toxic reagents (brucine, strychnine, etc.) to separate the enantiomers. At the same time, there are some known cases when the racemic compound is separated by one of its derivatives. In these cases the resolving agent can be obtained from the useless byproduct enantiomer. It is supposed that the most favourable resolving agents of a particular compound can be found among their own derivatives. This is explained by examples of very good enatiomeric separation, and by the fact that the diastereomeric salt crystallized from the reaction mixture contains one or both enantiomers. In these cases quasi-racemic and quasi-enantiomeric ionic pairs are formed, which remind of the conglomeratic or racemic behaviour of the initial racemic compound.



R$_1$: racemic bases
H
o-CH$_3$
m-CH$_3$
p-CH$_3$
m-OCH$_3$
p-OCH$_3$
p-Cl
p-Br

R$_2$: resolving agents *(R)*
OCCOOH
OCCH$_2$COOH
OCCH$_2$ CH$_2$COOH
OCCH$_2$ CH$_2$ CH$_2$COOH
o-OC-Ph-COOH

Based on these results, we tried to enlarge the range of the own derivative resolving agents and we worked on experiments to study the regularities of resolution. We examined whether the derivative resolving agent is necessary needed for the good enantiomeric separation, and we studied if a homologous resolving agent line can be used just only in special cases or it can be applied generally.

We resolved the racemic bases with the resolving agents shown on the table. We reached 99–100% enantiomeric enrichment in every case.

EXAMINATION OF RIDGE REGRESSION USING SIMULATED AND REAL DATA

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Computing the parameters of a model from experimental data is a frequent task in chemical engineering. The goal is to achieve accordance among estimated and true parameters with high probability.

The estimators are divided into two groups: unbiased (the expected values of the parameters are equal to the true parameters), like in the least squares method; and biased, like in the ridge regression. It can be advantageous, if we use a slightly biased estimator with smaller variance than an unbiased one with large variance.

I compared the ridge regression with the method of least squares using both simulated data (the true parameters are known) and real data. In the computation we used three data processing methods: without transformation, with centralisation and with standardisation. The calculations were made with the softwares Mathematica and Statistica. Due to the difficulties of using Mathematica with external, large data matrices, I wrote Visual Basic for Statistica macros to perform the ridge trace.

The results show that the structure of the data has great influence on efficiency, but in three cases from among the examined four ones the results of the ridge regression were better then those obtained by the least squares methods.

A NEW EFFICIENT ZEOLITE CATALYST IN ORGANIC SYNTHESES

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The examination of the applicability of different mineral-based reagents and catalysts in organic syntheses seems to be an important field of the research work in the preparative organic chemistry even from the practical point of view. Natural clays have several advantages as they are environmentally-friendly, non-toxic, recoverable, reusable and inexpensive, nevertheless they are efficient mild catalysts.

The aim of our work was to check whether a new zeolite-type product family, Ersorb is applicable in organic syntheses, e.g. as catalyst or condensing agent. Ersorb-4 (E4) is a weakly acidic clinoptylolite-type zeolite material with pore size of 4 Å. It can adsorb small molecules such as water, hydrochloric acid, ammonia, methanol or hydrogen sulfide.

Reaction of free amino acids with acid chlorides in dioxane in the presence of modified E4 results in the formation of the appropriate N-acyl derivatives. High yields were obtained with aryl chlorides and poorer with aliphatic ones.

Similarly, in the presence of E4 aromatic carboxylic acids and 2-aminoalcohols give the appropriate 2-aryl-oxazolines with good yield.

Aromatic aldoximes were converted to the corresponding nitriles in a microwave oven in the presence of E4 under solvent-free conditions.

In conclusion, in these cases simple, cheap and environmentally friendly syntheses were developed. The work-up of the reaction mixtures is very simple, the catalyst can be recycled without any loss of activity.

THE STRUCTURE OF 1,4-DIPHOSPHATRIAFULVENE

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The structure and properties of 1,4-diphosphatriafulvene have been studied with high level ab-initio and DFT methods (QCISD, CCSD, MP4, MP2, B3LYP for geometries and energies, B3LYP and MP2 for other properties, CBS-Q for activation barriers and reaction energy calculation).

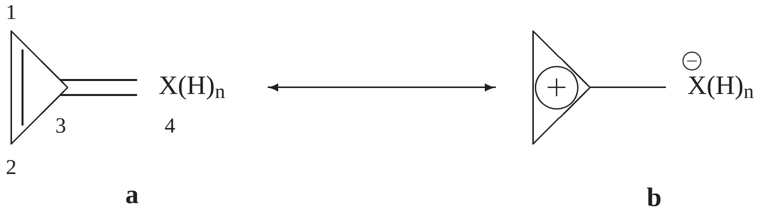

Fig. 1. The structure of triafulvenes

As shown in *Fig. 1* triafulvenes contain a three membered ring and a heteroatom double bonded to the ring. There are two resonance structures, the right one is aromatic, the left is not, which indicates that triafulvenes are partially aromatic compounds. In case of the aromatic structure the X heteroatom has a partial negative charge, so this atom has nucleophilic character, in spite of the fact that X can be more electropositive than the carbon atom (for example $X =$ Si or P).

1,4-diphosphatriafulvene is the newest member of the few known triafulvenes synthesized by Masaaki Yoshifuji in 2001.

In contrast to 4-silatriafulvene, 1,4-diphosphatriafulvene is a rigid molecule which has a planar structure. The bond order (Wiberg index) of phosphorus-carbon bond, formally a double bond, is less than two, the bond order of the single bond is more than one. According to the NBO analysis the ring has a partial positive charge, and the phosphorus atom at the 4th position is partially negative. 1,4-diphosphatriafulvene compared to the other triafulvenes has a large dipole moment (2.39 D, B3LYP/cc-pVTZ).

This molecule has two isomers (E and Z), but the inversion barrier between them is very high: 167.04 kJ/mol (CBS-Q), therefore the two isomers can expectedly be isolated. The inversion barrier is lower in the case of 4-silyl-1,4-diphosphatriafulvene (114.10 kJ/mol) and higher for 4-metil–1,4–diphosphatriafulvene (187.89 kJ/mol). The Z isomer is thermodynamically more stable than the E isomer, but the difference is very small (2.56 kJ/mol), so the properties of these compounds are the same.

The aromaticity indices (Bird, NICS and ΣCC indices and isodesmic energies) do not correlate very well, but the calculations agree that the phosphorus atom in the ring decreases the aromaticity. This effect is small, and 1,4-diphosphatriafulvene is a partially aromatic molecule.

1,4-diphosphatriafulvene is a strong basis, its proton affinity is 872.6 kJ/mol. The protonated compound has a trans bent structure. The protonated form is flexible, the inversion and the rotation barrier is low (51.43 and 24.72 kJ/mol, CBS-Q).

Studying the [$C_2P_2H_2$] potential energy surface 12 structural isomers were found.

THE ROLE OF NON-NUCLEAR ATTRACTORS IN EXCITED MOLECULES

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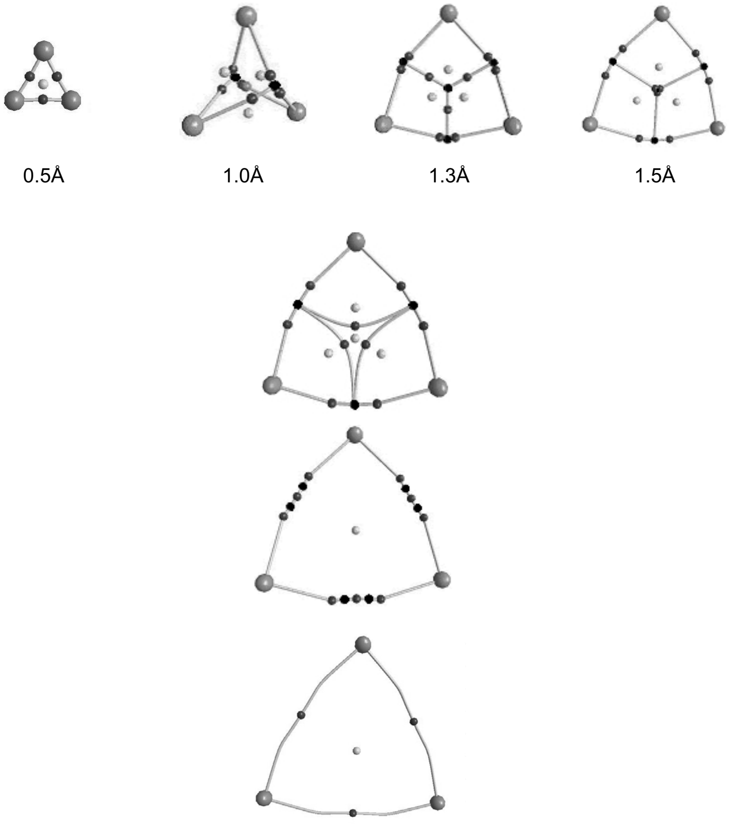

0.5Å 1.0Å 1.3Å 1.5Å

1.6Å
1.82Å
2.0Å

Fig. 2. The structure of $Li_3\ {}^4A'_1$

The electron density of small lithium-clusters ($^3\Sigma_u$ state of Li_2, the $^2A'_1$ and $^4A'_1$ states of Li_3 and the $^1A'_1$ state of Li_3^+) and $H_2X = XH_2$, $HX \equiv XH$ (X = C, Si, Ge) have been studied with high level ab-initio and DFTcalculations (with restricted, unrestricted and restricted open shell QCISD(Full), B3LYP, HF and at several atomic distance CASSCF methods) and a large basis set ($6-311++$G(3df,2pd)). The geometry of Li_3 clusters was selected to be a regular triangle.

In case of the lithium clusters we studied the electron density in the ground and in the first excited states at several atomic distances (from 0.8Å to 4.0Å). The topology of the electron density is very similar in the ground and excited states. When the atomic distance is lower than 1.2Å or larger than 3.2Å, the topology is the classical one: there is lithium–lithium bond in all clusters, and only one bond critical point is existing among the nuclei.

The structure of Li_3 $^4A'_1$ at several atomic distances (lithium distance from the middle of the triangle is given) is shown in *Fig. 2*. The NNA window is the same as in Li_2 $^1\Sigma_g$. The structure is related to other states of Li_3 clusters.

Li_2 $^3\Sigma_u$ is especially interesting, because there are formal rings in this molecule from 1.7 to 2.5 Å.

We examined the influence of bond order and substituents on the existence of the non-nuclear attractors. It was found that the bond order had no influence for the NNA window.

PRETREATMENT AND ENZYMATIC HYDROLYSIS OF CORN STOVER, ENERGY GRASS, AND WHEAT BRAN WITH THE INTENTION OF BIOETHANOL PRODUCTION

Gergely KÁLMÁN

Supervisors: Kati Réczey
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Department of Agricultural Chemical Technology

Among renewable energy sources, bioethanol seems to be the most promising for near-term commercial application. Nowadays bioethanol is manufactured from sugar cane and corn starch. However, it is not possible to significantly increase ethanol production from these raw materials, due to production limitations. The biomass, which is already being produced in huge quantities without further utilization, is lignocellulosic biomass.

This work focused on three lignocellulosic raw materials: corn stover, energy grass, and wheat bran. Dilute sulphuric acid pretreatment was used to pretreat the raw materials before enzymatic hydrolysis. Dilute acids bring hemicelluloses into solution in the form of monosaccharides, thus they make cellulose enzymatically digestible. Relatively low reaction temperature (120 °C), and long residence times (60–120 minutes) were used in order to avoid breakdown of carbohydrates. Results showed that the pretreatment increased the conversion of the enzymatic hydrolysis from ca. 15% to 40–70%, depending on raw material, concentration of sulphuric acid, and residence time during pretreatment. The samples, which were pretreated with acid in concentration of 2% for 90 minutes, reached the same glucose yield during enzymatic hydrolysis, as samples pretreated with higher severity. At the same time, 2% acid reached hemicellulose yields close to theoretical during pretreatments.

QUALITY DEVELOPMENT OF ‘STEAM-CRACKING’ FEEDSTOCK

János KEREZSI

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Department of Chemical Technology BUTE

A laboratory apparatus was built and tested for the pyrolysis, with other name, for the steam-cracking of naphta and gasoil. The apparatus consists of dosing pumps, a preheater, an electric heated pyrolysis furnace, a quench cooler, a separator, a low temperature cooler and a gasometer. The analysis of the product stream was carried out with three steps (H_2 and CH_4 determination, C1–C4 analysis, $>$ C4 analysis) gas chromatography. The apparatus was tested with gasoline and gasoil samples and afforded product composition and amount near to the industrial values. The good simulation results made possible to use the steam-cracking apparatus for characterisation of different gasoline and gasoil feedstocks, moreover to test the pyrolysis of low-polymerisation grade polyethylene, dissolved in gasoil.

SYNTHESIS OF NEW PROTON-IONIZABLE CROWN ETHERS CONTAINING SUBSTITUTED 1*H*–PYRIDINE–4–ONE SUBCYCLIC UNITS FOR COMPLEXATION AND TRANSPORT STUDIES

Júlia KERTÉSZ

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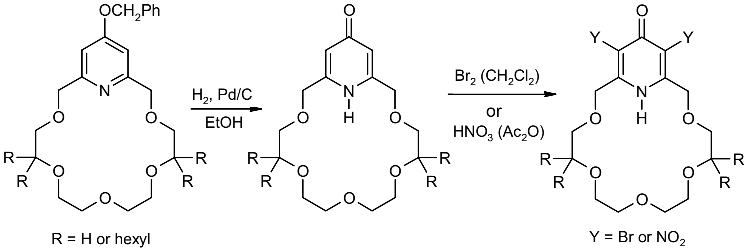
We are interested in crown ethers having a proton-ionizable moiety as a part of the macroring. These ionophores increase the cation-crown ether complex stability and if they are lipophilic enough, allow selective proton-coupled transport of metal ions through various membrane systems without the need for an anion to accompany the macrocycle-cation complex.



Five novel pyridino–18–crown-6 and two new benzyloxy-substituted pyridino–18–crown–6 ligands have been prepared. First methyl benzyloxyacetate was treated with hexyl-magnesium bromide, then the resulting alcohol was treated with diethylene glycol ditosylate in strong basic conditions to obtain the dibenzyl-protected and tetrahexyl-substituted tetraethylene glycol. Removal of the protecting groups from the latter by catalytic hydrogenation gave the tetrahexyl-substituted tetraethylene glycol. The disodium salt of the tetrahexyl-substituted tetraethylene glycol was treated with 4–benzyloxy-2,6–pyridinedimethanol ditosylate to render the lipophilic benzyloxy-pyridino-crown ether.

The parent non-lipophilic crown ether was obtained by treating the disodium salt of 4–benzyloxy–2,6–pyridinedimethanol with tetraethylene glycol ditosylate.

By the catalytic hydrogenative removal of the *O*-benzyl group attached to the pyridine ring, both the lipophil and the non-lipophil pyridino-18-crown-6 ethers were obtained. The latter ligands were transformed to their 3,5–dibromo- and 3,5–dinitro derivatives by treatment with bromine in methylene chloride and nitric acid in acetic anhydride, respectively. The latter proton-ionizable crown ethers have pK_a values as low as 6.0. Thus, they are good candidates for complexation and proton-coupled transport of selected cations.

A report of the complexation and cation-transport properties of these novel macrocycles will be published when that work is finished.

A STUDY ON THE ACTIVITY MEASUREMENT OF CELLULASES

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Due to environmental considerations, interest towards alternative energy resources has considerably increased during the past decades. Producing energy from biomass has an uncontroversial advantage, i.e. carbon dioxide emission neutrality, when compared to conventional fossil fuel based energy utilization. If biomass is used to provide energy, the carbon dioxide released during utilization will not contribute to the atmosphere's carbon dioxide level, because it is reused via photosynthesis in order to produce new biomass supply. Today, mainly the transportation sector can be held responsible for the continuously increasing carbon dioxide emission. Therefore, introducing alternative fuels such as ethanol from renewable resource would significantly reduce the contribution to the atmosphere's greenhouse gas content. Ethanol can be produced cost efficiently from lignocellulosic biomass, however, the competitiveness with gasoline is still questionable. Sensitivity analysis of a lignocellulose based fuel ethanol technology has shown that the main factor influencing the total production cost is the ethanol yield. Furthermore, if the process alternative of enzymatic conversion of cellulose is chosen, the other main contributor to the high production cost is the price of cellulase enzymes. For the complete hydrolysis of cellulose synchronized work of many enzymes, i.e. cellulases, is needed. The other characteristic of the cellulose hydrolysis is that while most enzymatic reactions took place in solutions, this one is a heterogeneous reaction involving solid – liquid interface, since cellulose is not water-soluble. For these reasons it is not surprising that methods available for cellulase activity measurements are numerous, which makes the comparison of results published by different research groups difficult. From a process point of view incorrectly measured enzyme activity could result in overdosage of the cellulases, which therefore would be reflected in the production cost of ethanol.

The cellulase enzyme system can be grouped into three classes based on the site of action of the enzymes. These major groups are: endoglucanases (EG), cellobiohydrolases (CBH) and ß-glucosidase or cellobiase. Strictly speaking, the cellobiase enzyme does not belong to cellulases, because it does not act on the cellulose itself. However, due to its specificity to ß-1,4-glucosidic bonds and its important role in the hydrolysis process, i.e. by converting cellobiose to glucose, thereby reducing the inhibition effect of cellobiose on the other cellulases, it is often mentioned as a cellulase. One of the most often used methods for cellulase activity measurements is called the filter paper activity (FPA), which was worked out by Mandels et al. In this activity measurement the enzyme solution is incubated in a buffered solution together with a standard quality of filter paper strip. The sugars released during the measurement are determined using a non-specific reagent, dinitro-salicilic-acid (DNS), which is suitable for the determination of the amount of reducing ends in saccharides. The main problem with this activity measurement is that the effect of the different amounts of cellobiase in the cellulase enzymes is not taken into account. For example if an enzyme preparation has a low activity of cellobiase, the main product released by the cellulases is cellobiose, while in the case of high concentration of cellobiase enzyme glucose is expected to be the final product. According to the Mandels procedure the DNS solution is calibrated using glucose standards. Therefore, depending on the cellobiase content of the cellulase enzyme solutions to be determined, different cellulase activities could be measured, even at constant EG and CBH concentration.

In the present study the effect of cellobiase concentration on the FPA measurement was examined using the non-selective DNS as well as a selective HPLC sugar determination method. It has been shown that increasing the amount of cellobiase added to constant amount of other cellulases (EG, CBH), the FPA activity was increased about 2-folds. Using the selective HPLC sugar determination method revealed that not only the glucose/cellobiose ratio found in the supernatant of the activity measurement was increased by higher cellobiase concentration but also the total amount of sugars liberated by the enzymes expressed in glucose equivalent was significantly increased. This indicated that the inhibition of cellobiose has to be eliminated, which can be achieved by cellobiase dosage from external sources. As the consequence of the study a new approach to FPA measurement has been shown and a recommendation for a new, more reliable technique has been given.

MATHEMATICAL MODEL OF THE AUTOTHERMAL THERMOPHILIC AEROBIC DIGESTION (ATAD)

Róbert KOVÁCS

Supervisor: Zsolt Csikor
Environmental Pilot Laboratory

ATAD is a stabilization process which is able to produce stable and pathogen-free product from raw sewage sludge. During the treatment the thermophilic microorganisms degrade the substrates in the sludge fed into the reactor and the produced heat raises the temperature into the thermophilic range.

In order to reveal the mechanism of the degradation and to make easier the planning of new ATAD reactors we tried to find the mathematical model of the process. In order to do this we performed lab-scale batch experiments at 55 °C followed by respirometry.

Based on these experiments we proved that the IWA's ASM3, which we used as starting point for the modelling, cannot describe the thermophilic process well. Our experimental results showed that there were considerable amounts of facultatively thermophilic cells in the fed sludge which became active thermophilic microbes following the feed. After the completion of the original model with the new component (facultative thermophiles) and the new process (activation) the new model was successfully calibrated and verified, so we got a new powerful tool that is able to predict the behaviour of ATAD reactors among different conditions.

CELLULASE ENZYME PRODUCTION WITH *TRICHODERMA REESEI* RUT C30 WITH UTILIZATION OF CHEAP ALTERNATIVE SUBSTRATES

Krisztina KOZMA

Supervisors: Kati Réczey
Nóra Szijártó
Department of Agricultural Chemical Technology

The high cost of cellulase enzymes and the successful utilization of cellulosic material as a renewable carbon source depends on the development of economically feasible process technologies for the production of the cellulase enzyme complex. As the enzyme production cost varies with the carbon source used, utilization of cheap alternative substrates is considered as an attractive way to improve process economics. With regards to their availability at no extra cost, lignocellulosic wastes have gained considerable interest to be used as carbon sources in cellulase enzyme fermentation processes.

In this study the potential utilization of old corrugated cardboard (OCC) as a novel fermentation substrate has been investigated and the possible replacement of Mandels salts by stillage concentrate has been studied in cellulase enzyme fermentation experiments of *Trichoderma reesei* RUT C30. The utilization of stillage from various sources (i.e. spirit and yeast industry) was of major interest since this is a readily available source of cheap salt supply for industrial-scale microbial fermentation. However, according to its general composition stillage may lack the sufficient levels of inorganic phosphate, thus during the course of this study special emphasis was taken on the need of additional phosphate supplementation, while the main focus was directed to define the sufficient stillage concentration in shake flasks and a laboratory fermenter.

When an OCC concentration corresponding to 10 g/l cellulose was applied together with 20 g/l stillage, the highest cellulase enzyme activity observed in shake flasks was in the range of 1.6 IU/ml and 1.9 IU/ml in the presence and the absence of additional mono ammonium phosphate, respectively. Promising results of preliminary studies allowed the scale up of the process, which resulted in a maximal enzyme activity of 1.4 IU/ml in a 30 L laboratory fermenter.

PREPARATION OF THE ELECTRON EMISSION MATERIAL $Ba_3Y_2WO_9$ FOR HIGH PRESSURE SODIUM LAMPS WITH HIGH TEMPERATURE SINTERING AND OPTIMALISATION OF THE SINTERING PROCESS

Henriett LOVAS

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Institute of General and Analytical Chemistry
Miklós Győr
GE Consumer Products Hungary RT.

The High Pressure Sodium (HPS) lamps, belonging to the family of High Intensity Discharge (HID) lamps, nowadays is a very popular lamp type because of its high efficacy. They are well suitable for street lighting, industrial, as well as horticultural applications. Previously, they were used for the illumination of outdoor areas only, but now they are used indoors, too. HPS lamps have an advantage over the incandescent lamps because they turn more than 50% of the consumed electrical energy into visible light.

The light is emitted from a discharge zone between the two tungsten electrodes. The electrodes are covered with a sort of electron emission enhancing material. These are relatively stable barium compounds, which may cover the electrodes with barium film formed at the high (2000 °C) operational temperature of the electrodes [1].

My purpose was to prepare an emission enhancing material barium yttrium tungstate ($Ba_3Y_2WO_9$) in a high temperature sintering furnace and to optimize the sintering process [2-5]. The phases formed during the sintering have been identified with X-ray diffraction after cooling down the samples [6]. Additionally, I tried to estimate the thermal stability of the samples [4,7].

I have applied repeated milling and by choosing the suitable sintering temperature I have obtained a product that contained, beside others, the target compound $Ba_3Y_2WO_9$ [8]. Afterwards, I have tried to optimalize the milling process to reach better results. I have tried another method for the sintering by using excess Y_2O_3 to get a product that contains more $Ba_3Y_2WO_9$ and is crystallized in a greater extent [3]. In addition, I have made another sintering, with 5 weight % of tungsten powder added the starting powder mix of stoichiometric composition. During the sintering process I worked with two parallel samples: I milled one of the samples between each sintering step of different temperatures, while the other one remained unmilled. My purpose was to observe if the milling between the two sintering steps has an influence on this solid phase reaction.

My sintering experiments showed that at about 800 °C most of the starting materials remained unreacted. At about 1100 °C, $BaWO_4$ appears in the product, most probably as a temporary intermediate species. The amount of the $BaWO_4$ formed depends on the milling of the powder mix. The expected end product $Ba_3Y_2WO_9$ has appeared after sintering at 1340 °C. The product has became crystallized in a greater extent if I repeated the 1340 °C sintering step. After the sintering experiment with Y_2O_3 excess, I have observed that the end product appears partially after the sintering step at 1100 °C, but only in low percentage. It seems that the role of Y_2O_3 in the system is to reduce the nucleation temperature of $Ba_3Y_2WO_9$.

In summary, my conclusion from the experiments is that combination of the milling between the sintering steps, presence of Y_2O_3 excess, and the applied high temperature of 1340 °C leads to the expected reaction product. It is also an important observation, that the reaction can be promoted towards higher yields with increasing Y_2O_3 excess and repeated sintering at 1340 °C.

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UV RADIATION DECREASING OF COMPACT FLUORESCENT LAMPS

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Department of Atomic Physics
Zsolt Vincze
GE Lighting

This research project, bound to the CFL development in GE Lighting, aims the reduction of undesired UV radiation emitted by commercial CFL-s. Since the UV radiation is harmful for the human organism, a PET value is defined, which gives the number of hours without health damage at 500 lux CFL illumination. Our purpose is to increase the PET value, which is not trivial in the case of CFL's, whose basic operation is to transform UV radiation into visible by fluorescing powders.

Dependence of the emitted UV on several factors such as lamp position, glass thickness, conversion efficiency and active material thickness was evaluated during the experimental investigation. It was detected that, since glass thickness is essential in UV absorption, the actual lamp forming technology greatly reduces the glass thickness at curved parts and the UV emission can be higher at these locations. Technology changes were initialised in order to keep the glass thickness uniform and to avoid peeling off of the fluorescent powder.

Increased UV absorption can be obtained also by using special layers. The effect of CeO_2 layer has been experimentally investigated and serious efforts have been made to achieve a uniform layer on the lamp inner surface. The technology involves chemical reaction of $CeNO_3$ around 300 °C, whereas the most serious problem is the uniformity and continuity of the formed layer. We created layers on experimental lamps, with 30% higher PET parameter value and unchanged emitted visible light power.

COMPARISON OF STABILIZER EFFICIENCY IN METALLOCENE POLYETHYLENE

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Joint Laboratory of Polymer Physical Chemistry
Institute of Chemistry, Chemical Research Center
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Department of Plastics and Rubber Industries

The synthesis of polyolefins by metallocene catalysts is one of the most recent developments in the plastics industry. Although these new products are more and more widely applied, several problems are still unsolved. One of them is the efficient stabilization of the polymer. In the present work the efficiency of two different stabilizer systems containing phosphoric antioxidants was compared in metallocene polyethylene (mPE). Processing caused changes in the chemical, physical and rheological properties of the polymer were determined and evaluated with respect to the chemical transformation of the phosphoric stabilizers.

The number of unsaturated groups, representing the weakest points, was lower by one order of magnitude in the mPE studied than in the conventional Phillips type polyethylenes. As a consequence the experimental results proved that the stabilizers were more efficient in mPE.

Quantitative relationship was found between the degree of oxidation of the phosphite stabilizer and changes in the properties of mPE. During processing, both breaking and coupling of the polymer chains happen simultaneously. The direction of the reactions is affected by the type of the phosphoric stabilizer. The phosphonite type antioxidant hinders the recombination of macroradicals more efficiently than the phosphite molecules.

RAMAN-MICROSCOPIC ANALYSIS OF MULTICOMPONENT SYSTEMS

Béla Botond MAROSFŐI

Supervisor: György Marosi
Department of Organic Chemical Technology

The aim of this work was to examine the possibilities of using the Raman microscope in quantitative analysis especially in the field of pharmaceutical quality control.

Important tasks in pharmaceutical processes are to maintain the contents of pills at the specified level and to keep the quality of the packaging materials. Accordingly, the experiments included two main research parts: quantitative analysis of drug delivery components and determination of the composition and structure of multilayer packaging materials.

The first part of the work started with recording the Raman spectra of pure drug components; followed by the quantitative analysis of binary powder mixtures; and calculating the calibration curves. The selected materials are widely used components in pharmaceutical manufacture: cornstarch, lactose-monohydrate and calcium-hydrogen-phosphate.

In the second series of experiments two- and three-layered packaging films, used in pharmaceutical industry, were to be examined by Raman microscope.

Based on the results, it could be concluded that the Raman microscope with a proper examination method is suitable for quantitative and qualitative analysis of mixtures and multilayer films. The error of the methods could be decreased from the initial 90% to the 2–8% interval. With the proper use of inner or outer standards further reduction of the error and improvement of the linearity of the calibration curve are expected.

ENVIRONMENTALLY FRIENDLY TECHNOLOGY FOR THE RESOLUTION OF RACEMIC *TRANS*-2-CHLOROCYCLOHEXANE-1-OL

Péter MOLNÁR

Supervisors: Béla Simándi
Edit Székely
Department of Chemical Engineering
Elemér Fogassy
Department of Organic Chemistry Technology

Nowadays, beside many other requirements, it is essential for new technologies not to pollute the environment.

As it is well known, the effect of enantiomers can be different, therefore the separation of them is very important. A possible way for separation is the resolution.

A new technology of environmentally friendly resolution was developed in my work using supercritical extraction. A racemic alcohol was studied as model compound and (–)–(2R,3R)–O,O'–dibenzoyl-tartaric acid monohydrate ($DBTA \cdot H_2O$) was used as resolving agent, in less than equivalent molar ratio, (mr) $=$ ($DBBS \cdot H_2O$/racemic alcohol). Melting-state crystallisation was used to create the diastereomeric complex, therefore using of poisonous organic solvents and the loss of material by evaporation were avoidable.

This complex was exclusively decomposed in the extractor by optimal setting of extraction parameters (EPs), thus both enantiomers were obtained in the separator.

The effect of (mr) was determined for the efficiency of separation, and the influence of EPs was examined for optical purity (OP). The best separation was obtained at 100 bar, 33 °C; OP $= -52\%$ in the extract of the first extraction step.

The problem of further purification of enantiomers was solved too. One repeated resolution gave 30% better purity.

Almost the same good separation was obtained in experiments reusing the resolving agent.

My primary aim was to create an environmentally friendly resolution technology, moreover I succeeded to purify these enantiomers very well.

SYNTHESIS OF α-AMINOPHOSPHONIC ACID DERIVATIVES

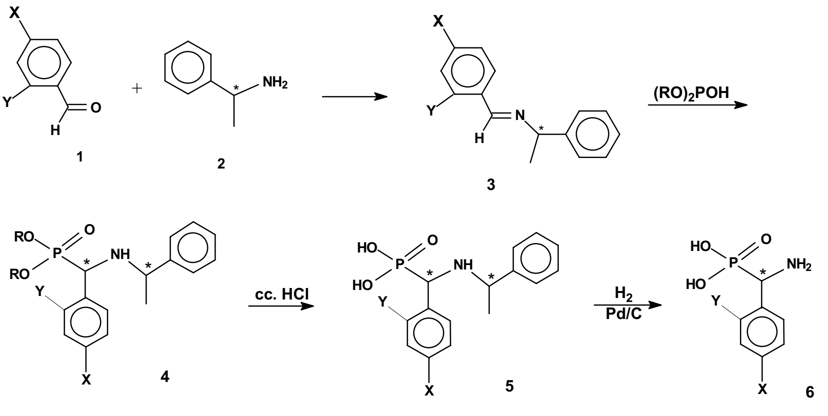
Éva NAGY

Supervisors: Imre Petneházy
Andrea Szabó
Department of Organic Chemical Technology

The synthesis of α-aminophosphonic acids has an increasing interest because of their biological activity and structural analogy to α-amino acids, especially in cases their α-carbon atom is a chiral centre.

Although, the α-aminophosphonic acid derivatives can be synthesised in numerous ways, chiral syntheses were published only in the last few years.

These compounds can be prepared by Kabachnik–Field reaction via nucleofilic addition of phosphite to a $C = N$ double bond. Chirality of formation of stereogenic α-carbon atom was exerted by using α-phenylethyl group in imines as a powerful stereodirecting group which induces good to high diastereoselectivity.



R: Et, iPr; Y: H, Cl, NO$_2$, Me; X: H, Cl, NO$_2$, Me

At first, a couple of chiral imines from optically active α-phenylethyl amine and substituted benzaldehyde were produced at a yield over 90%. Most of them are non-published and they were characterised by ^{1}H-NMR and IR spectroscopy.

New α-aminophosphonates were formed by addition of dialkyl-phosphite to imines. The desired product was formed at good yields and at good to high diastereoselectivity. Diastereomeric ratio of **4** was characterised by ^{31}P-NMR in each case.

Deprotection of **4** results in α-aminophosphonic acid **6**. It has to be noted, that performing the hydrolysis of **4** by concentrated hydrochloric acid never caused any racemization. The removal of the chiral auxiliary group by catalytic hydrogenation is in progress.

SCREENING FOR *TRICHODERMA HARZIANUM* ISOLATES CAPABLE OF PRODUCING CHITINASE BY SOLID SUBSTRATE FERMENTATION

Viviána NAGY

Supervisor: György Szakács
Department of Agricultural Chemical Technology

Chitin is produced in enormous quantities in the biosphere, chiefly as the major structural component of most fungi and invertebrates. Chitin, a β-1,4-linked N-acetyl-D-glucosamine (NAGA) homopolymer is mainly utilized in industry for its mono- and oligosaccharides. Oligomers of chitin are valuable as fine chemicals and as potential pharmaceuticals. As most fungal and invertebrate pests and pathogens have chitin as an essential structural component, chitinase activity could have an important place in biological control.

More than 40 *Trichoderma harzianum* isolates have been tested in solid state fermentation (SSF) for chitinase production. SSF involves the growth of a microorganism, most commonly the filamentous fungi, on water-insoluble moist substrate, in the absence of free water. Strains were isolated from Asian soil and tree bark samples. Identification was performed in Austria and in Canada by using classical and taxonomical molecular methods.

Four SSF media were used for screening, they contained wheat bran, crude chitin and different salt solutions for wetting the substrate. The best strains (TUB F–691, TUB F–699, TUB F–700, TUB F–900, TUB F–927, TUB F–947) produced 2–6 Unit/g dry matter (DM) chitinase.

Trichoderma harzianum TUB F–927 was selected for further optimization. During the optimization the following parameters were examined: moisture content, additional carbon, nitrogen and phosphorus sources, different substrates (carriers). The optimal temperature and pH for chitinase enzyme was also determined.

The optimum moisture content of the substrate was found to be 67%. Higher chitinase production was observed by using chitin than by other additional carbon sources. From the tested organic and inorganic N-sources only NH_4^+ had a significant and positive effect on enzyme production, the tested P-source had no significant effect. Beside wheat bran, ground corn-cob also proved to be an appropriate substrate-carrier for chitinase production. Optimal temperature and pH of chitinase enzyme were 55 °C and 4.5, respectively.

EXTRACTION OF GROUND PAPRIKA (*CAPSICUM ANNUUM* L.) AND QUALITATIVE ANALYSIS OF THE EXTRACTS

Edina PETŐ

Supervisors: Béla Simándi
Erika Vági
Department of Chemical Engineering

The aim of this work was to compare the different extraction methods, the extraction yields and to make qualitative comparison in function of the ground paprika samples with different moisture contents. Another aim was to map the different flows (concentration changes) in the extractor during the supercritical fluid extraction (SFE).

The soluble compounds were extracted by Soxhlet extraction in laboratory apparatus with ethanol and *n*-hexane solvents as well as by SFE with fluid CO_2. The supercritical fluid extraction was carried out at 450 bar pressure, 50 °C and 80 °C temperatures. To obtain higher extraction yield the higher temperature and lower moisture content was efficient. Samples containing high amount of moisture can not be extracted by supercritical CO_2. The packed extractor column was separated into ten parts with filter discs. In these experiments the distribution of the different compounds can be followed in the function of their location.

In the analytical experiments five different paprika samples were examined. According to the data of spectrophotometric analysis the highest overall carotenoid content was obtained with supercritical CO_2 in the fully exhausted paprika extraction. For characterisation of ground paprika powder and the extracts obtained by solvents and $scCO_2$ the ASTA measurement has been used. The amount of the pungent and colour components in paprika extracts and in their residual powders were analysed by HPLC. High amount of capsantin was found in the residual powders.

SYNTHESIS OF PYRROLO[3,4-C]QUINOLINES BY 1,5-ELECTROCYCLISATION OF NON-STABILISED AZOMETHINE YLIDES

Áron PINTÉR

Supervisor: Miklós Nyerges
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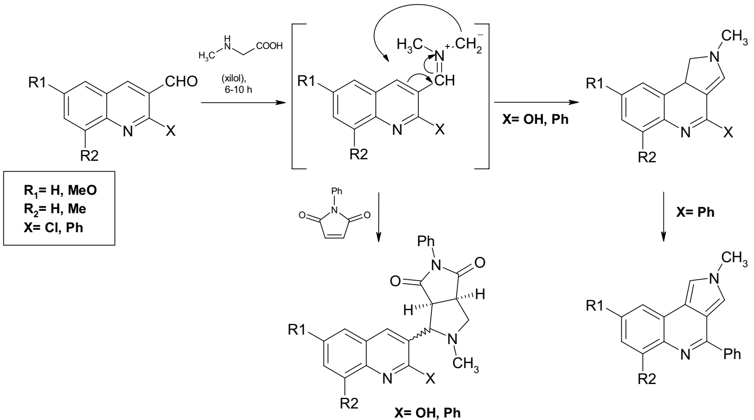

Azomethine ylides are planar molecules composed of one nitrogen and two terminal sp^2 carbons. The synthetic importance of azomethine ylides stems mainly from their use for the prepartion of five membered nitrogen heterocycles, which are ubiqitous in nature and often found as subunits of bioactive natural products. In this work we have studied the electrocyclisation reaction of azomethine ylides generated from 2–chlorine- and 2–phenylquinoline–3–carbaldehydes *via* decarboxylation method. The explored rearrangement gives a direct route to the otherwise hardly accessible pyrrolo[3,4–*c*]quinoline ring system.

The quinolines were prepared from the corresponding acetanilides by treatment with *Vilsmeier* reagent in a single step. The reaction of 2–chloro–3–formylquinolines with sarcosine in refluxing xylene gave 2–methyl–2,4,5,9*b*–tetrahydro–1*H*–pyrrolo[3,4–*c*]quinoline–4–one in acceptable yield *via* the expected 1,5–electrocyclisation reaction accompanied with the hydrolysis of chlorine function under the applied reaction conditions.

We performed a series of experiments with 2–phenyl–3–formyl-quinolines, obtained in three steps from 2–chloro–3–formyl-quinolines including a palladium catalysed Suzuki coupling with phenylboronic acid. The reaction of the resulted quinolines with sarcosine gave the fully aromatised 2–methyl–4–phenyl–1*H*–pyrrolo [3,4–*c*]quinolines as products in a moderate yield.

In all cases the intermediacy of azomethine ylides was shown by the trapping of the proposed dipoles with *N*-phenyl-maleimide as a dipolarophile to give a mixture of two isomeric cycloadducts.

MECHANISM OF INTERACTION IN PP/MONTMORILLONITE NANOCOMPOSITES CONTAINING A MALEINATED POLYMER

Béla Pukánszky Jr.

Supervisor: Béla Pukánszky
Department of Plastics and Rubber Industries

Recently the interest in nanocomposites increased both in industry and academia [1]. This class of composites claimed to have numerous advantages. The dispersed clay layers increase strength already at very low filler contents. Further advantages of these materials are their low flammability [1], increased dimensional stability and decreased permeability. Inspite of their potentials technical problems hinder the application of these materials.

A major problem of nanocomposites is that their strength remains below the expected value. The silicate must be surface treated to increase the distance between its galleries and facilitate exfoliation. However, treatment leads to low interaction with the matrix.

Recently, several attempts were made to improve adhesion between the treated silicate and the polymer matrix by the introduction of a modified polymer [2,3]. The maleinated polymer is claimed to improve intercalation through interdiffusion and formation of entanglements. However, this explanation raises several questions. The maleic anhydride group cannot chemically react with the surface of the filler. Moreover, the surface is covered by the organic cation, usually a quaternary ammonium ion.

Our goal was to find an answer to the questions raised above. Model reactions were carried out with maleinated polypropylene and various compounds used for the treatment of layered silicates. The reaction was followed by FTIR spectroscopy and DSC measurements. The results indicate that maleinated PP and the amine surfactant react with each other with the formation of imides. The study continues in order to determine the mechanism of interaction between the modified polymer and the filler.

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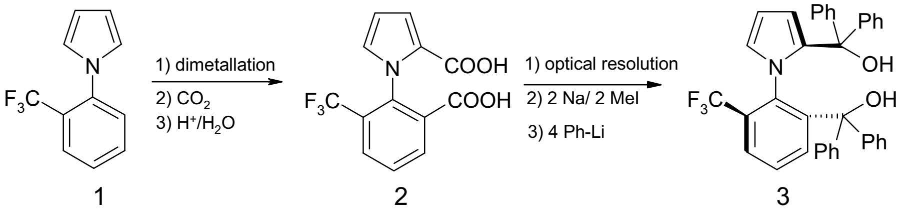
SYNTHESIS OF A NEW CHIRAL LIGAND FROM 1-[2-(TRIFLUOROMETHYL)PHENYL]PYRROLE AND ITS APPLICATION IN ENANTIOSELECTIVE REACTIONS

Tamás SÁNDOR

Supervisors: Ferenc Faigl
Angelika Thurner
Department of Organic Chemical Technology

Functionalised biaryls such as 1,1’-binaphthalene-2,2’-diol (BINAPHTHOL) or the tartaric acid derivatives (like TADDOL) are well-known representatives of chiral ligands of enantioselective catalysts having C_2 symmetry. The corresponding 1-phenyl-pyrrole derivatives could be used as completely asymmetric analogues of the above mentioned ligands if we could substitute both the phenyl and the pyrrole rings in *ortho* and α positions, respectively. In order to achieve this goal regioselective mono- and dimetalation of 1-[2-(trifluoromethyl)phenyl]pyrrole (**1**) have been developed in our laboratory. Molecular modelling calculations predicted that the enantiomers of the prepared dicarboxylic acid (**2**) are stable at ordinary temperature. According to this fact we were able to separate the mirror image atropisomers by optical resolution. Consecutive esterification and phenyllithium addition resulted in the corresponding optically active tetraphenyl diol derivative (**3**) without any racemization.



Asymmetric induction power of this ligand was tested in a Michael-type addition of 2-nitropropane to (E)-1,3-diphenyl-2-propen-1-one.

The ligand was converted into the mono- and the dilithium alcoholates. The rate of the Michael addition was small in both cases but we achieved 5% enantiomeric excess (ee) using the dialcoholate.The monoalcoholate catalysed reaction provided the desired product in 27% ee.

SYNTHESIS OF NEW P-HETEROCYCLES BY THE MODIFICATION OF 1,2-DIHYDROPHOSPHININE-OXIDES

Melinda SIPOS

Supervisors: György Keglevich
Dénes Szieberth
Department of Inorganic Chemistry

Our aim was to synthesise 1,2-dihydrophosphinine-oxides with different substituents on the phosphorus atom and to modify their saturation by hydrogenation or by substitution.

The ring enlargement of 1–(2,4,6-trialkylphenyl-)2,5-dihydro-1H-phosphole oxide via the 6,6-dichloro-3-phosphabicyclo[3.1.0]hexane afforded the double-bond isomers of the corresponding 1,2-dihydrophosphinine-oxides. Catalytic hydrogenation of the isomeric 1-(di-tert-butyltolyl)-1,2-dihydrophosphinine-oxides gave the diastereomers of the corresponding hexahydrophosphinine oxide, while that of the 1-(triisopropylphenyl) isomers led predominantly to the isomers of phospholane oxides formed by a novel type of ring contraction.

The anions generated from diphenylphosphine oxide or dialkyl phosphites added easily onto the α, β-double-bond of 1,2-dihydrophosphinine-oxides to afford a single diastereomer of 3-substituted tetrahydrophosphinine oxides. The diastereoselectivity of the Michael-type addition is connected with the preference of the $P(O)Y_2$ substituent to occupy an axial position in the twist-boat conformation providing the possibility for an intramolecular stabilisation.

The corresponding disulfide derivative was prepared by oxygen-sulfur exchange, while deoxygenation led to a bisphosphine that was stabilized as bisphosphine-borane complex. Complexation reaction of the bisphosphine with dichlorodibenzonitrile platinum was also studied.

The new heterocycles with the exocyclic P-function are of interest due to their potential bioactivity.

ETHANOL PRODUCTION FROM AGRICULTURAL BY-PRODUCTS THE ANALYSIS OF LIGNOCELLULOSIC MATERIALS

Norbert SOÓS

Supervisor: Kati Réczey
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As the result of extensive burning of fossil fuels, the amount of carbon dioxide keeps increasing in the atmosphere. The accumulation of carbon dioxide in the atmosphere can lead to the so called greenhouse-effect, which could cause, through global warming, dramatic changes in the earth’s climate. Since the transportation sector produces the largest fraction of released carbon dioxide, substituting fossil fuels with so called alternative fuels would result in a significantly reduced carbon dioxide emission. Such alternative fuels are bioethanol or biodiesel, which can be produced from biomass. The main advantage of using biomass as the source of energy is that the carbon dioxide discharged during production and utilization will be reused through photosynthesis when new biomass is grown. The main scope of this study was to review the available technologies for the production of fuel ethanol from agricultural by-products, and to develop a new method for chemical analysis of various lignocellulosic substrates.

The analysis of complex biological materials such as lignocellulosics, is quite a sophisticated, time consuming process, which therefore is not adequate for serial measurement of large number of samples.

The analytical method, which has been investigated in this study, was worked out by Hägglund in 1951 for the determination of acid insoluble lignin content (Klason lignin). This assay is based on a three-step sulfuric acid hydrolysis, during which all the carbohydrate type components (cellulose, hemicellulose) are broken down. From the supernatant of the hydrolysis the concentrations of various sugars can be determined using appropriate HPLC column and detection system. The composition of the sample can be calculated from the measured concentrations. The whole procedure, including sample preparation, can take as long as three days.

The main objective of this study was to develop a procedure with a considerably shorter time, which gives accurate result, when compared to the original method. Varying the sample amount, the amount of acid added and reducing the hydrolysis steps to two while increasing the temperature of the hydrolysis the processing time was reduced to one day. When the results of the new optimized assay were compared to those of the traditional Hägglund method, there was no significant difference observed.

It can be concluded that by varying the parameters of the original method an assay was achieved that is as accurate as the original one while the processing time was reduced to one third.

CONCEPTIONAL DESIGN OF MODULE-LIKE LIGHT SOURCE PRODUCER UNITS

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This year the General Electric Company (hereinafter GE) accepted four Aschner scholarship applicants on the announced topic. For this reason our projects contain overlaps, in fact major part of the work was done in teamwork. Accordingly, we summarised the results together.

In the light source factories of GE, the different-sized light sources are produced on production lines that include indexing machines. The machines in the factories were redesigned many times throughout the years and new constructions were developed. They can be classified into four different groups yet none of them fulfil 100% the expectations of GE.

The goal of GE is the production of a base machine design, with flexible application possibilities, and the creation of a standard unit library, inherent to the machine, which contains the manipulator units that ensure the most often used movements.

Our research consisted of two parts:

- We got acquainted with the currently used base machines, and worked on the new base machine design.
- We surveyed the movements and kinematics of the units of a working production line and made suggestions on its integration.

In the first part of the research we had to get acquainted with the different types of base machines on each production line. The different base machine types are as follows: traditional, racecourse shaped, hybrid and standard. We examined the field of application, the motional conditions and the manipulators of these base machines. According to given aspects we surveyed the advantages and disadvantages of the machines and we analysed them with the help of the Cause-and-Effect Diagram (fishbone) within the frame of teamwork. After the evaluation of all the base machines, we prepared a general problem exposure and a demand list. Based on these we individually produced several new base machine drafts.

The GE supervisor evaluated the solutions, which resulted in some ideas being pushed aside and some needing further consideration. The remaining solutions went through detailed development. The designs contain the geometry of the new base machine, the drives of the indexing turret and the actuators of manipulator units. The variants were modelled in 3D.

The best base machine design drafts took part individually in the contest, with four other base machine constructions, which were compared with the help of a professional team.

The task of the second part of the work was the standardisation of manipulators used on different production machines. First we created an integrated symbol system to easily and explicitly define as well as to make reproducible all the spatial movements. The system also makes possible the comparison with other researches in the same field.

We examined the console producer, the stem and mount exhaust and capping machines. We collected *125 manipulator movements* that we summed-up in tabular form. According to the results, we chose the most often used manipulator movements. These movements will be accomplished by the units that are in the unit library. The result of own activities is a summary which can be the base of the new standardised library of frequently used manipulators.

EVOLVED GAS ANALYSIS (TG-TFIR, TG/DTA-MS), INFRARED SPECTROSCOPIC AND X-RAY DIFFRACTION STUDY OF THE THERMAL DECOMPOSITION OF A RAW MATERIAL USED IN TUNGSTEN POWDER METALLURGY

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The first step of lamp filament tungsten wire production, the thermal decomposition of ammonium paratungstate (APT), $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 4H_2O$ was studied by thermogravimetric and differential thermal analysis in air, helium and 10% H_2/He atmospheres. The gaseous products were analysed by on-line TG/DTA-MS, TG-FTIR techniques. Intermediate solid products were obtained by the calcination of APT in 10% H_2/Ar atmosphere at 170, 240, 365, 390, 450 °C and were analysed by FTIR spectroscopy and X-ray diffraction.

In air the formation of two new gaseous products (NO and N_2O) was observed besides the previously known formation of water and ammonia. With the detection of the former gases the catalysed combustion of the formed ammonia was proved, i.e. NO and N_2O are the combustion products of ammonia. The two exothermic DTA peaks at 342, 443 °C, not accurately interpreted earlier, were assigned to ammonia combustion.

The formerly described formation of water from the solid phase at the fourth decomposition part in air (376 – 470 °C) and in 10% H_2/He (365 – 480 °C) was not detected.

In reductive atmosphere the previously not explained exothermic peak around 400 °C on the DTA curve turned out to be the crystallisation heat of the intermediate product ‘blue oxide’.