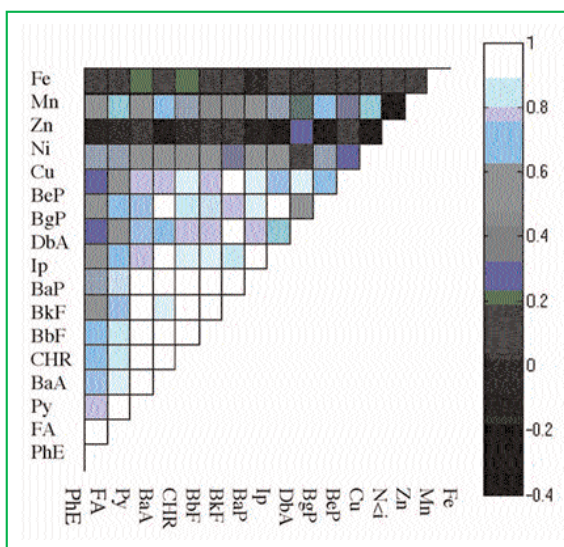


The Particulate Matter and Heavy Metals

in the Atmosphere of Bari

by M. Caselli, P. Ielpo, G. de Gennaro, M. de Rienzo, E. Filippo, D. Manno

This research aims to study size distribution and elemental composition of the smaller fractions of the particulate matter of Bari focussing attention particularly on heavy metals. Daily samplings were performed monthly for a week overall the 2002 spring season in three different sampling locations. The particulate sampling was performed by using a high volume pumping device (Graseby-Andersen) equipped with quartz filters. PM₁₀ analysis was performed using gravimetric method. Heavy metals and PAHs analysis and Sem measurements were performed on different parts of the filter. After digestion by a microwave system (Ethos D-Milestone) heavy metals (Cu, Ni, Zn, Co, Fe, Mn, Cd, Fe and Pb) were separated and detected by ion chromatography. A post-column derivatization system was used for detection. Analysis of PHAs was performed by a GC-MS, using a 30 m x 0.25 mm id HP 5-MS, operating in Select Ion Mode; the use of a Ptv (Programmable temperature vaporisation), as injector system, enhanced the sensitivity of the analytical procedure. Correlation between heavy metals and PHA has been investigated. The microscopic analysis it was performed by Jeol-Sem (Scanning electron microscope) 5410 LW equipped with Oxford microanalysis X system. In the Figure a strong correlation among the concentrations of higher molecular weight PAHs is displayed. On the contrary concentrations of higher molecular weight PAHs (BaA through BgP) present a poor correlation with the lower molecular weight PAHs (FA through



Correlation table between PAHs and heavy metals in the samples collected in the Cavour avenue (city centre of Bari) during the spring season

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Py) ones. Cu shows a high correlation with PAHs (BaA through BeP), while Ni and Mn are correlated only to some PAHs. Zn and Fe are not correlated with PAHs: this evidence indicates a different source for this compounds. By Sem experiments the diameter size distribution of the particles of some samples was obtained: this distribution can be fitted by four gaussian curves. In addition the mass size distribution of some elements (like copper and iron) contained in the particles was obtained: elements have essentially a bimodal size distribution. The information obtained by chemical analysis and Sem experiments will be used for the receptor models to determine the apportionment of the pollutants concentrations.

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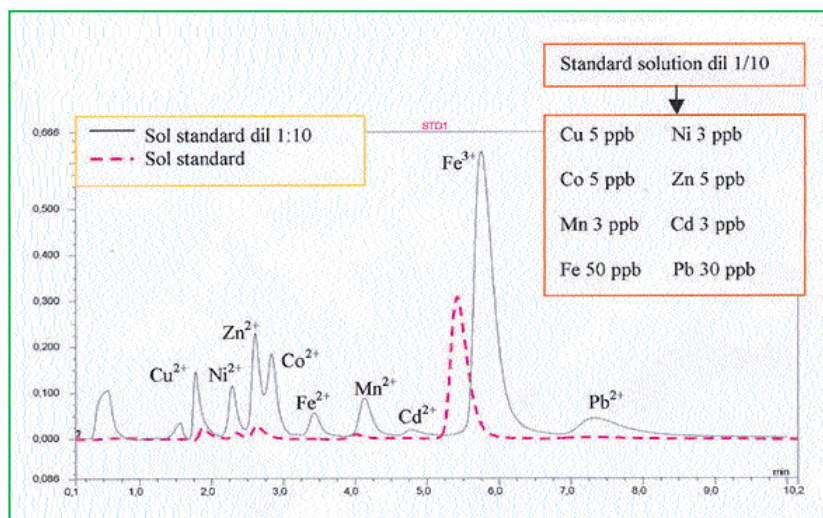
Ion Chromatography Analysis of Preconcentrated Metals

by M. Caselli, G. De Gennaro, P. Ielpo, T. Ladisa

Heavy metals, normally present in atmospheric particulate can be separated and detected in isocratic mode by ion chromatography with post-column reaction and spectrophotometric detection. This method uses a bifunctional ion-exchange column (CS5A Dionex) exploiting the different charge due to the different degrees of association between the metal

and a chelating agent. The metals separated are Cu, Ni, Zn, Co, Mn, Cd, Fe and Pb [1]. Unfortunately nickel and lead concentration in the urban sample is under the quantification limit. Furthermore cadmium and cobalt concentration is under the detection limit of the method. Method modification is required to achieve accurate quantitative results. Lower detection limits are achieved by concentrating from larger sample volumes. For this purpose, concentrator columns are used. They are short columns (typically 35-50 mm in length), which

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contain a stationary phase that is similar to the analytical column used for the analysis. The function of a concentrator column is to strip ions from a measured volume of a relatively clean aqueous sample matrix. This means that also a simple guard column can be used as a concentrator column [2]. The tested guard column is IonPac CG5A (Dionex). Usually the guard column is placed prior to the analytical column to pre-

vent possible sample contaminants from fouling this one. To use the guard column as a concentrator column it has been located in the loop position. Further instrumental modifications are necessary. In our configuration the ion chromatograph (Dionex-600) has been implemented with a six port valve and a piston pump. The valve is connected to a sample loop. The loop is filled with the sample and then delivered to the concentrator column using water as a carrier solution: the analytes of interest are retained on the concentrator column. Finally the eluent is switched through the concentrator to the analytical column. In the Figure two chromatograms are compared. They are referred to the same standard solution: the first one is obtained with the previous method, the second one shows the result obtained by the new method on the same solution diluted 1:10. The sample inject volume is 10 ml. This method will be validated by certified material and then tested on real samples.

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Principles and Applications of Secm

by F. Longobardi, P. Cosma, A. Agostano, A.J. Bard

Secm is based on the movement of a very small electrode (the tip) near the surface of a conductive or insulating substrate. In amperometric Secm experiments, the tip is usually a conventional ultramicroelectrode (Ume) fabricated as a conductive disk of metal or carbon in an insulating sheath of glass or polymer. Potentiometric Secm experiments with ion-selective tips are also possible. In amperometric experiments, the tip current is perturbed by the presence of the substrate. When the tip is far (i.e. greater than several tip diameters) from the substrate the steady-state current, $i_{T,\infty}$, is given by

$$i_{T,\infty} = 4nFDc_a$$

in which F is the Faraday constant, n the number of electrons transferred in the tip reaction ($O + ne \rightarrow R$), D the diffusion coefficient of species O , C is the concentration, and a is the tip radius. When the tip is moved toward the surface of an insulating substrate, the tip current, i_T , decreases because the insulating sheath of the tip blocks diffusion of O to the tip from the bulk solution. The closer the tip gets to the substrate, the smaller i_T becomes. On the other hand, with a conductive substrate, species R can be oxidized back to O . This produces an additional flux of O to the tip and hence an increase in i_T . In this case, the smaller is the value of d , the larger is i_T , with $i_T \rightarrow \infty$ as $d \rightarrow 0$, if the oxidation of R on the substrate is diffusion-limited. These simple principles form the basis for the feedback mode of the Secm operations. When the tip is

rastered in the x-y plane above the substrate, the tip current variation represents changes in topography or conductivity (or reactivity). One can separate topographic effects from conductivity effects by noting that over an insulator i_T is always less than $i_{T,\infty}$, while over a conductor i_T is always greater than $i_{T,\infty}$. In the feedback mode of the Secm operation as stated above, the overall redox process is essentially confined to the thin layer between the tip and the substrate. In the substrate-generation/tip-collection (SG/TC) mode (when the substrate is a generator and the tip is a collector), the tip travels within a thin diffusion layer generated by the substrate electrode. The tip-generation/substrate-collection (TG/SC) mode is advisable for kinetic measurements, while SG/TC can be used for monitoring enzymatic reactions, corrosion, and other heterogeneous processes at the substrate surface.

Biological applications of Secm

The transport of species through membranes, tissues and pores is a general phenomenon underpinning a number of major processes in biological systems. Key questions concerning the transport process need to be addressed:

- 1) is the rate of transport uniform across a tissue or membrane, or is it spatially localized?
- 2) if transport is localized, where are the transport sites and can the local transport rate be measured quantitatively?
- 3) what factors govern the rate of transport?

Scanning electrochemical microscopy (Secm) is particularly suited to addressing these questions since, under conditions where the Ume is held at a potential to drive the electrolysis of a target solution species, the magnitude of the current flowing at the tip depends only on the local rate of mass transport. By measuring the tip current as a function of position in the x-y plane as the tip is scanned over a target interface, regions

of high mass transport are identifiable from an enhancement in the tip current compared to the response when the tip sits above an area of the interface where there is no transport.

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Vicarious Nucleophilic Substitution of Chloroalkylheterocycles with Nitroarenes

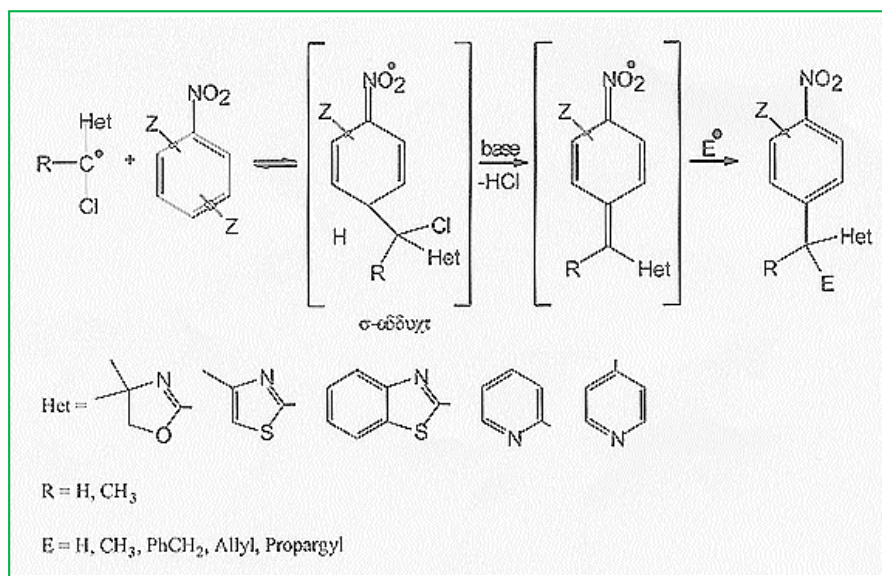
by P. Lorusso, S. Florio, C. Granito, L. Troisi, L. Ronzini

Vicarious Nucleophilic Substitution of hydrogen (Vns) [1] in aromatic compounds is a process, by means of which hydrogen atoms in nitroarenes can be replaced with functionalized alkyl substituents. The nucleophile in the reaction is a carbanion moiety bearing both a leaving group and an electron-withdrawing group which, in this communication, correspond to a heterocycle.

Potassium azaenolates derived from 2-chloroalkyl-2-oxazoline, 2-chloroalkylthiazole, 2-chloromethylbenzothiazole, 2- and 4-chloromethylpyridines add cleanly to nitrobenzenes giving a series of *ortho*- and *para*-heteroalkylsubstituted nitrobenzenes. The reaction proceeds *via* fast and reversible addition of the carbanions, containing chlorine as leaving group at the carbanionic center, to the nitroaromatic ring, followed by base-induced β -elimination of HCl from the intermediate σ -adduct. The regioselectivity of the reaction is overwhelmingly controlled by steric factors. Carbanions derived from a methylene group (R=H) generally replace hydrogen both *ortho* and *para* to the nitro group; methynic carbanions (R=CH₃) replace hydrogen almost exclusively in the *para* position.

The selection of base and solvent is crucial for the Vns reaction to occur: among the various possibilities we found *t*-BuOK in DMSO to be the more convenient, using at least two mol of base for each mole of acidic proton to ensure deprotonation of the nucleophile and fast subsequent β -elimination. The acidic quenching of the reaction mixture affords nitrophenylalkylheterocycles (E=H); moreover the Vns reaction may be quenched with a series of alkyl halides offering a useful pathway to construct α -aryl quaternary centers (E \neq H). We found that the benzylic carbanion derived from the reaction of

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the potassium anion of 2-chloroethyloxazoline is actually generated, as it undergoes methylation, allylation, benzylation and propargylation. This represents a good route to α -substituted nitrobenzylheterocycles bearing a quaternary center *via* one-pot three-component coupling reaction [2]. However the benzylic anion does not react efficiently with carbonyl compounds, but we observed, in the presence of air, and warming up the reaction mixture to 50 °C, the formation of a compound identified as the *p*-nitrophenyloxazoliny ethanol [3].

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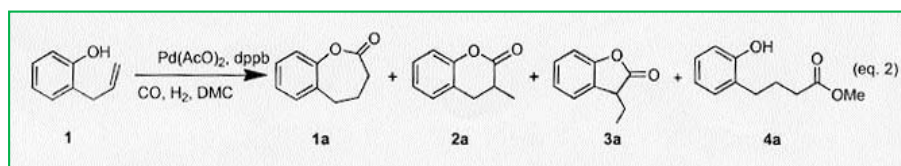
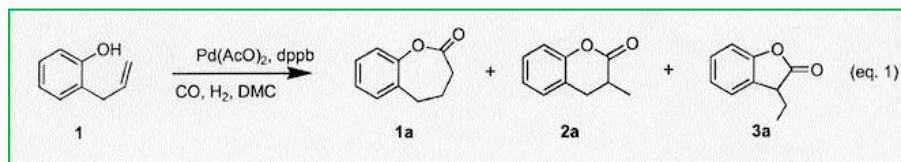
Dimethylcarbonate

as Eco-Friendly Solvent in Cyclocarbonylation Reactions

by A. Maffei, G. Mele,
G. Vasapollo

Cyclocarbonylation reactions catalysed by transition metal complexes represent an interesting synthetic strategy for the synthesis of cyclocarbonylated compounds such as, for example, lactones and lactams. Recently, some of us reported that palladium-phosphine complexes are effective catalysts for the regioselective cyclocarbonylation reactions of allyl phenols affording selectively 5, 6, 7 membered rings lactones and bis lactones [1-6]. On the other hand, it is well known that dimethyl carbonate (DMC) can be used not only as an alternative and eco-friendly solvent; but also as the reactant. Continuing our research in cyclocarbonylation reactions we have observed that $\text{Pd}(\text{OAc})_2$ -dppb [dppb= 1,4- bis(diphenylphosphino) butane] is an efficient catalysts for cyclocarbonylation reactions of allyl phenols using alternative solvent having a low environmental impact such as for example dimethyl carbonate. So that, in this communication we report our results concerning the use of dimethyl carbonate as solvent in cyclocarbonylation reactions of allyl phenols catalysed by $\text{Pd}(\text{OAc})_2$ and dppb under various reaction conditions. As reported previously, treatment of 2-allyl phenol **1** with $\text{Pd}(\text{OAc})_2$ and dppb in toluene under 1/5 carbon monoxide and hydrogen resulted in 90% of conversion with good selectivity toward the seven-membered ring lactone with trace amounts of 6- and 5-membered ring lactones. (eq. 1). In a similar manner, performing the reaction in dimethyl carbonate in place of toluene, the yields toward the seven mem-

A. Maffei, G. Mele, G. Vasapollo, Consorzio INCA-Venezia and Dipartimento di Ingegneria dell'Innovazione - Università di Lecce. This research was supported by Progetto 5 Cluster 11-A, Legge 488.



bered ring lactone **1a** were maintained high as well as the selectivity. Trace amounts of 6- and 5-membered ring lactones **2a** and **3a** were also present and in some case, depending on the reaction conditions, the ring opening specie **4a**, involving DMC as reactant, was also observed with longer reaction times (eq. 2). Other substrates, such as for example 2-allyl-4-hydroxybenzaldehyde and 1-allyl-naphthalen-2-ol were also considered for such transformation. In summary, cyclocarbonylation reactions performed in DMC have maintained yield and regioselectivity for 7-membered ring lactone similar to those performed in toluene under analogous reaction conditions (temperature, reaction times and CO/H_2 molar ratio). Differently to the other solvents, DMC behaved, at high temperature and longer reaction time, as reactant and promoted the formation of a methoxycarbonyl compound.

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Addition vs. Substitution in the Reaction Of Cisplatin Analogs

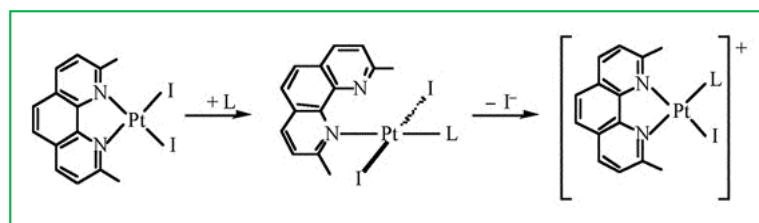
with Sterically Hindered 1,10-Phenanthrolines and Aromatic Bases or Nucleobase Derivatives

by N. Margiotta,
A. Boccarelli, M. Coluccia,
F.P. Fanizzi, G. Natile

The complex *cis*-[PtCl₂(NH₃)₂] (Cisplatin) is one of the three most widely used antitumor drugs in developed Countries [1]. With the aim of preparing "new generation" Cis-

platin analogs able to circumvent tumor resistance arising from increased cellular detoxification, platinum complexes with sterically hindered aromatic bases have been synthe-

sized (*i.e.* 2-picoline for AMD473) [2]. The square planar complex $[\text{PtI}_2(\text{Me}_2\text{phen})]$ ($\text{Me}_2\text{phen} = 2,9\text{-Me}_2\text{-}1,10\text{-phenanthroline}$) is characterized by a large steric hindrance of the methyl substituents. The resulting structure is highly strained and makes this complex to behave as a spring trap towards an extra ligand (L) forming an addition product $[\text{PtI}_2(\text{L})(\text{Me}_2\text{phen})]$ in which Me_2phen is singly bonded to the metal. For unsubstituted pyridine the addition product is indefinitely stable in chloroform solution, while for 2-amino-pyridine the iodo ligand can be displaced by the free end of Me_2phen to form the cationic species $[\text{PtI}(\text{L})(\text{Me}_2\text{phen})]^+$ [3]. 1-Me-cytosine behaves like the 2-amino-pyridine forming the cationic substitution product. The isolated cationic complexes



have a highly shielded metal center and preliminary cytotoxicity data obtained for the complex with $\text{L} = 1\text{-Me-cytosine}$ have shown a good activity against human ovarian, colon, and breast cancer cell lines as compared to that of Cisplatin.

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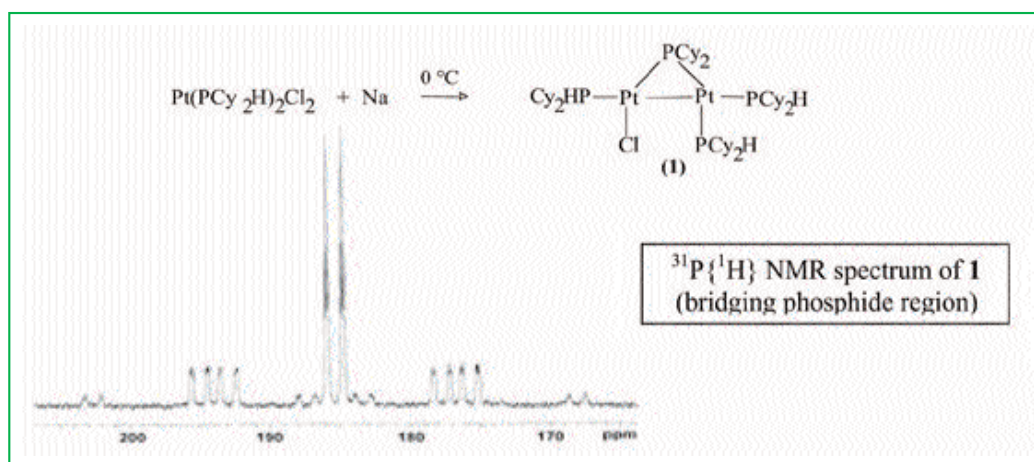
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Synthesis and Characterization of the Dinuclear Complex

$[(\text{PHCy}_2)(\text{Cl})\text{Pt}(\mu\text{-PCy}_2)\text{Pt}(\text{PHCy}_2)_2] (\text{Pt-Pt})$

by M. Latronico, P. Mastroilli, C.F. Nobile, F. Fanizzi

The synthesis of "molecular fragments" containing metal centres with non-conventional oxidation states is well documented. In this perspective we have investigated the reactivity of complexes of formula ML_2X_2 [1] ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$; $\text{L} = \text{PR}_3, \text{PHR}_2$, $\text{X} = \text{Cl}, \text{Br}$) or $\text{Ni}(\text{dp})\text{Cl}_2$ [$\text{dp} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}, 1,2\text{-bis}(\text{diethylphosphino})\text{ethane}, 1,2\text{-bis}(\text{dicyclohexylphosphino})\text{ethane}, 1,3\text{-bis}(\text{dicyclohexylphosphino})\text{propane}, 1,4\text{-bis}(\text{dicyclohexylphosphino})\text{butane}$] in reductions with sodium metal. Our recent investigations deal with the reduction of *cis*- $\text{PtCl}_2(\text{PHCy}_2)_2$ which was found to be temperature dependent. When carried out at 0°C , the reaction leads to the new binuclear complex $[(\text{PHCy}_2)(\text{Cl})\text{Pt}(\mu\text{-PCy}_2)\text{Pt}(\text{PHCy}_2)_2] (\text{Pt-Pt})$ (1) [2]. Complex 1 was isolated and fully characterised by multinuclear and dynamic Nmr.



The comparison with the analogous palladium-based complex [3], previously synthesised by us and characterised also by means of Xrd analysis, reveals that the fluxional processes typically observed in molecules embodying bulky phosphines are more pronounced in the case of the palladium complex.

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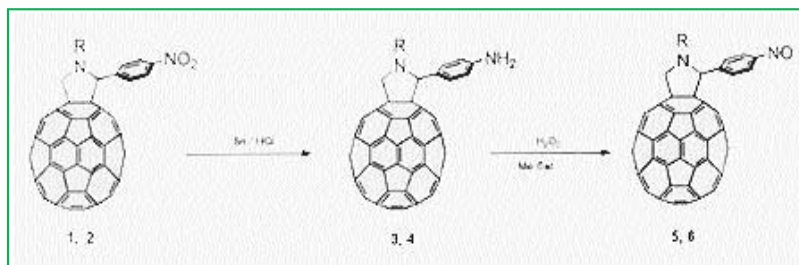
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Synthesis and Characterization of Nitroso-Fulleropyrrolidines

by G. Vasapollo, G. Mele, L. Longo, R. Ianne, B.G. Gowenlock, K.G. Orrell

In the recent years many fundamental properties of fullerene derivatives have been discovered and have evidenced interesting properties such as superconductivity or charge - transfer behaviour and so on. It is well known also that the ball-like structure of C_{60} molecules is very rigid, hydrophobic, and exhibit peculiar properties totally different from those of rod-like self-assembling amphiphilic molecules. The use of highly organized fullerene derivatives in the form of supramolecular array (thin films, nanotubes *etc.*) could offer new technological potentialities and one of the most common approaches to control the architecture of organized thin films containing the fullerene moiety [1-2] is the functionalisation of C_{60} [3]. On the other hand, there are many interesting studies concerning the structure of a variety of C-nitroso compounds both in the solid and in solution [4-6] but there are no reports on C_{60} -nitroso derivatives. The introduction of a nitroso group, as a suitable ligand for a large variety of metals into C_{60} -containing structures offers the possibility to prepare new molecules with potential features. We have therefore pursued the strategy of preparing new molecules that contain both the fullerene and the nitroso group in order to synthesize nitroso fullerene compounds with potential utility as a source for new materials or biologically active compounds. In this context we report here the preparation of nitroso fullerene compounds together with a simple procedure that involves the reduction sequence $RNO_2 \rightarrow RNH_2 \rightarrow RNO$ [7]. The compounds 1 and 2 (1: $R=CH_3$; 2: $R=C_6H_5$) have been prepared according to the literature (Scheme) by the condensation reaction of α -amino acids (*N*-methyl-



glycine or *N*-phenylglycine), with aldehydes and C_{60} through a typical 1,3 dipolar addition reaction of azomethine ylides generated in situ [8]. *N*-methyl-2-(4-aminophenyl)-fulleropyrrolidine 3 ($R=CH_3$) and *N*-phenyl-2-(4-aminophenyl)-fulleropyrrolidine 4 ($R=C_6H_5$) were synthesized respectively by simple reduction of 1 and 2, in chloroform with powdered Sn and H_2O/HCl mixture. The compounds 5 and 6 were prepared by selective oxidation of primary aromatic amines 3 and 4 using H_2O_2 in the presence of $[Mo(O)(O_2)_2(H_2O)(hmpa)]$ (*hmpa*=hexamethyl-phosphoramide) as catalyst. A nitroso group spaced by a long alkyl chain from the fulleropyrrolidine was also prepared. The presence of a long alkyl chain groups significantly improves its solubility in organic solvents and certainly influence also the interfacial properties of the fullerene derivatives on the water surface specially when is required the formation of thin films.

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Determination of Ochratoxin A in Meat Products

Using Solid Phase Extraction and Hplc Coupled to Fluorimetric Detection

by L. Monaci, A. Netti, G. Tantillo, F. Palmisano

Ochratoxin-A (OTA) is a toxic metabolite produced by several species of *Aspergillus* and *Penicillium* genera and represent a frequent contaminant of different commodities. Since it has been classified by the IARC [1] as a possible carcinogen toward humans, a steady exposure to this mycotoxin must be considered an hazard to the health. OTA enters the

food chain either through cereals, oilseeds and fruits and also through products of animal origin if animals like swine and poultry are fed with OTA-contaminated feed. Recently, the German Federal Ministry for Health has started a study aimed to determine the exposure of the consumer to OTA and level of contamination in foods. This study, performed over a peri-

od of 2.5 years, highlighted the wide presence of OTA-contaminated foods in European countries focusing the attention on meat products that are considered as a special problem [2]; about the 57% of 6476 food samples analyzed contained OTA. The Joint Fao/Who Expert Committee on Food Additives (Jecfa) [3], after evaluation of the toxic effect of OTA, proposed a provisional maximum tolerable weekly intake of 0.1 µg/kg body mass for this mycotoxin.

Swine is the most sensitive animal toward OTA exposure since the biotransformation rate of this mycotoxin appear to be slow, with a half life of 89 hours [4]. OTA was found to accumulate in kidney with the highest residual levels ranging around 50 µg/kg, followed by liver and muscle that contained much lower levels. Available analytical methods for OTA detection in animal products need to be improved and forthcoming studies are desirable in this direction, since the Official method at present in use has a range of applicability of 5-50 ng/g [5], while the Italian legislation has recently set a limit of 1 ng/g. In this work a method using Hplc coupled to fluorimetric detection has been developed for the determination of OTA in meat products. The sample pretreatment was based on solid phase extraction clean up on C18 column that represents a

good and cheaper alternative to immunoaffinity columns. Compared to the Official methods, detection limits were lowered by one order of magnitude reducing, at the same time, the sample amounts requested (2,5 g instead of 50 g)

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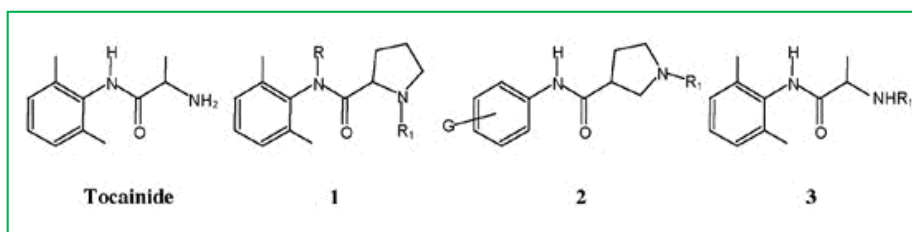
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Structure-Activity Relationships in Tocainide Chiral Analogues

by M. Muraglia, A. Catalano, F. Corbo, C. Franchini, A. Scilimati, V. Tortorella, A. De Luca, D. Conte Camerino

Mytotic syndromes are skeletal muscle diseases caused by either dominant or recessive forms of sodium channelopathies. Various mutations impair the normal functions leading to both spasmodic and involuntary muscle contractions, which occur after a voluntary contraction. The current therapy for all forms of myotonia is symptomatic

and it is based on the use of sodium channel blockers such as Mexiletine and Tocainide. Even if these compounds have a good bioavailability and an acceptable plasma half-life, they have poor selectivity being also endowed with analgesic and antiarrhythmic activity. Searching for safer and more specific drugs against myotonia, we synthesized a large number of Tocainide analogues in their racemic and optically active forms (1-3). Although structural requirements affecting for the use-dependent block on sodium channels have not yet been fully clarified, it has been proposed that lipophilicity and basicity ($pK_{a} \approx 9$) are fundamental molecular properties affecting drug-receptor interaction. Compounds 1, 2 and 3 seem to satisfy both the requirements. These new compounds were screened in voltage



clamp on sodium currents of frog skeletal muscle fibres, both in tonic and phasic block conditions. The phasic block of sodium channels is related to the use-dependent behaviour, namely an improved capability to exert a greater potency on sodium channels of tissues with excessive firing of action potentials than on tissues showing normal excitability.

The increase of lipophilicity, obtained by the introduction of the benzyl group, determines a great increase of potency, whereas the constraint of stereogenic centre of tocainide in a pyrrolidine ring increases both potency and use dependency of action. Synthetic methodologies, pharmacological results and the rationale behind these results will be presented.

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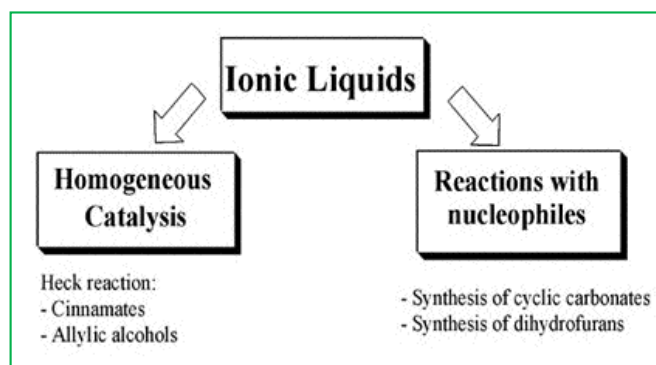
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Ionic liquids Solvents and Catalysts for Organic Syntheses

by V. Caló, A. Nacci, A. Monopoli, P. Dambruoso

The scientific community was recently attracted by ionic liquids (ILs) for their excellent solvent properties for a wide range of inorganic, organic and polymeric materials. Possessing a negligible vapour pressure, they also represent a "greener", valid alternative to toxic and volatile organic solvents (Vocs) [1]. Nevertheless, to date the study of the most part of organic reactions in ILs is still at an undeveloped stage and represents a new fascinating challenge for research area sensible to environmental problems. Our research interests concern the development of new environmentally friendly processes by using ionic liquids both as solvents and catalysts. The main fields investigated by us are *homogeneous catalysis* [2], where ILs proved to be very efficient in activating and stabilizing the metal catalyst, and *reactions with nucleophiles* [3]. In the latter case solvating effect exerted by ILs improves the nucleophilicity of anions. We report the synthetic applications of ILs to the Pd-catalysed Heck arylations of cinnamates and allylic alcohols, carbon dioxide fixation and stereoselective synthesis of 2,3-dihydrofurans.



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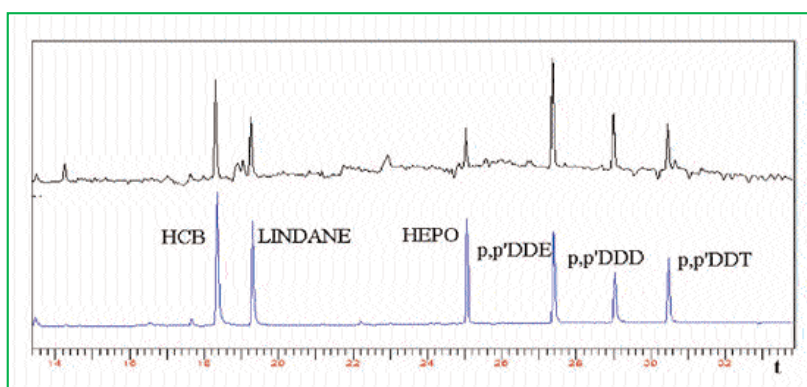
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Rapid Multiresidue Extraction Method of Organochlorinated Pesticides from Fish Feed

by C. Palermo, D. Centonze, V. Nardelli

The increasing interest for the sea culture farms has boosted remarkably modern techniques of intensive breeding, with a particular focus on the rationalization of feeding systems. Nevertheless, the use of highly nutritious feed requires accurate sanitary controls of Public Health. In fact, in such matrixes it is frequent to find highly toxic chemical products or substances not permitted, added for a preventive purpose or as growth promoters.

Fish feed are very complex matrixes for the presence, among the other components, of animal origin products, too. For this reason the aim of our work has been the developing of a rapid extraction method with a high efficiency, followed by the gas chromatographic determination (see Figure) of the HCB, Lindane, HEPO, p,p'-DDE and p,p'-DDD residues. In this procedure, the fat, previously extracted from feed, has been purified in a single step, combining the use of n-hexane, concentrated sulphuric acid (90.0%) [1-2] and ENVI-carb [3], a graphitized non porous carbon material. This mixture has been centrifuged



Overlay of a spiked blank sample (a) and a standard solution (b) of organochlorinated pesticides at a 100 ng/g concentration

and then the upper clear solution has been evaporated. Finally, the residue, obtained in about 50 min, was dissolved in 1 ml of isooctane and analyzed by gas chromatography with electron capture detector (Ecd). The identification of extracted pesticides has been confirmed by gas chromatography-mass spectrometry (GC/MS). Calibration curves of the analyzed pesticides present a good regression line ($r > 0.999$) in the range of

explored concentrations (3.0-6.0-12.5-25.0-50.0-100.0 ng/g), from the detection limit to 100 ng/g. Owing to this rapid clean-up clear and colorless solutions were obtained, allowing the persistent pesticides to be detected at low levels. In fact, the detection limit is equal to 3.0 ng/g related to fat, for each individual standard. Accuracy has been validated through a series of recovery experiments at four fortification levels in the order of 12.5-25.0-50.0-100.0 ng/g. Average recoveries are in the range 80.0-120.0% apart from HEPO (not greater than 60.0%) that, in our opinion, undergoes a conversion into the corre-

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spondent diol due to the acid treatment. The described multiresidue method is very useful for the analytical screening of organochlorinated pesticides in fish feed, being a low-cost and simple procedure, based on rapid and safe operations.

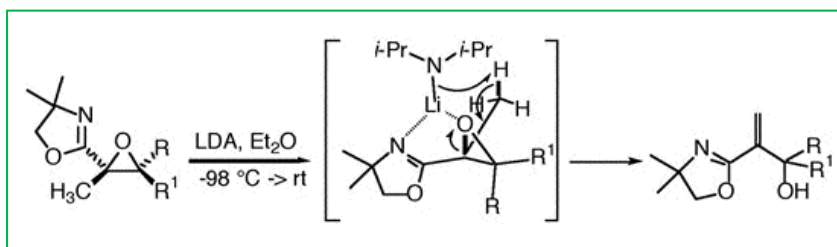
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Synthesis and Reactivity of Oxazolinyl Allylic Alcohols

by F.M. Perna, V. Capriati,
S. Florio, R. Luisi

The base-promoted rearrangement of oxiranes often provides a convenient method of preparation of allylic alcohols [1] which are useful intermediates in synthetic organic chemistry. In the present communication we report a quite simple route to functionalized oxazolinyl allylic alcohols (which can be considered masked Baylis-Hillman adducts) based on the base-promoted [(LDA) or *s*-BuLi/TMEDA in Et₂O at -98 °C] isomerization reaction of tri- and tetrasubstituted oxazolinyl alkyloxiranes. An E₂-E₁cb-like syn β-elimination involving the α-methyl group and the oxygen of the oxirane ring has been proposed [2] to explain the above-mentioned isomerization. The coordinative assistance of the nitrogen oxazolinyl

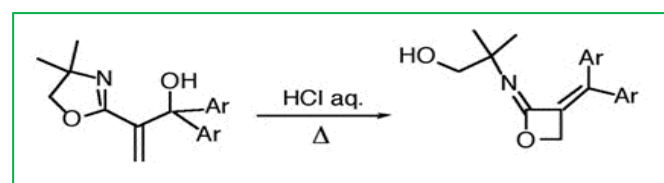


ring is also expected to facilitate the β-elimination process. An unexpected acid-promoted transformation of oxazolinyl allylic alcohols β,β-diaryl substituted into interesting 3-alkylidene-2-iminoxetanes will be discussed as well.

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Semiconductor Nanocrystals

Applied to Energy Photoconversion

The increasing interest toward quantum-sized nanoparticles due to their unique optical, electronic, magnetic and photocatalytic properties has led to develop a wide range of chemical preparation routes. The aim of our research is the synthesis and characterisation of nanostructured semiconductors and their application to solar energy conversion. To elucidate peculiar properties of these new materials, synthetic routes able to controlling size-distribution, morphology, crystallinity, and agglomeration of

by R. Comparelli, A. Petrella,
M.L. Curri, M. Striccoli, A. Agostiano

particles during and after the synthesis are needed. The key point to fulfil is the separation of nucleation from nanocluster growth that can be obtained using colloid chemistry. Recently new synthetic methods exploiting thermal decomposition of organic precursors in co-ordinating solvents have appeared in literature. This technique provides nanocrystals with a narrow size-distribution, high crystallinity, soluble in most of common solvents and with high quantum efficiency in band edge emission. The development

of organised assembly to design and construct "environmental friendly" photovoltaic device is an example of the great number of application of these materials. Novel type of device, which is under study in recent years, operates on different principles with respect to conventional solar cells: light adsorption and charge separation represents two separated steps. Light absorption is performed by a monolayer of dye absorbed chemically at the semiconductor surface. Electron-hole pair are generated in the dye, whose molecular properties are specifically engineered for the task, and while electrons are injected into the conduction band of the semiconductor, holes are collected from glass deposited ITO. Semiconductors with large band gaps better fit the requirements for this application and, in particular nanocrystalline semiconductors due to their reduced dimensions. Several organic molecules, such as eosins, phtalocyanines and few classes of photosynthetic molecules, as chlorophylls and carotenoids have been indicated and are under investigation as possible sensitizers for nanocrystalline semiconductors. Moreover nanomaterials can be employed in improving a photodegradative process belonging to Advanced Oxidation Process class. Semiconductors metal oxides could catalyse these degradation reactions. Red-ox processes, able to degrade organic pollutants, take place when electron-hole pairs are generated in semiconductor materials by light radiation having a frequency higher than a threshold value related to semiconductor band gap energy. Semiconductor with a larger band gap

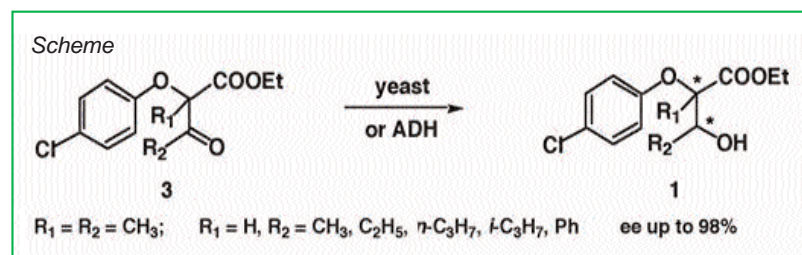
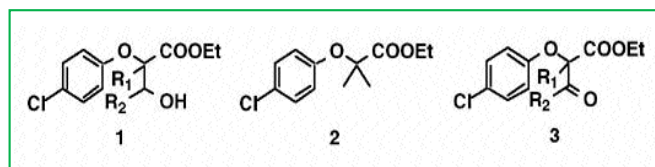
would enlarge the range of degradable compounds, but at the same time would decrease the fraction of solar light able to generate electron-hole pairs. Semiconductor nanomaterials could represent an effective route to solve this problem since their size-dependent band gap. Further, as photocatalytic process occurs at nanoparticles surface, their high surface to volume ratio will contribute to increase the decomposition rate. Among the metal oxides, anatase TiO_2 is at the moment the most utilised photocatalyst, although ZnO appears very promising for degradation of organic solutes in aqueous systems. The photocatalytic efficiency of nanocrystalline ZnO and TiO_2 has been compared to that of the commercially available bulk material in order to achieve the degradation of the dye Methyl Red. The experiments have been carried out using metal oxides both in suspension and immobilised onto substrates, under UV and visible light illumination. The influence of various experimental factors, as pH, concentration of dye, presence of O_2 , etc. have been investigated. The results show that nanostructured ZnO and TiO_2 present a higher efficiency for dye photodegradation compared with their commercial equivalent, and nanostructured TiO_2 shows enhanced capability with respect to ZnO nanoparticles in degradation treatment, conversely to what reported for commercial TiO_2 and ZnO.

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Lipid-Modifying Agents by Yeasts and a Novel ADH-mediated Reduction of 3-Oxoesters

by M.G. Perrone, E. Santandrea, C. Syldatk, V. Tortorella, A. Scilimati

New antilipidemic agents 1, [S. Ferorelli *et al.*, *Tetrahedron: Asymmetry*, 2001, **12**, 853] analogues of clofibrate 2, have been developed. Key step in their preparation is the diastereo- and enantio-selective bio-assisted reduction of the carbonyl function of the oxoesters 3, that was accomplished by using both the reductive ability of some yeasts in growing and resting cell condi-



tions and a novel alcohol dehydrogenase (ADH) isolated by us (Scheme). The results of the reduction of the ethyl 2-(4-chlorophenoxy)-3-oxobutanoate 3 performed in different conditions will be presented.

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The Study of Genetic Resources by Using Capillary Electrophoresis

by A.R. Piergiovanni, G. Taranto, N. Volpe, G. Laghetti

Characterisation and evaluation of genetic resources are basic steps for their utilisation in breeding programmes. Seed storage proteins are commonly used to study the diversity associated to germplasm collections. The end-use of

wheat varieties primarily depends on their technological quality, which in turn, depends upon the quantity and quality of gluten. Gliadins comprise about half of the gluten. They are about 50 proteins that share structural homology and similar physicochemical properties. Because of this high heterogeneity, powerful separation techniques are needed to gliadin characterisation. Various types of chromatographic and electrophoretic techniques are currently used. One of the newest electrophoretic technique is capillary electrophoresis (CE).

The hulled wheats *Triticum monococcum* L. (einkorn), *T. dicoccon* Schrank (emmer) and *T. spelta* L. (spelt) are among the oldest domesticated species. Recently, interest in these ancient wheats is increased due to their adaptability to poor soils, attractive nutritional attributes, potential therapeutic properties and source of useful genes. The genetic diversity of gliadins in hulled wheat species has been little studied [1, 2]. This work investigated the gliadin variation in emmer and spelt by using CE. Twenty-four lines of emmer and ten of spelt were analysed. Gliadin analysis was achieved by using uncoated fused-silica capillaries and isoelectric buffers [3]. From 21 to 30 peaks were resolved in less than 15 min., the major peaks eluted between 4.5 and 8.5 min.

The collected data showed that CE allows the detection of major and minor qualitative as well as quantitative differences. The elaboration of this information makes possible the varietal identification as well as the characterisation of each line. The capacities of CE are underlined by the absence of identical electrophoregrams. The α -gliadins showed four patterns in emmer, while two patterns were observed in spelt.

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The β -gliadin fraction consisted of several peaks whose number and area varied from line to line in both species. The lowest variation was associated to γ -gliadins. The γ -fraction of emmer lines consisted of 3 peaks partially overlapped, the 3rd was the prominent. One prominent peak was the most frequent γ -pattern in spelt. The ω -gliadins showed to have, along with the β -fraction, a very high individual character. Spelt ω -fraction was characterised by a higher number of peaks distributed almost on the entire range of investigated migration time. Lines belonging to the same species can be differentiated mainly on the bases of β - and ω -gliadin patterns. The γ - and ω -gliadins are more useful in the discrimination of emmer from spelt. CE of gliadins is useless to differentiate hulled and unhulled species. Qualitative and quantitative differences of gliadin fractions have been related to the technological properties of wheat flour. Lines showing balanced amount of (α - + β -): γ : ω -fractions and others characterised by unbalanced composition were identified. This suggests that different technological quality could be associated to the tested lines.

The gliadin variation observed in this study confirm that both emmer and spelt are a rich source of genome diversity for breeders. The short time of CE analysis strongly suggests the use of this technique in the screening of large collections. Familiarity with the traits of hulled wheat germplasm is fundamental for its utilisation.

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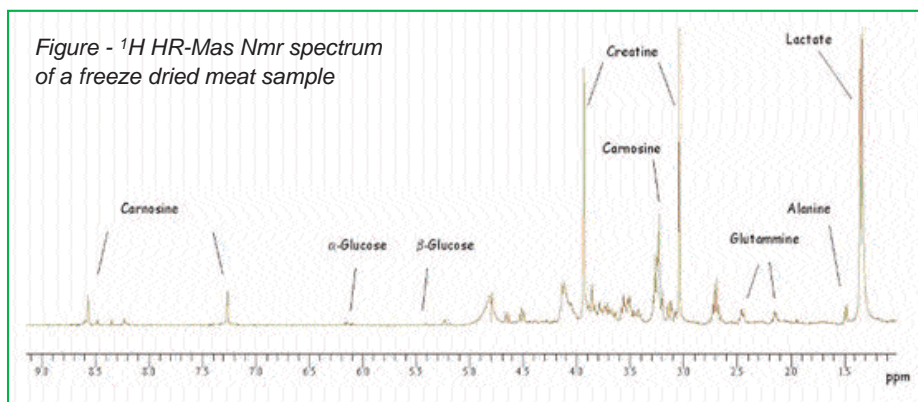
High Resolution Nmr Spectroscopy

Studies on Meat Composition and Features: Potentialities and Prospects

by A. Sgaramella, A. Caputi Jambrenghi, D. Sacco

The EC has promoted programmes to boost the recognition of typical primary products by endorsing the Protected designation of origin (PDO), and the Protected Geographical Indication (Pgi) trademarks. In the last few years, the application of innovative techniques in the analysis of food products has been developed. Among these, nuclear magnetic resonance spectroscopy (Nmr) has grown to a relevant position.

In particular, ¹H HR-Mas Nmr technique brings an important advantage consisting in an easy preparation of the sample, since it permits to introduce the solid directly in the rotor. Moreover, it gives a resolution comparable to that of a meat extract spectrum and needs shorter experimental time to obtain



a good signal to noise ratio (M.A. Brescia *et al.*, *Ital. J. Anim. Sci.*, 2002, **1**, 151). In this communication we present a preliminary ¹H HR-Mas Nmr investigation on meat, trying to show the potentialities and the prospective of this technique. A typical ¹H Hr-Mas spectrum of a meat sample is shown in the Figure. It

contains a large number of signals due to different meat components. The spectrum contains resonances from amino acids and sugars. 2D-Nmr experiments (Tocsy and ^1H - ^{13}C hetero-correlated) were performed in order to assign unknown peaks. A partial assignment of the signals present in the mono-dimensional ^1H -HR Mas spectrum is reported in the Figure. ^1H HR-Mas Nmr was performed using a 400 MHz instrument (Bruker Avance), on 55 meat samples coming from three different location of Apulia (Capitanata, Salento and Murgia). Explorative da-

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ta analysis (principal component analysis, Pca) was performed on the intensity of selected peaks. It permitted to individuate a separation of the samples in three groups according to their geographical origin. This preliminary approach has shown how it is possible to obtain information on a high number of meat metabolites through a single Nmr spectrum. Moreover, other advantages of this innovative technique consist in a) easy preparation of the sample; b) a short analysis time. In this manner hundreds of samples could be analysed in an acceptable time. This is the necessary condition for the statistical applications that are essential for the characterisation of the geographical origin of meat samples.

Influence of Hydrodynamics on Mass Response of a Flow-Through Qcm System for Sensor Applications

by C. Malitesta, E. Sion

Piezoelectric transduction (through quartz crystal microbalance, Qcm) is widely used in sensor field due to its simplicity (low cost) and versatility (for a review see e.g. [1]). Detection of gases has been early developed since in this case only mass loading affects sensor response. A more complex behaviour of Qcm is observed in liquids, where the response depends on additional factors such as viscoelastic effects, conductivity, etc. Different strategies (*dip and dry*, *batch* and *flow* mode) have been proposed for overcoming this problem. Among them the flow mode seems more promising since couples the possibility of subtracting constant (base) contributes from the response to the speed of analysis. Several different flow Qcm systems are reported in the literature (see e.g. [2]) and others are commercially available. Even if different geometries/hydrodynamics have been employed, the reasons for the specific choices are not clearly stated. A home-made transparent flow Qcm system has been developed on the basis of common flow-cell geometries. Viscoelastic responses to glucose solutions have shown peak dura-

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tions much longer than theoretical residence time. This result could be rationalised considering the peculiar flow pattern established in the cell. In fact, the passage of permanganate plugs through the cell permitted to evidence that the plug keeps unmodified until the cell exit is reached, then it mixes with the carrier and leaves the cell by successive dilutions. The system obeys Kanazawa-Gordon equation for viscoelastic effect and Sauerbrey equation for mass loading. The mass sensitivity (7.8 ng/Hz) resulted *ca.* one order of magnitude higher than the correspondent value in batch mode. This interesting result can be explained considering that the peculiar flow of undiluted analyte probes mainly the central part of Qcm (see above) for which a distinctly higher sensitivity has been reported [3]. The developed system is being applied to detection of water pollutants.

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Examples of Electroactive Polymers: Floating Layers, Langmuir-Schäfer Films and Gas Sensing Properties of a Polyphenylenethienylene Derivative

by F. Babudri, D. Colangiuli, G.M. Farinola, F. Naso, R. Rella, R. Tafuro,

There has been enormous attention in recent years in floating films of amphiphiles on the water surface and, in suitable instances, in the transfer of such floating films onto

solid substrates (by Langmuir-Blodgett, LB, or Langmuir-Schäfer, LS, methods) [1]. Such films are not only of interest as specimens of organised structures, but they also have

promising applications in various fields, such as polymer diodes, transistors or resistive chemical sensors [2-4]. Notwithstanding the LB or LS multilayers of numerous non-polymeric amphiphiles are very ordered, regrettably they are susceptible of molecular rearrangement [5]. This consideration stimulated us to study floating layers of preformed polymers and the derived multilayered films. Such polymeric films are generally more stable and physically more robust than those derived from the non-polymeric counterpart.

Gas sensors using conducting polymers as the sensing layers have been sellably constructed since a decade [6]. In comparison with inorganic oxide based devices they evidence noticeable sensitivity to different gases even when working at room or low temperature [7]. Moreover the chance of varying by simple chemical modifications the polymer structures allows to modulate the film properties and to engineer the preparation of sensing devices. In this work, we report on the investigation performed on LS films (30 layers) of poly(2,5-dioctyl-1,4-phenylene-alt-2,5-thienylene) [POPT]. The floating layer at the air-water interface was analysed by Langmuir isotherms, reflection spectroscopy, and Brewster Angle Microscopy (Bam) on the water surface.

The limiting area per molecule in the Langmuir curve indicates that the floating layer is not monomolecular in thickness. The Bam observations put in evidence that aggregates are on the water surface just after solvent evaporation and

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the RefSpec analysis also confirmed the presence of such domains. The bathochromic effect observed in comparison with the solution absorption spectra (from 469 nm to 512 nm) suggests that the rings in the polymer chain are in a more coplanar arrangement at the air-water interface, thus increasing the conjugation. The absorption spectra performed on the LS multilayers reveal a maximum at 494 nm, thus indicating that, as a consequence of the transfer, the coplanarity of the rings has been lowered by the effect of the two *n*-octyl substituents in each repeat unit. Finally these LS multilayers were used in resistive chemical sensors for the detection of nitrogen dioxide in dry atmosphere. The revelation limit is in the ppb range, while the response is not influenced by the contemporary presence of other toxic gases in the atmosphere. This observation reveals the high selectivity of this polymer towards nitrogen dioxide. The response is reproducible and stable, and has an optimum working temperature at 60 °C. Also response and recovery times are very promising for future application in a functioning device.

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Zeolite Synthesis in Soils Amended with Coal Fly Ash Evaluation of their Role in the Stabilization of Heavy Metals in Polluted Soils

by R. Terzano, M. Spagnuolo, L. Medici, F. Tateo, P. Ruggiero

The use of zeolites for the remediation of polluted soils is a widespread and effective technique for the stabilization of heavy metals in contaminated soils. So far, in order to minimize heavy metals mobility and, consequently, their bioavailability and migration toward other environmental compartments, only the cation exchange capacity property of these minerals has been exploited.

Conversely, this research aims to study the possibility of entrapping heavy metals inside the characteristic structures of zeolites during their synthetic process in soils amended with fly ashes obtained from thermoelectric plants as residuals of coal combustion. The synthesis of Zeolite X (zeolite belonging

to the Fujasite series) has been performed by an alkaline hydrothermal process at 60 °C for 4 days using fly ashes pre-treated with NaOH for 1 h at 550 °C. The synthesis of Zeolite X has been also obtained at 25 °C in 17 days. Xrd and Sem-Eds analysis confirmed the occurred synthesis of zeolites even in the presence of considerable amounts of typical soil clay minerals such as montmorillonite and kaolinite (fly ash/mineral ratio: 1/10). However, the zeolite synthesized under these conditions was mainly Zeolite P (zeolite belonging to the Gismondine series). The crystallization of zeolites is particularly favoured in the experimental conditions adopted and it is very likely that the type of synthesized zeolite is dependent on the pedological substrate involved.

In order to study the interaction among heavy metals and zeolites during their synthesis process, the Zeolite X has been synthesized in solutions containing 2,500 ppm of Cu(II), Ni(II), Co(II), Cd(II), Pb(II) and Zn(II) in separate experiments. Xrd

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and Sem-Eds analysis confirmed the crystallization of the Zeolite X in the presence of each metal listed above. As far as Cu(II), Ni(II), Co(II) and Cd(II) are concerned, it has been noticed a reduction of their total concentration in solution (evaluated by Icp-Oes analysis) of 83.0%, 99.5%, 99.9% and 99.8%, respectively, as a consequence of the zeolite crystallization. Conversely, Pb(II) and Zn(II) concentrations in solution remained unchanged. Epr analysis of Zeolite X synthesized with Cu(II) revealed the presence of the metal in isolated and rigid positions inside the aluminosilicate structure. The treatment of the sample by a NH₃ saturated atmosphere (3 h and 24 h) revealed a remarkable signal change probably ascribed to the presence of Cu(OH)₂ in a separate phase.

The first spectroscopic data obtained suggest that some of the considered metals predominantly precipitate as hydroxides. However, it is likely that a fraction of the metals could be entrapped, during the crystallization process, inside the zeolite characteristic cages in isolated positions or as clusters. The zeolite synthetic process in soils amended with pre-treated fly ashes could be an effective method for the stabilization of

heavy metals in polluted soils. Detailed studies on the zeolite synthetic processes and stability, following fly ash spreading on soil, are developing. Moreover, the speciation of heavy metals in these zeolitic structures and the evaluation of the heavy metals stabilization process over time in soils amended with coal fly ashes are also under investigation. At last, these neo-formed zeolites are being assessed for their catalytic capacity in degradation processes of organic xenobiotics in soil.

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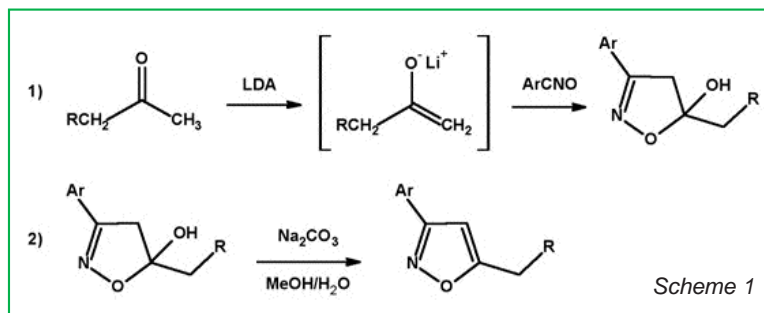
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Synthesis of 3-Aryl-5-Vinylisoxazoles

A Preliminary Investigation

by L. Di Nunno, A. Scilimati, P. Vitale

Synthesis and elaboration of isoxazoles constitute an interesting field of investigation due to their importance both from pharmaceutical [1] and synthetic [2] point of view. Recently we have discovered a new efficient approach to the synthesis of 3-aryl-5-alkyl-5-hydroxy-2-isoxazolines and, by their dehydration-aromatization under basic conditions (Na₂CO₃, MeOH/H₂O), of the corresponding isoxazoles (Scheme 1) [3]. These, in turn, could be transformed into other isoxazole derivatives *via* alfa-metallation of the side-chain followed by reaction with various electrophiles. Extension of the above procedure to the synthesis of 3-aryl-5-vinylisoxazoles, which are valuable starting compounds for the side-chain elaboration at both alfa- and beta-position, revealed however interesting unprecedented aspects concerning the base-induced dehydra-



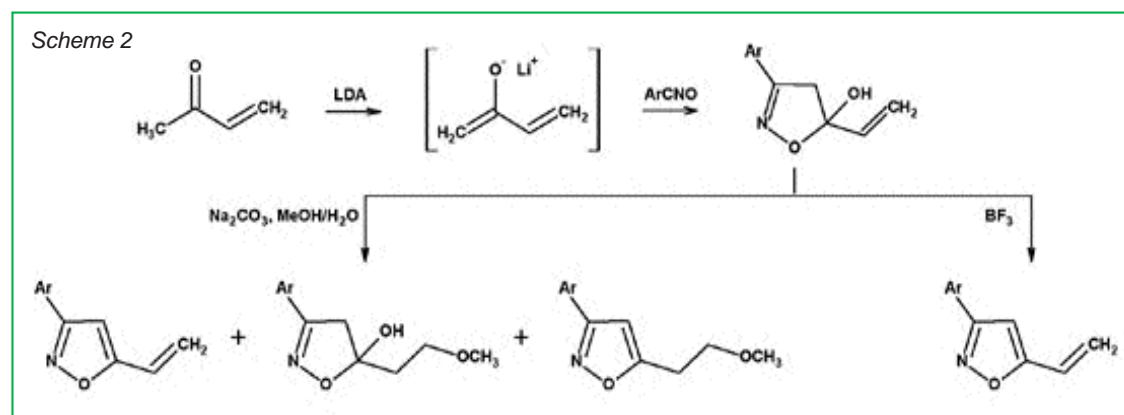
Scheme 1

tion-aromatization of 5-hydroxyisoxazolines intermediates (Scheme 2). Details as well as a possible mechanistic explanation of the new observed behaviour will be discussed.

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Analytical Work On Real Environmental Samples at Istituto Tecnico Industriale "Pacinotti" - Taranto

by E. Paradiso, S. Mancini, M. Campanella, O. Cipriano, S. Galeandro, C. Dragone

The research aimed to acquaint our students with problems related to the analysis of real samples of environmental interest. Students of the Environmental Chemistry curriculum, already trained in volumetric and instrumental analysis, have been responsible for the entire analytical process (searching for official methods, sampling plan, measurements, etc.). Water samples were drawn from Mar Piccolo. Soil samples were collected both within industrial zone (Ilva) and within agricultural zone (Fragagnano, Lizzano, Ginosa) in Taranto area. The following contents were determined in water samples by the specified analytical methods: dissolved oxygen (DO, Win-

kler method), chloride (Mohr method), nitrite (Griess method), ammonia (Nessler method), phosphate (Molybdenum Blue method), pH

(pH-meter). As far as soil samples are concerned, pH, density, total limestone, cationic exchange capacity (Cec), metals (Zn, Cu, Cd, Pb, Ni, Cr) contents (Atomic Absorption Spectroscopy) were determined. Tables 1 and 2 summarises the obtained results. By the performed activities the students experienced the wide difference existing in the determination of analytes in real and simulated samples.

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Table 1 - Water samples results

pH	8.2
DO (ppm)	10
Cl ⁻ (mg/l)	22.2*
NO ₂ ⁻	traces
NH ₃	traces
PO ₄ ³⁻	nd**

* Fresh water sources (< value for Mar Grande)
** nd = not detectable

Table 2 - Soil samples results

	Industrial	Agricultural	Average
pH			8.8
d (g cm ⁻³)			2.65
total limestone (%)			1-10
CEC (meq/100 g)	25-52	36-63	
Zn (ppb)	nd*	nd*	
Cu (ppb)	30	16	
Hg (ppb)	50	45	
Cd (ppb)	5.5	4	
Cr (ppb)	11	9	
Ni (ppb)	28	22	

* nd = not detectable
Notes: PH acid soil: <6.5, alkaline soil: >7.5

Investigation on Environmental Pollution in Taranto Area Within a High School Curriculum

by E. Paradiso, M. Oliva, C. Fratini, R. Quarta, V. Morelli, T. Guastella, G. Sigismondo, S. Tamborrino

This project aimed to increase consciousness of students about environmental pollution and its causes through their involvement in determination of environmental parameters in their living area. Participating students has followed a one-year course of general chemistry with some organic chemistry elements. Environmental and Analytical Chemistry are not normally included in their curriculum.

Water samples were drawn in the period January-March from Ajedda Channel which feeds Mar Piccolo. Students analysed them for dissolved oxygen (DO), chloride, phosphate, nitrite, ammonia and pH. The Table reports the obtained findings. Their environmental significance was illustrated to participating

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	January	February	March	Average	Significance
pH				7.75	
DO (ppm)	6.9	4.34	1.32		Pollution
Cl ⁻ (ppm)				20	Contribute from sea water
NO ₂ ⁻ (ppm)	1.82	0.39	0.65		Pollution
NH ₃ (ppm)	12.5	18.8	16.6		Faecal wastes
PO ₄ ³⁻ (ppm)	1.25	2.13			Urban and/or agricultural wastes

students. Faecal pollution was confirmed by microbiological tests performed by the students. Air pollution data (CO, NO_x, SO₂, O₃) were obtained from investigations described at an Internet address. Acoustic pollution was evaluated measuring sound intensity by a phonometer in a zone of intensive traffic. An average value of 75 dB with peaks of about 95 dB were recorded. Thorough information on state-of-art of knowledge on electromagnetic pollution was presented. After this work students appeared more sensitive to environmental problems.