# ADDITIVES IN COMPOSITE MATERIALS: SYNTHESIS AND CHARACTERIZATION OF INNOVATIVE PROMOTERS IN POLYURETHANE BLENDS

**Federico Vittorio Rossi**

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**Química**

Orientadores: Prof Pedro Paulo de Lacerda e Oliveira Santos
Prof. Enrico Marcantoni
Dr. Serena Gabrielli
Dr. Giovanna Biondi

## Juri

Presidente: Profª. Maria Matilde Soares Duarte Marques
Orientadores: Prof Pedro Paulo de Lacerda e Oliveira Santos
Vogais: Corrado Bacciocchi
Profª Dulce Elizabete Bornes Teixeira Pereira Simão

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# *Abstract*

Composite materials, namely materials made of two or more different components, regained a fundamental role both in everyday life and in industrial applications. In the last years the increasing development of the electric industry has meant that there is a huge request for insulation materials, which have the function of covering conductor materials, able to ensure high performances and excellent physico-chemical properties. Among these insulation systems, a particular attention is placed on coatings for metallic wires. Polyurethane enamels appear to be widely used at an industrial level because they are derived from readily available cheap raw materials. From a synthetic point of view, polyurethane production has been widely explored through the years, but the increasing necessity for better performing materials has meant that inorganic and organic additives find a fundamental role in the polyurethane compound formulation: promoters, catalysts, primers, UV-absorbents, flame retardants, plasticizers, anti-oxidants and dispersants bring an improvement in the materials' mechanic and physico-chemical properties. Promoters and catalysts result to be very important from a synthetic point of view because they favour and speed up the cross linking reactions between polymeric chains. This thesis work is focused on the importance of these promoters, in particular on the condensation product between aniline and butyraldheyde, in the formulation of polyurethane blends, their synthesis and their characterization, in order to improve the solderability and the thermal resistance.

**Keywords:** Additives, Aldimine, Dean-Stark apparatus, GC-MS, Polyurethanes.

# *Resumo*

Os materiais compósitos, em particular os constituídos por dois ou mais componentes, têm vindo a recuperar um papel fundamental tanto na vida do dia-a-dia como para aplicações industriais. Nos últimos anos, o grande desenvolvimento das indústrias eléctricas resultou numa necessidade acrescida de materiais isolantes, com a função de revestir materiais condutores de modo a assegurar desempenhos elevados e excelentes propriedades físico-químicas. De entre estes sistemas isolantes, é dada particular atenção a revestimentos para fios metálicos. Os materiais baseados em poliuretano parecem ser largamente utilizados na indústria devido a serem facilmente produzidos a partir de matérias primas pouco dispendiosas. Do ponto de vista sintético, a produção de poliuretanos tem sido muito explorada ao longo dos anos mas a necessidade crescente de materiais com melhor desempenho significa que aditivos orgânicos e inorgânicos têm um papel fundamental na formulação de poliuretanos, como promotores, catalisadores, estruturas de base, elementos com capacidade de absorção no UV, retardadores de chama, plastificantes, anti-oxidantes e dispersantes, que podem melhorar as propriedades mecânicas e físico-químicas daqueles materiais. Tanto promotores como catalisadores são de grande importância na síntese porque favorecem e aceleram o estabelecimento de ligações cruzadas entre as cadeias poliméricas. O trabalho desenvolvido nesta tese foca-se na importância dos promotores, e em particular no produto de condensação entre a anilina e o butiraldeído para formulação de poliuretanos, com vista a melhorar a adesão dos componentes e a resistência térmica.

**Palavras-Chave:** Aditivos, Aldimina, Dispositivo de Dean-Stark, GC-MS, Poliuretanos.

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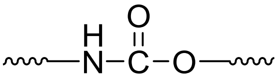
# CHAPTER 1.

# ENAMELS IN MODERN ELECTRIC INDUSTRY

In the 1900s, there were very few of the synthetic polymers we have grown accustomed to now. During succeeding years, polymer science experienced explosive growth with the invention of polyvinyl chloride (PVC, 1913), polyethylene (1933), polyvinylidene chloride (Saran, 1933), polyamides (nylon, 1934), and polytetrafluoroethylene (Teflon, 1938). In addition, during the 1930s, the polymer family known as polyurethanes was invented. Polyurethanes, and all the polymers developed during this period, have become an integral part of modern life. In particular, polyurethanes surround us and they are present in everyday life, in fact: shoes, seat cushions, fibers of clothings, insulation of walls roofs , refrigerators, dishwashers, water heaters, automotive seatings, automotive structural foams, automotive paints and coatings, furniture coatings, *etc.,* are made of, or contain polyurethanes. Specially, in this chapter, the attention will be focused on wire enamels in modern electric industry.[1] From a structural point view, polyurethane is the generic name of polymers with urethane interunit linkage in the chain as shown in Figure 1. For what concern the synthetic methodologies, the reactivity and the building block of this polyurethane, they will be exploited in the Chapter 4. However, the general polyurethane formation reaction is based on a polycondensation between a di- or polyisocyanate and a hydroxyl containing compound (e.g, polyols).



$$\sim\!\sim\overset{H}{N}-\overset{\overset{O}{\|}}{C}-O\sim\!\sim$$

**Figure 1:** Urethane interunit linkage.

The polyurethane, was discovered by O. Bayer and this poly-condensation product opened a new chapter in the varnish and wire enamel chemistry. During the Second World War, Bayer AG developed the use of isocyanates and polyurethanes for coatings. The first polyurethane wire enamel (PU-WE), introduced in the 1950, consisted of an alkyd or polyol, made of dicarboxilic acids, three functional alcohols, like glycerine, and Desmodur AP stable, a phenol blocked trimethylol propane-toluene diisocyanate adduct.These polyurethane coatings were ductile, had high electrical properties, good abrasion and chemical resistence. Moreover, PU-WE have the advantage of easy solderability, they cure at low temperature and the wire can be enamelled at faster rates, and this is an important feature for the industrial production. In the 1950s' the principal wire enamels were the poly(vinyl formal) resins combined with a phenolic resin (as reported in Figure 2) in a solvent mixture of cresylic acid and naptha.[2]

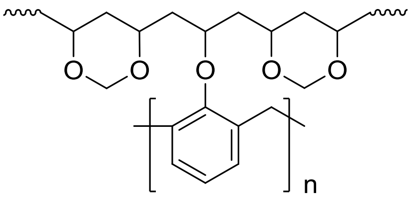


**Figure 2:** Poly (vinyl formal)-phenolic resin.

The long term temperature resistance of this insulation was 105°C. These enamels were substituted by polyurethane, especially in the fine wire segment. These coatings are characterized by an high soldering temperature of 360°C, leaving a clean wire surface for the solder to adhere to it.[3] The combination of poly(vinyl formal) and polyurethane wire enamels brings an improvement in their properties such as resistance to organic solvents stability and breakdown voltage. In the early 1960s, there was the introduction of terepthalic acid polyesters and polyester imides as high thermal stability wire enamels by Dr. Beck & Co. GmbH (Figure 3).[4]

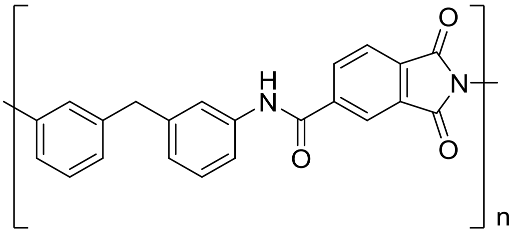


**Figure 3:** Polyester imides.

In this contest there were the possibilities to modify PU-WE, in a particular way, a thermal resistance upgrade of these coatings. In the middle of the 1970s, the first class-F (TI = 155°C) PU-WE were developed by Dr. Wiedeking GmbH and Schweizerische Isola-Werke using a polyester imide as polyol. The increase of the imide content of the polyester imide resins and using diphenyl methane diisocyanate (MDI) instead of toluene diisocyanate (TDI) allowed in the 1980s, to the introduction of a class-H (TI = 180°C) PU-WE by the Dr. Wiedeking GmbH. Nowadays, this class-H PU-WE represents the top performing version of the commercially available polyurethane wire enamels.[5] The composition of a polyurethane wire enamel consists of a blocked polyisocyanate adduct, a polyester polyol, a catalyst, solvents and additives.

## 1.1 BLOCKED ISOCYANATE ADDUCTS

The first blocked diisocyanate adduct used in wire enamels was Desmodur® AP stable, a phenol blocked trimethylol propane-toluene diisocyanate adduct from Bayer AG (Figure 4).

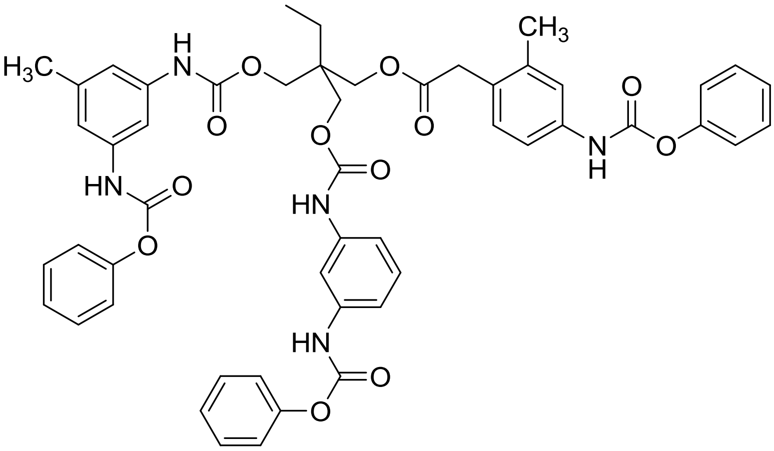


**Figure 4:** Desmodur® AP stable.

For polyurethane wire enamels, aromatic isocyanates are used, because they have higher thermal stability and reactivity, compared to the aliphatic ones. Typical isocyanates, which are used for PU-WE are shown in Figure 5.

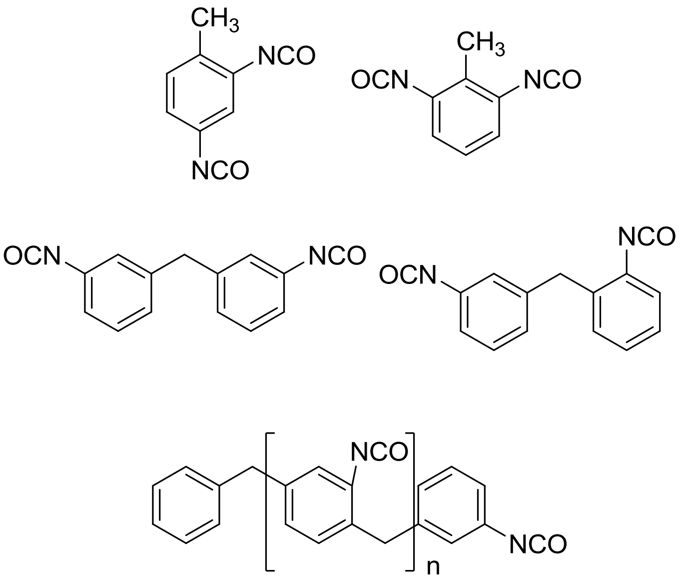
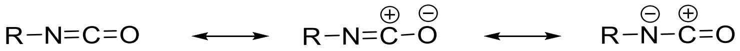


**Figure 5:** Typical isocyanates for PU-WE.

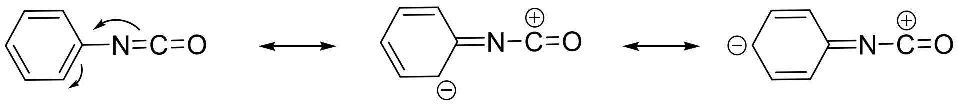
The electron distribution of the isocyanate group it is represented by the mesomeric structures in Scheme 1.



$$R{-}N{=}C{=}O \longleftrightarrow R{-}N{=}\overset{\oplus}{C}{-}\overset{\ominus}{O} \longleftrightarrow R{-}\overset{\ominus}{N}{-}\overset{\oplus}{C}{=}O$$

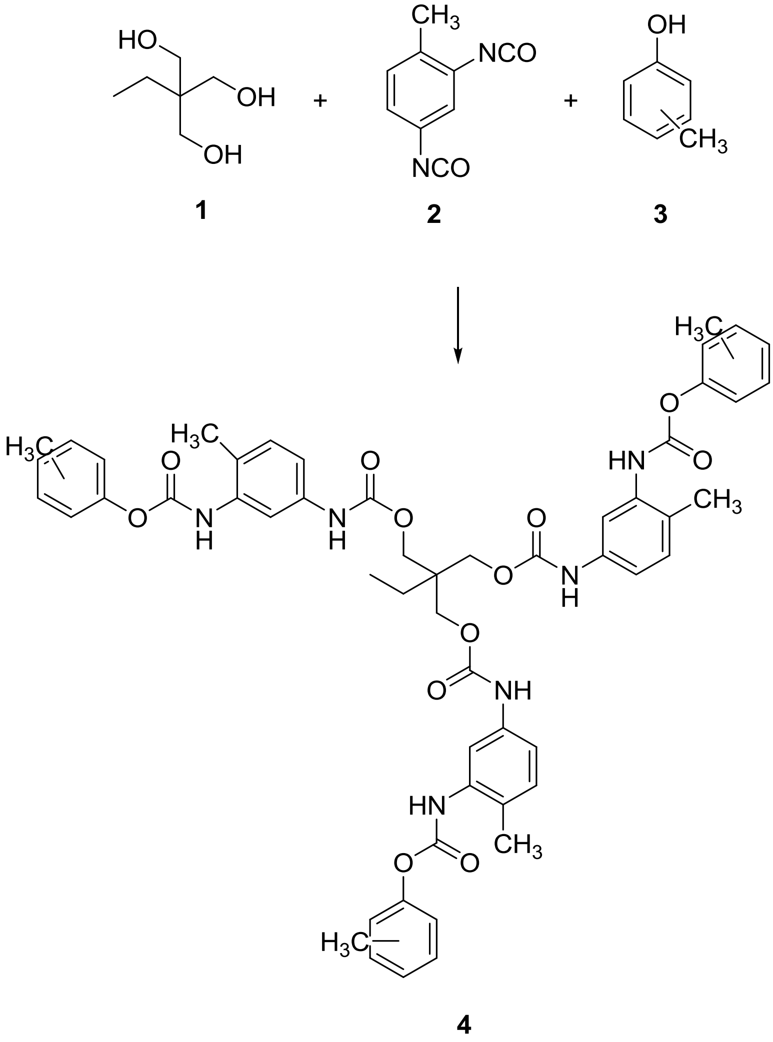
**Scheme 1:** Mesomeric structure of NCO.

From the resonance structure the carbon atom results electrophilic site, while the nitrogen and the oxygen atom result nuclephile site. In this way the carbon atom can be attacked by a nucleophilic partner, while the nitrogen and oxygen atoms are free for an electrophilic addition. The mesomeric effect on the aromatic ring increases the positive charge at carbon atom and the reactivity thereby (Scheme 2).



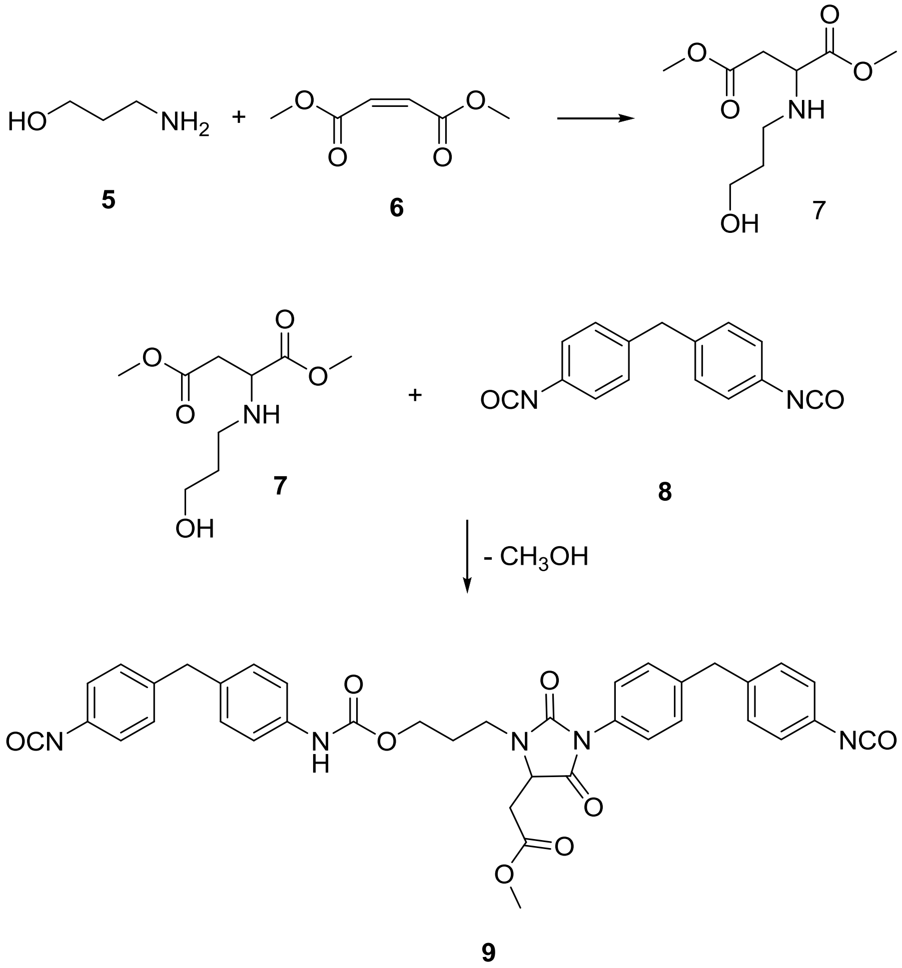
**Scheme 2:** Mesomeric structure of aromatic NCO.

The aromatic isocyanate **2** is not used pure in the formulations. They react with aliphatic triols like trimethylolpropane (TMP) **1** or diols in a ratio of alipathic hydroxyl group to di- or polyisocianates of 1:1. The reaction leads to a product mixture **4** having a molecular weight distribution. The remaining free NCO groups are blocked using phenols **3** and cresylic acids as blocking agents (Scheme 3).



**Scheme 3:** Blocked isocyanate adduct synthesis.

There are three principal reasons to explain why blocked isocyanate adducts, instead of pure isocyanates in PU-WE formulations.[6] Some isocyanates, especially toluene diisocyanate (TDI), have low vapour pressure (TDI = $2.3 \times 10^{-2}$ Torr at 25°C), which causes healty problems to workers. This problem is easily solved using isocyanates with a higher molecular weight.[7] The formation of the adduct allows the increase of the molecular weight, branching density and functionality. This leads to a high cross-linking density on the wire with a high hardness and chemical resistance. The use of phenols as bloking agents, lead to a product with long shelf life; the main blocking agents are: phenols, cresylic acids, caprolactam, imidazole, malonic esters and oximes. The steric hindrance and the acid character of the blocking agent, lead to thermal labile bonds to the isocyanate, in this way, phenols result the best blocking agent.[8] The de-blocking process occurs in the oven at high temperature (more than 120°C) and the free isocyanate groups react with the polyester polyol, forming stronger urethane bonds. In particular, the solderability of PU-WE is based on the splitting of urethane groups, higher is the temperature of the splitting of urethane groups better is the solderability. The highly cross-linked and polymeric structure as well as the secondary structure, increase the splitting temperature, on the other side the amount of urethane bonds improve the solderability. In order to increase the mechanical properties some structure modifications were made. Bayer introduced in 1966, a hydantoin modified polyisocyanate to increase the thermal resistance of the resulting wire enamel. The reaction of primary aminic alcohol **5** with ethylene-1,2-dicarboxylic acid ester **6**, leads to the asparginic acid ester **7**. After the following reaction of these ester with diisocyanate **8** hydantoin modified polyisocyante **9** was obtained (Scheme 4).

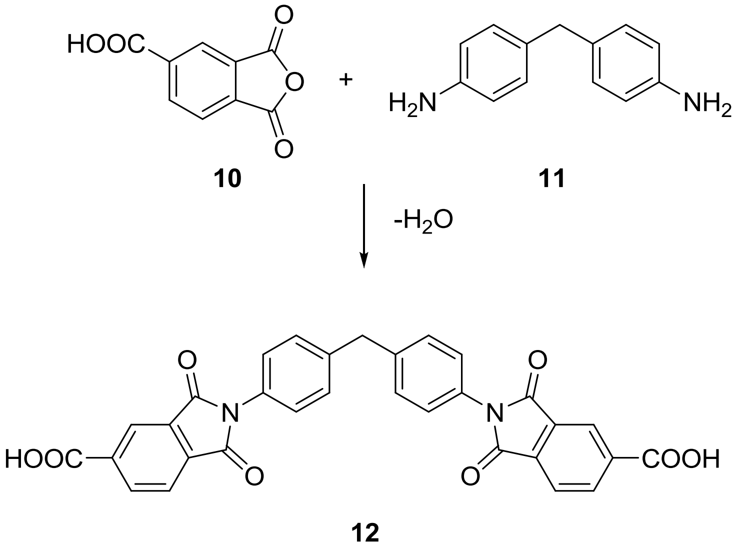


**Scheme 4:** Hydantoin modified isocyanate.

Wires with good brazability, heat and crazing resistance were obtained using a spiroacetal glycol MDI reaction product blocked with cresol and a epoxy resin. Carbodiimide modified blocked isocyanates allows an higher enamelling speed. With hydroxyl group containing reaction partners, solderable PU-WE were obtained; with carboxylic containing partners cross-linked, non solderable wire enamels were obtained.

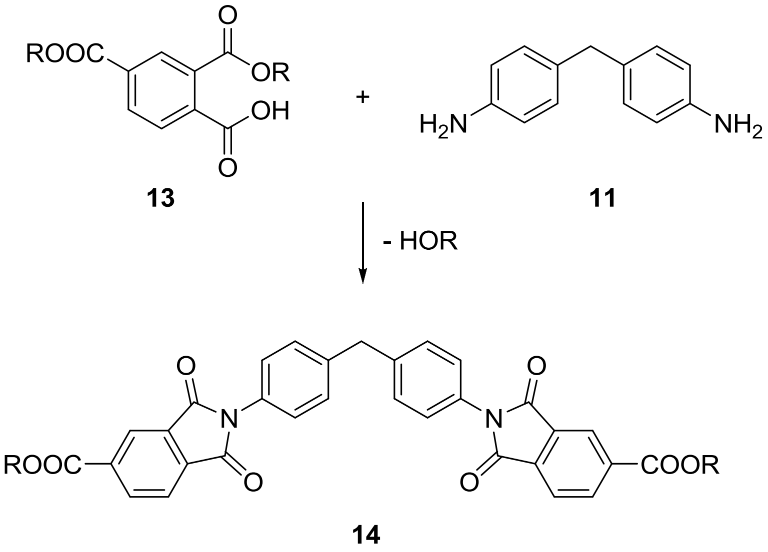
## 1.2 POLYESTER-POLYOLS

The composition of polyurethane wire enamels is characterized, as it was reported in the Chapetr 1.2, by a blocked isocyanate adduct (e.g, Desmodur® AP stable), but also by polyester polyols. In particular polyester polyols react with isocyanates molecules such as imides. Polyesters are characterized by a high thermal stability and an high oxidation resistance. For class A and class B PU-WE, alkyd resins and simple polyesters out of ethylene glycol, diethylene glycol, triethylene glycol, glycerine, TMP, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, adipic acid, phtalic acids and their esters and anhydrides are used. The synthetic route of these building blocks is based on a poly condensation reaction between a diacid and a di- or trifunctional alcohol. This reaction can be catalyzed by metal such as Pb, Zn, Sn, Mn or salts as acetates and octoates or titanates. This process is controlled by measuring the viscosity and the acidic sites and hydroxy numbers by titration. In particular, the number of hydroxyl groups is always in excess with regard to the number of carboxylic acid groups in the synthesis, to ensure that the polyester has enough free hydroxyl groups for the reaction with the polyisocianate. Moreover, unreacted hydroxyl groups are responsible for a good adhesion on the copper surface of wires. During the formulation are usually used aliphatic alcohols because they show a high reactivity towards isocianates due to their inductive effect and on the other side aromatic acids are used. This choice ensures a good thermal stability, flexibility and breakdown resistance. The introduction of polyester imides influenced polyurethane chemistry. The first polyurethane wire enamel reachimg class F was available in 1975, invented by Dr. Wiedeking GmbH and Schweizerische Isola-Werke. This polyurethane was prepared from a blocked isocyanate adduct and a polyester imide as hydroxyl polyol component. The polyester imide was synthesized starting from *p,p*-diaminodiphenylmethane (DADM) **11**, glycine, trimellitic acid anhydride (TMA) **10** and diols and triols like glycols and 1,1,1,-trimethylol propane (TMP). The imide formation is based on the reaction represented in the Scheme 5.



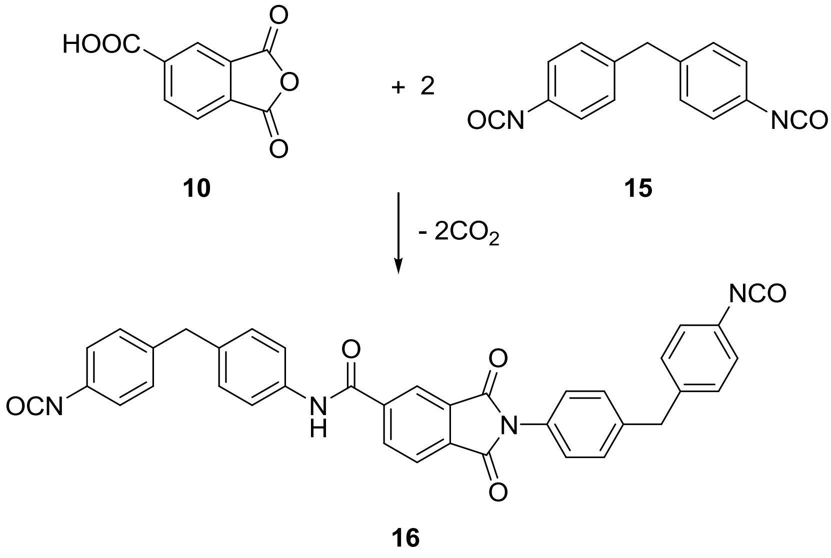
**Scheme 5:** Imide formation.

The primary amine is reacted with an aromatic anhydride, leading to rapid formation of amic acid intermediate, occurring at room temperature. The imide group **12** is formed after the ring closure of the amic acid. This process occurs at elevated temperature, but may also occur in traces at room temperature. Due to the different reactivity of the two functional groups of TMA towards amines (carboxylic acid, anhydride), the formation of amic acid occurs faster with respect to the amide formation (reaction of amine with carboxylic acid). The reaction of the formed acid with alcohols leads to polyester imide polyols. The reaction can be carried out in a two step reaction (firstly, imide formation and secondly esterification) or in a single stage. Since the imide formation is thermodynamically preferable, the amine can form the imide also with already esterified TMA **13** (Scheme 6).



**Scheme 6:** Imide formation of esterefied TMA.

Instead of diamines (several aromatic amines are carcinogenic) the corresponding diisocyanates **15** can be used. An advantage of this reaction is the formation of carbon dioxide as byproduct which can be easily removed (Scheme 7).



**Scheme 7:** Imide formation starting from diisocyanates.

Polyamide-imide modified polyurethane as well as hydantoin modification of PU-WE allows to higher thermal values.[6]

## CHAPTER 2.

## ADDITIVES CHEMISTRY

The European Commission defines as additive a substance which is incorporated into plastics to achieve a technical effect in the finished product, and is intended to be an essential part of the finished article. From an industrial point of view very few polymers are technologically used in their chemically pure form. It is generally necessary to modify their behaviour by the incorporation of additives; in particular some useful materials could only be obtained if certain additives are incorporated into the polymer matrix, in a process normally known as "*compounding*". Additives confer on materials significant extensions of properties in one or more directions, such as durability, stiffness and strength, impact resistance, thermal resistance, resistance to flexure and wear, acoustic isolation *etc.* The steady increase in demand for plastic materials by industry and consumers shows that this kind of products are becoming more performing. This evolution is also reflected in higher service temperature, dynamic and mechanical strength, stronger resistance against chemicals and radiation and odourless formulations. Consequently, a modern plastic part often represents a high technology product of where the additives play a very important role to define material's properties. In the formulation an additive represents a primary ingredient which forms an integral part of the final product, or a secondary ingredient which improves performance and/or durability. Additives are needed not only to make resins processable but also to improve the properties of the moulded product during use. In the last years the range of additives is increased a lot and the number of them in use today runs to many thousands and their chemistry is often extremely complex and not all additives are suitable for the same material. Most commercial additives are single compounds, but there are case where additives are oligomeric or technical mixtures. Example of this complex additives are: Irgafos P-EPQ containing seven compounds, Anchor DNPD, technical grade technical grade glyceryl-monestearate and various HAS oligomers. Particularly Flame retardants are often used as a mixture and the surfactants rarely occur as pure compounds. For what concern the different additives type they may be monomeric, oligomeric or high polymeric ( typically: impact modifiers and processing aids). They may be liquid-like or high-melting and therefore show very different viscosity compared to the polymer melt in which they are dispersed.[9] Generally additives can be broadly grouped into three major types based on what characteristic is being modified: *chemical* - antioxidants, UV absorbers, thermal stabilizers; *physical* – flow aids, rheology modifiers, de-foamers, dispersants; *biological* – antimicrobials, antifungals, algaecides. Another important aspect related to the additive functions is the working environment. The ability of all these additives to fulfil their roles is greatly impacted by the environment in which they operate. If the additive sees specific chemical or hydrophobic interactions or partitions into a discontinuous phase it may not be available.[10] In this chapter not all the additives will be taken into account but only the principal additives used in for wire enamels, in particular flame retardants, levelling agents and corrosion inhibitors.

## 2.1 FLAME RETARDANTS

It is known from literature that hydrocarbon-based plastics are combustible, this is due to the presence of hydrogen in the carbon backbone which, in presence of oxygen and heat, can produce fire. In Figure 6 is reported a general scheme of what happens during the polymer combustion.

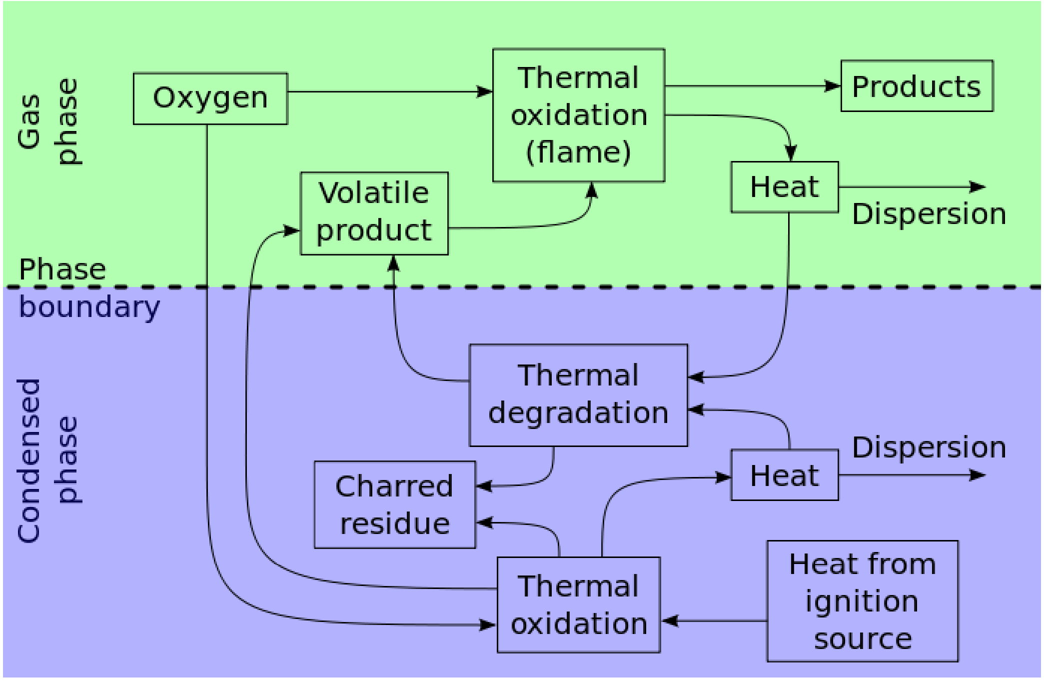


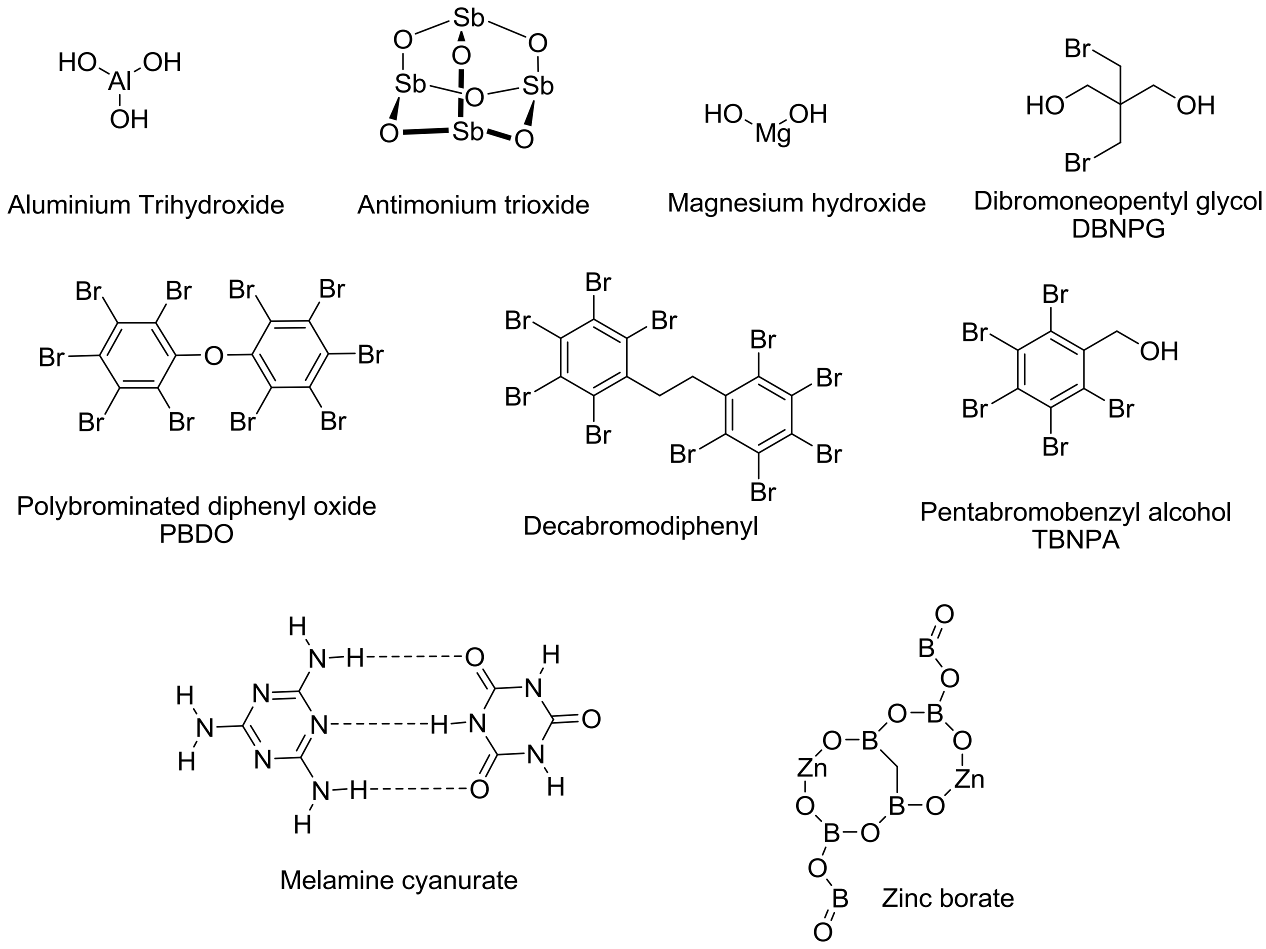
**Figure 6:** General scheme of polymer combustion.

In order to make them safe for use in vary applications such as electronic equipment, they need to be made incombustible, or difficult to ignite and burn at the very least. Some thermoplastics, such as PCV, and modified PPO, have some inherent resistance resistance to burning, but may need to be supplemented by additives. Flame retardant additives work by breaking one of the links that produce and support combustion – heat, fuel and air. They can quench a flame by depriving it of oxygen or may absorb heat and produce water, which reduces the temperature. When flame retardants are combined, then can provide a synergistic effect. Flame retardants act after combustion has started and operate by interfering with the combustion process. This can be by cooling the flame (often by releasing water), or to starve it of oxygen by releasing nitrogen or halogens, or by forming a carbonaceous char layer over the burning plastic. Some flame retardants can perform more than one of these actions, or can be combined to produce a sequence of useful reactions in a fire. As well as controlling and smothering the flame, the flame retardant system must not produce toxic, dense, or noxious smoke and fumes. It also needs to assist in preventing burning material from dripping and spreading the fire, as well as reducing the afterglow. There are three key tests for flame retardants: the peak rate of heat release indicates how far and rapidly a fire will spread, the limiting oxygen index (LOI) determines the relative flammability of polymeric materials, the higher the LOI value is the more flame retardant will be active into the plastic specimen. Finally, smoke suppression indicates the relative hazard from inhalation of smoke and toxic fumes.

Flame retardants can be inorganic, such as aluminium trihydrate (ATH), antimony oxide or zinc borate, or organic, such as  phosphate esters or halogenated compounds. There are three main types of flame retardants chemicals: additive flame retardants, active flame retardants and intumescent flame retardants. Most additive flame retardants contain bromine, chlorine, phosphorous, antimony or aluminium.[11] The main types of additive flame retardants include brominated hydrocarbons such as chlorinated paraffins and cycloaliphatics; non halogenated and halogenated phosphate esters, antimony oxide-trioxide and pentoxide. Also melamine, zinc borate and silicone polymer are considered good flame retardant agents. Reactive flame retardants are usually introduced during the polymerization stage and copolymerized together with other monomers. These flame retardants have a minimal effect on mechanical properties. Examples include tetrabromobisphenol A, diibromoneopentyl glycol, vinyl chloride and bromo- or dibromostyrene.

Reactive flame retardants are mainly relevant to thermosettings resins, such as unsaturated polyesters and epoxies. For polyesters, the main reactive flame retardants are HET acid (Chlorendic acid) or dibromoneopentyl glycol. Brominated flame retardants are claimed to be 70% more efficient than HET acid. Reactive phosphorous organic compounds are often considered the best system for epoxies. These are toxicologically harmless in fire and are chemically linked to the resin matrix, so that mechanical and chemical properties are not affected. On the other hand, additive flame retardants are introduced during compounding. These include chlorinated paraffins, brominated organics, phosphate esters, aluminium trihydrate magnesium hydroxide, borates and antimony trioxide. A third approach employs an additive that will intumesce under high heat. This involves forming a barrier, which is both non-combustible and acts as a thermal insulator to protect the substrate.

Additive flame retardants are more frequently used and there are a great many to choose from, depending on the precise conditions in wich the additive is expected to operate, and also the desired cost level. The cheapest additive is aluminium trihydrate, which is largely used in polymers that are processed at low temperatures, such as epoxy resins, unsaturated polyesters, polyethylene and PVC. High loadings are required, wich can affect the physical properties of the polymer. Chlorinated paraffins offers low cost and application in all the polymers that are processed at less than 240°C. Bromine is a more effective flame retardant but, on cost/performance, chlorinate paraffins can be more effective the aromatic bromines. The structure of the main flame retardant additives are reported in Figure 7**.**[11,12]


Aluminium Trihydroxide

Antimonium trioxide

Magnesium hydroxide

Dibromoneopentyl glycol
DBNPG

Polybrominated diphenyl oxide
PBDO

Decabromodiphenyl

Pentabromobenzyl alcohol
TBNPA

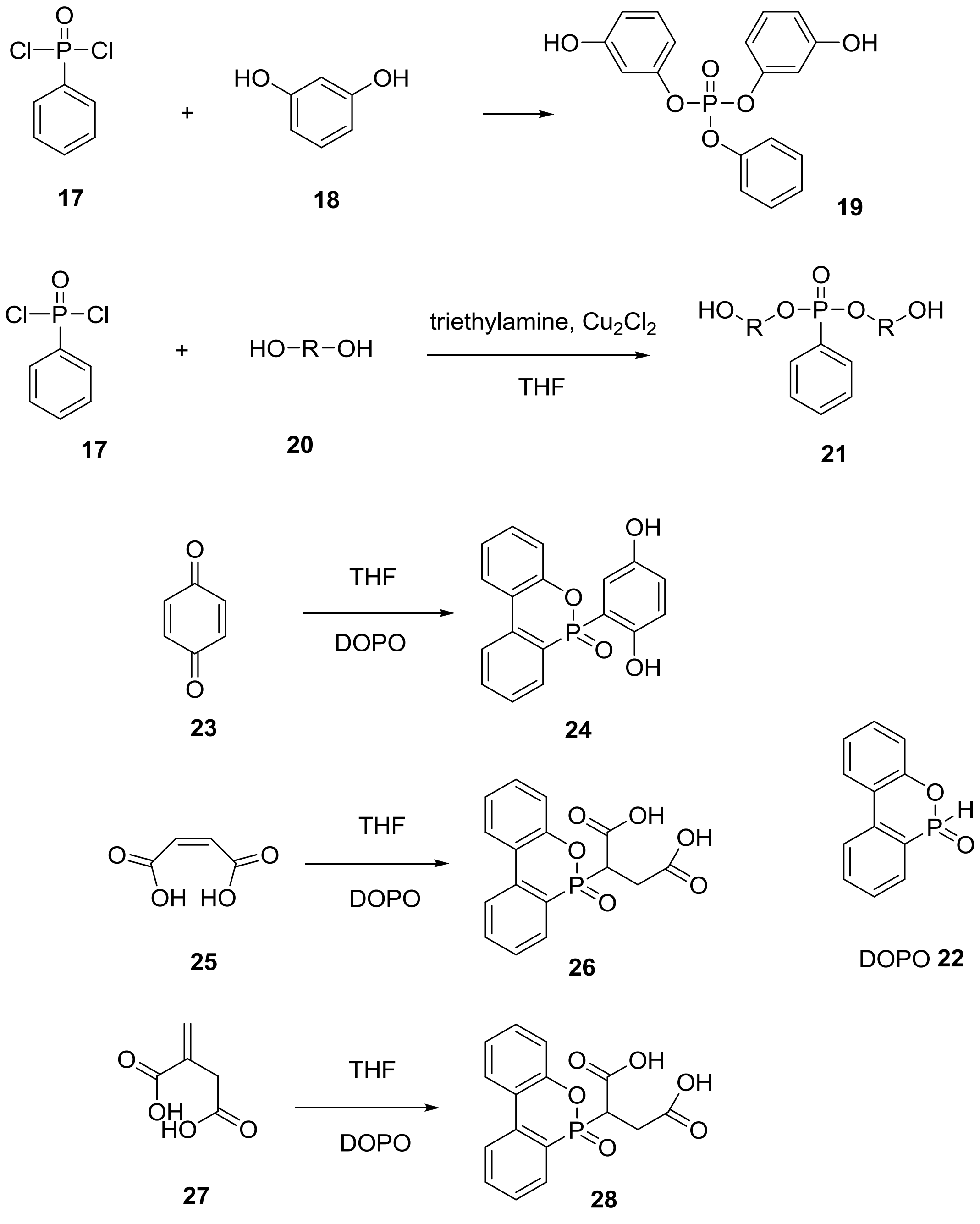
Melamine cyanurate

Zinc borate

**Figure 7:** Main flame retardants additives structures.

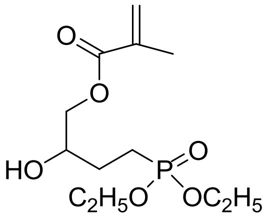
Flame retardants and their properties result to be very important additives in coating and enamel formulation. Flame retardant coatings are non combustible materials, which prevent or delay flashover from the coating surface of combustibles. The history of flame retardant materials was spurred by an important research on flame retardant military clothing used by US during the World War II.[13] As seen previously there are two general approaches to achieve flame retardancy in polymers known as additive and “reactive” types. For what concern coatings, the incorporation of phosphorus-containing chemical units into the PU backbone or in the side chain is the most effective way to improve flame retardance, because a phosphorus group accelerates crosslinked phosphorus and carbonaceous char formation. Therefore, PUs containing reactive type flame retardants char more easily during combustion than that containing additive type flame retardants, and results in higher flame retardancy.[14] Based on the flame retardant mechanism, these coatings can be classified into intumescent and non-intumescent, i.e., those that swell and char on exposure to a flame, and those that, respectively do not do so. At high temperature, the formed charred layer on the coating surface provides resistance to both heat and mass transfer, giving good heat insulation to the underlying binder. Intumescent systems consist of three main substances: an acid source (e.g., phosphorus-containing substance), a carbon source (e.g., polybasic alcohol), and a gas source (nitrogen containing substances).[15]

An increasing interest, in the flame retardants field, is given by organophosphorus compounds. Many of these compounds have been synthesized for using as flame retardants, and some of them are commercially available. Reactive phosphorus containing compounds, mainly polyols, are the most suitable flame retardants for an easy inclusion in the PU structure.[16] They not diffuse toward the surface of the polymeric material and remain more resistant against combustion for longer periods. Some structure, such as phenyl dichloro phosphate (BHPP) **17** and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) **22** shown in the Scheme 8 have attracted unique attention due to the presence of an electrophilic phosphorus center in all these structures. An organo modifier i.e., a nucleophile can modify these structures.[17]

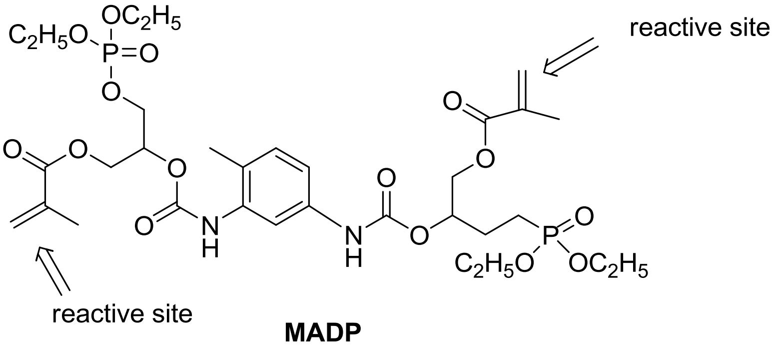


**Scheme 8:** Different organophosphorus reactive type flame retardants.

For example (Scheme 8) 1,3-dihydroxybenzene (resorcinol) **18** reacts with phenyl dichlorophosphate (BHPP) **17** to give bis(3-hydroxyphenyl) phenyl phosphate **19** which can be used in the reaction with NCO-capped PU. Another approach regards, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) **22** which can react, in the same fashion, with benzoquinone **23,** maleic acid **25** and 2-methylene succinic acid **27** to give the corresponding organophosphorus compounds **24**, **26** and **28**.[18] Z.L. Ma *et al.*[19] used for spirocyclic phosphate containing polyols as reactive type flame retardant material in PU coatings. P.L. Kuo *et al.*[20] synthesized oligomeric polyalkyl phosphate type polyols from phosphorus oxychloride, ethylene glycol and 1,4-butanediol. These polyols were then reacted with toluene diisocyanate (TDI) to form corresponding flame retardant PUs. Different phosphorus containing diols or triols were reacted with diisocyanates and produced NCO-capped monomers. These monomers were further reacted with hydroxyl group containing acrylates e.g., HEMA or HEA to produce unsaturated reactive type flame retardants. For example, methacrylated phosphate (MAP) and diphosphate (MADP) reactive flame retardant for UV-curable formulations were synthesized by S. Zhu and W. Shi.[21] In their study, phosphorus trichloride was reacted with ethanol and the resulting product $(C_2H_5O)_2$-POH was treated with sodium bicarbonate and potassium permanganate to get diethylphosphoric acid (DEPA). The reaction of DEPA with glycidyl methacrylate results in MAP, whereas treatment of MAP with TDI produce MADP (Figure 8).



**MAP**

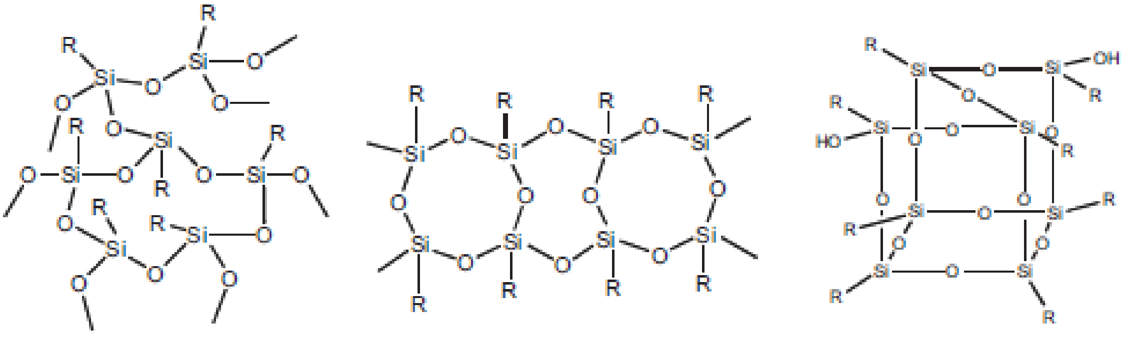


**MADP**

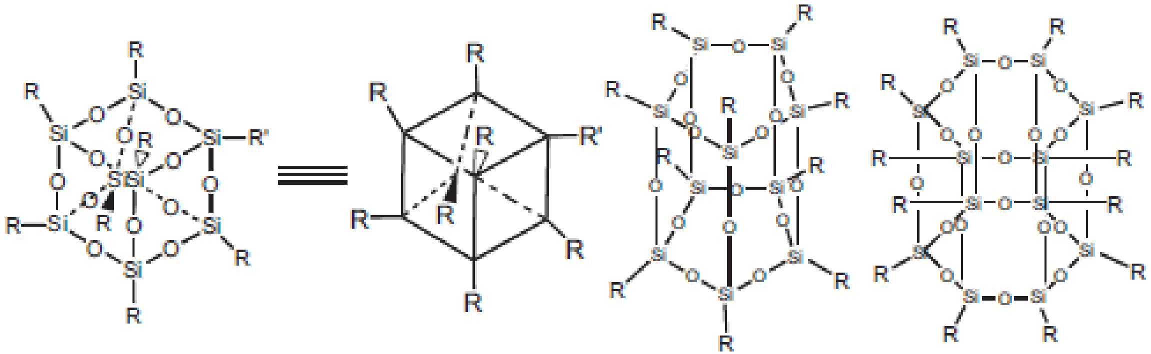
**Figure 8:** Structure of MADP, MAP and DMPE.

MADP contains terminal unsuturation which can be used for making PU-acrylate flame retardant formulation. Wang *et al.* copolymerized DPME with different acrylic monomers and prepared acrylic co-polyols, which they reacted with MDI for the preparation of flame retardant PUs.[22]

Another important flame retardant class is represented by silsequioxanes and organo-boranes. Silsesquionaxes impart flame retardancy on incorporation to PU structure. Silsesquinoxanes is the term for compounds with the formula $(RSiO_{1.5})_n$; they may form cage ladder, and sheet like oligomers and polymers. Their synthesis is based on the hydrolysis-condensation of $RSiX_3$ derivates (X= Cl, OMe, OEt, etc.). The hydrolysis of different trifunctional silanes may produce the diverse structure shown in Figure 9.[23]



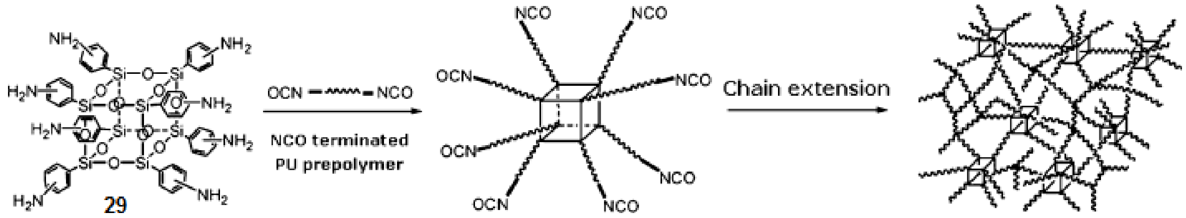
Random structure Ladder structure Partial cage structure



$T_8$ $T_{10}$ $T_{12}$

**Figure 9:** Generation of different structure during hydrolysis of trifunctional silane.

Nowadays, many studies are focused on polymers incorporating polyhedral oligomeric silsesquioxane (POSS), due to the simplicity of processing and the excellent comprehensive properties of this class of hybrid materials. The hybrid polymers show improved properties such as higher $T_g$ and modulus, a large increase in heat distortion, reduced flammability and enhanced mechanical strength.[24] Polyhedral silsesquioxane molecules are easy to prepare in high yield and standard organic manipulations can be applied to functionalize the exterior of the molecules, with retention of the silsesquioxane structure. In particular the incorporation of POSS into PU give materials with improved flame retardance, Liu and Zheng used octa aminophenyl polyhedral oligomeric silsesquioxane (OapPOSS) **29** to replace part of the aromatic amine crosslinking agent, and thus the POSS cages act as nanostructured crosslinking sites producing improved thermal stability (Scheme 9).[25]



**Scheme 9:** Polyurethane hybrid network containing POSS.

Talking about organoboron compounds they lead to significant improvement in flame retardancy. *Tris*(2-hydroxypropyl) borate **A** as reported in Figure 10 can be used in the PU formulation as a reactive flame retardant.

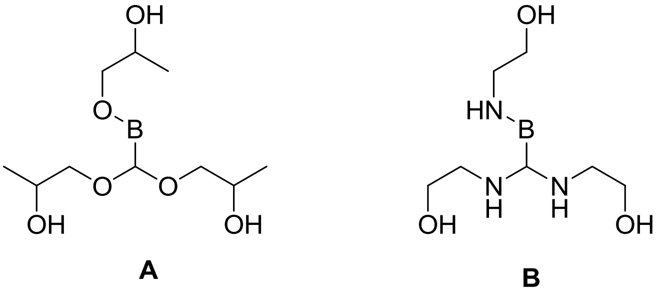
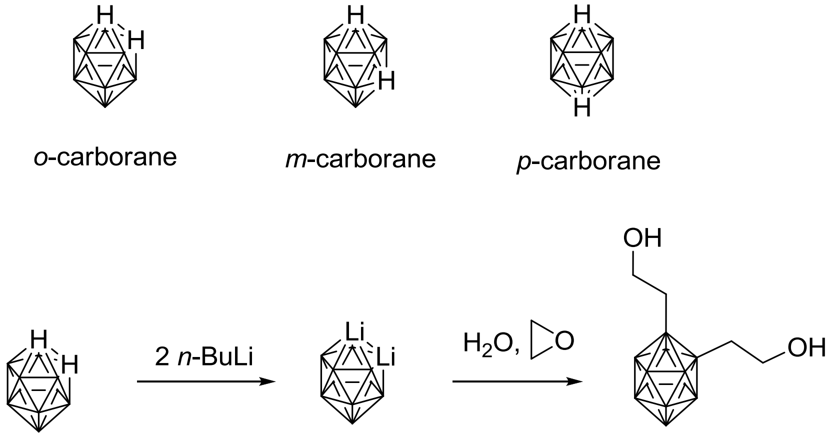


**Figure 10:** Strucutre of boron-containing reactive type flame retardant prepared from boric acid.

It was prepared from boric acid and 1,2-propanediol. Other example includes the reaction products of boric acid with 1,3-butanediol, monoethanolamine **B** and epichlorohydrin.[26]

Icosahedral carboranes (dicarba-closo-dodeca-boranes) are a class of carbon-containing boron-cluster compounds having remarkable thermal and chemical stability and exceptional hydrophobic character compared with other boron-containing compounds. These qualities, have made possible the development of extensive derivative and substitutions products. Most carborane derivatives of icosahedral ($C_2B_{10}$) or small cage ($C_2B_4$) systems are formed by varying the groups on the cage carbon atoms. The carborane cage is generally stable towards organic reactions and it is possible to carry out a variety of reactions on substituent groups attached to carborane while leaving the cage system intact. In carborane, the carbon bound hydrogen atoms are acidic and can be easily deprotonated, allowing the formation of numerous derivatives, including a wide variety of organic substituents. On the other hand the substitution at boron atoms is relatively difficult. The acidic hydrogen atom can be easily removed using alkyllithiums, LDA or *t*-BuOK giving rise to a highly nucleophilic carbanion with electrophile organo modifier, providing a convenient route to C-C bonds formation. For example, Cheung *et al*. preparared hydroxyalkyl *o*-carboranes by a very simple method: starting from closo dodecabornare *ortho* isomer **30**, it reacts with *n*-BuLi giving the lithiated *o*-carboranes **31** and in the last step there is the formation of hydroxyalkyl *o*-carboranes **32** using $H_2O$ and an epoxy ring (Scheme10).[27]



**30** **31** **32**

**Scheme 10:** Structure of carboranes and Cheung reaction.

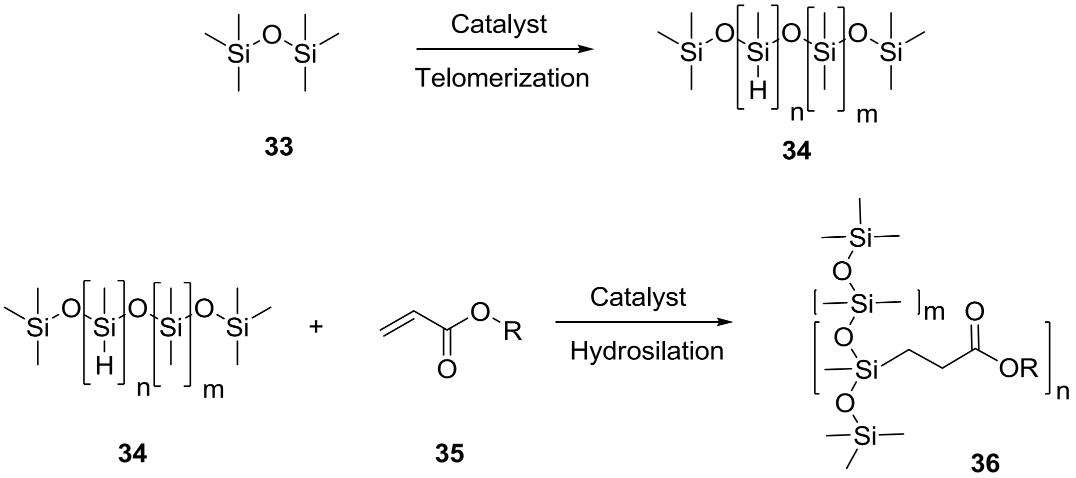
## 2.2 LEVELLING AGENTS

The terms “flow” and “levelling” mean something that deals with the even surface of a coating. This property is mostly judged on the basis of pure visual appearance. Typical surface problems which may have a negative influence on the overall surface property of good flow and levelling are for example: orange peel effect, structured surface, creater, fisheyes, crawling or air draught sensitivity, *etc.* Levelling and flow are very complex processes, the final result may be negatively influenced by several sources. Patton defined levelling as a purely viscosity dependent phenomenon.[28] Levelling can be determined with wet or with dried coating films. The levelling of wet coatings can be determined applying the liquid coating with various levelling gauges on contrast sheets. More important is the evaluation of the levelling of dry coatings, since the application process and application conditions (temperature, air humidity, film thickness, diluents, atomization, *etc.*) may have a very strong influence on the final result. The objective levelling evaluation “DOI” have been used for a long time and it is based on the evaluation of how much the mirror image is disturbed by the uneven surface of a coating. Another important measurements is based on the light scattering of a high-gloss coatings, so called “ALFA” values.[29] A coating film will obtain an even surface through the surface tension of the liquid coating which minimizes the surface area. Theoretically, the higher the surface tension is, the better the levelling will be, because a higher surface tension is accompanied with stronger physical forces that even out the surface. Surface control additives or levelling agents, are able to minimize the negative influences to flow and levelling. Experimental work proves that there is a correlation between reducing the surface tension by this kind of agents and the flow agents effectiveness.[30] Levelling additives, orient themselves at the liquid/air interface. This effect is caused by a limited compatibility and the low surface tension of this additive type. With a lower regular surface tension the wetting, levelling and flow is improved. The wetting is improved because liquids only wet a substrate if their surface tension is lower than the one of the substrate. The levelling is improved by creating a regular surface tension. Surface control agents orient themselves to interfaces and so evaporation of the solvents cannot cause gradients of surface tension. Without these gradients there is no flow to areas with a higher surface tension and the orange peel effect does not occur. All levelling agent should be carefully checked, because they can have positive or negative influences in the final system. Possible negative side effects can be: craters cause by overdose, interference in recoatability, foam stabilization telegraphing or loss of intercoat adhesion. After a careful check of the additive, some advantages can be provided, these benefits can be: control of gloss and orange peel effect due to a regular smooth surface. The substrate wetting control is improved by reducing the surface tension of the wet paint and in this way also critical surfaces can be wet and also the slip is enhanced by reducing the film surface roughness. During the drying process the additives becomes more concentrated at the surface, a closed film is formed facilitating hydrodynamic lubrification.[31]

An important class of levelling agents it is represented by polymeric levelling additives which create a physically uniform surface, hence reducing local surface tension differences. Among these levelling agent, polyacrylates are the most important. Moreover, they do not result in recoatability problems and they can be used without any risk of poor adhesion in primers and primer surfaces. These polyacrylate are homopolymeric or copolymeric materials, with a molecular weight between 5000 and 100000 Da and they have a glass transition temperature of -20°C or lower. Their levelling performance can be adjusted through variations in their chemical compositions, and their molecular weight. The solubility and compatibility in the coating are also dependent on these factors. Linear acrylic polymers are more incompatible that branched ones. Mainly *n*-butyl acrylate is used as the monomeric building block. Furthermore, copolymers are obtained, for example, from: ethyl acrylate, acrylic acid, or 2-hydroxyethyl acrylate.[32] Acrylic polymers, can be modified for waterborne applications with polar groups (i.e., carboxylic groups or polyethylene glycol). These products are mainly used in water soluble or hybrid coating systems (automotive coatings, primers surfacers, one coat systems), but they can also be applied in high-solids type polar solventborne coatings. Acrylic levelling additives are often used in solvent free systems such as unsaturated polyester resins or UV-curing systems. Commercial product examples are: Acronal4F, BYK-355, BYK-361, Modaflow, Resiflow,W-50, SER-AD FX 100 SF.

Many other polymeric materials are utilized, mostly not as all around products, but as speciality products, such as aromatic and aliphatic hydrocarbon resins, polymerized drying oils, high molecular weight butanol etherified melamine resins, modified polybutadienes, polyvinyl ether, polyvinyl butyrals, and modified polyalkylene glycols.

Another important levelling agent is represented by Silicones. Silicones (dimethylpolysiloxanes and modified dimethylpolysiloxanes) have been used in coating formulations since the early 1950s. Unmodified low-molwcular-weight, volatile silicones are used as levelling and surface flow control agents, but they also improve substrate wetting, anticrater performance, foam stabilization or defoaming, slip and mar resistance, and may other properties. Many important silicones properties such as compatibility, surface tension reduction, heat stability, slip and mobility in the paint film can be adjusted through chemical modification of the dimethylpolysiloxane chain. Most importantly, modifications can be done on the backbone or on the side chains. The modification of the polysiloxane backbone, can consist in replacing dimethylpolysiloxane units with methyl(alkyl)polysiloxanes or methyl(aryl)polysiloxanes. As side chains, polyethers such as polyethylene glycol or polypropylene glycol, or their combinations, as well as polyester, but also functional side chains carrying chemically reactive end groups (OH, acrylic) can be used. Commercial product examples: BYIS-300, BYK-3 10, BYK-320, BYK-333, BYK-370, Tego-Glide 444, Baysilonol PL, Paint Additive *56*.[30] Among the siloxanes copolymers containing poly(dimethylsiloxane) (PDMS) have received considerable attention. They find applications in the field of mechanical industry, chemical industry and even biomedical industry. Yang *et al.*[33] synthesizes PDMS grafted alkyl acrylate **35** *via* two well known and commonly reaction processes such as telomerisation and hydrosilylation (Scheme 11).



**Scheme 11:** Yang *et al.* PDMS synthesis.

## 2.3 CORROSION INHIBITORS

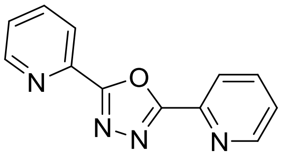
Metal corrosion related damage accounts for losses of 3 – 5% of the GNP (Gross National Product) in the industrialized nations. This enormous figure explains both the great interest in corrosion protection, as well as the significant efforts the industry is undertaking in developing both efficient and environmentally acceptable novel concepts. According to Kaesche the corrosion of metals can be defined as the destruction of a metal, commencing at the surface, by chemical reactions with components of its environment.[34] The protection of metal surfaces by organic coating is traditionally achieved with the following methods:

- The use of anticorrosive pigments;
- The application of barrier coatings;
- The applications of zinc rich coatings.

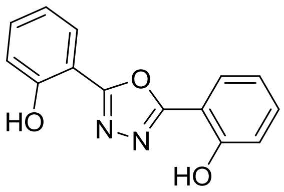
Nowadays, there is also the possibility to protect metal surface utilizing corrosions inhibitors. The use of these kind of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media.[35] The progress in this field has been phenomenal in the recent years and is borne out by the output of literature. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. The influence of these kind of organic compounds on the corrosion of steel in acidic solutions has been investigated by several works. The existing data, show that most organic inhibitors act by adsorption on the metal surface. The most important prerequisites for compounds to be efficient inhibitors are: forming a compact barrier film, chemisorption on metal surface high adsorption energy on metal surface and increasing layer thickness.[36] Corrosion inhibitors comprise a broad field, both in terms of the different chemical compound classes and chemical activities. Inhibitors are widely used in, e.g., liquid media such as lubricants, oil/water emulsions, or cooling/circulating systems. Others inhibition mechanism are based on:

- Shift of the potential at the anode (anodic inhibition);
- Shift of the potential at the catode (cathodic inhibition);
- Reduction of the porosity and the permeability of a coating towards water, oxygen and corrosion promoting ions (e.g, chlorides and sulphates);
- Improvement of the adhesion, especially of the wet adhesion between coating and metal surface.[30]

In PU enamel formulation, triazoles, tetrazoles, phosphates, imidazoles and their sulphur analogues are used as corrosion inhibitors. In particular Bentiss *et al.* studied the effect of a new class of corrosion inhinitors, namely 2,5-disubstituited-1,3,4-oxadiazoles (Figure 11) in acidic media.[37]



2,5-di(pyridin-2-yl)-1,3,4-oxadiazole



2,2'-(1,3,4-oxadiazole-2,5-diyl)diphenol

**Figure 11:** 2,5-disubstituited-1,3,4-oxadiazoles structures.

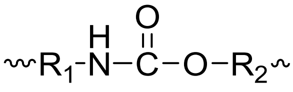
# CHAPTER 3.

# POLYURETHANES CHEMISTRY AND THEIR CATALYSTS

The myriad of applications related to polyurethane coatings, foams, fibers, moldings and elastomers demonstrate the versatility and the magnitude of urethane chemistry and the creativity of polymer scientist.[38] Otto Bayer and co-workers at I. G. Ferbenindustri Germany in 1937 were the first to discover PUs in response to the competitive challenge arising from Catohers's work on polyamides, or nylons, at E. I. Dupont.[39] The successful development of high molecular weight polyamides at E. I. Dupont stimulated Bayer to investigate similar materials. The initial work was the reaction between aliphatic isocyanate with a diamine to form polyurea which was infusible and hydrophilic. Further research on this subject demonstrated that the reaction of an aliphatic isocyanate with a glycol produces new materials with interesting properties. Dupont and ICI soon recognized the desiderable elastic properties of PUs. The industrial scale production of PU started in 1940 but market growth of PU was seriously impacted by World War II. A noticeable improvement in the elastomeric properties of PU waited until 1952, when polyisoyanate, especially toluene diisocyanate (TDI), became commercially available. In 1952–1954, Bayer developed different polyester-polyisocyanate system.[40] With the development of low cost polyether polyols, PU coatings opened the door for automotive applications. The PU coating industry has entered a stage of stable progress and advanced technological exploitation. Today, PU coatings can be found on many different materials, to improve their appearance and lifespan. The wide applicability of PU coatings is due to the versatility in selection of monomeric materials from a huge list of macrodiols, diisocyanates and chain extender (CE). The chemistry involved in the PU synthesis is focused on the isocyanate chemical structure characterized by the positive character of the carbon atom. In fact the synthesis of polyurethanes involve a simple reaction between a di- or polyisocynate with a di- and/or polyol.[41]

## 3.1 POLYURETHANES CHEMISTRY AND RAW MATERIALS

From a chemical point of view linear polyurethanes (PU) are polymers in which the principal chain structure is composed of aliphatic or aromatic sections $R_1$ and $R_2$ fixed together with polar urethane groups (Figure 12).



$$\sim R_1\text{-}\overset{H}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R_2\sim$$

**Figure 12:** Polyurethane general structure.

$R_1$ it's an aliphatic, aromatic or alicyclic radical derived from the isocyanate monomer, $R_2$ is a more complex group derived from the polyol component (polyether or polyester). The commercial manufacture of polyurethanes is nearly based on polyaddition process which involves diisocyanates and bi-functional or multifunctional polyols with hydroxyl terminal groups (Equation 1)

$$nOCN\text{-}R_1\text{-}NCO + nHO\text{-}R_2\text{-}OH \longrightarrow ...\text{-}(\text{-}O\text{-}R_2\text{-}O\text{-}OC\text{-}NH\text{-}R_1\text{-}NH\text{-}CO\text{-})\text{-}_n$$

**Equation 1**

The possible presence of multifunctional components, e.g. triisocyanates obtained from trimerisation process of isocyanate monomers, or the use of branched hydroxyl polyols, will yield polyurethane with three dimensional cross-linking in order to obtain materials with different mechanical properties. Moreover, it is a frequent practice that a prepolymer is initially synthesised and an excess of one component is used as reported in Equation 2.

$$2B + A \longrightarrow BAB$$

$$3B + 2A \longrightarrow BABAB$$

B = isocyanate
A= polyol

**Equation 2**

In this equation an excess of **B** has been used in relation to polyol **A**. When the polyol component is added to the diisocyanate, the molar ratio of the reacting substances is decisive for obtained size of the isocyanate prepolymer macro-molecules.

The synthesised urethane-isocyanate prepolymer BAB or BABAB can be further extended at the next reaction step by means of a low molecular weight diol. High molecular weight polyurethanes are produced in this way, and the size of the final macro molecule is controlled by the molar ratio of reacting functional groups (Equation 3)

$$\text{nOCN-BABAB-NCO + nHO-}CH_2\text{-}CH_2\text{-}CH_2\text{-OH}$$

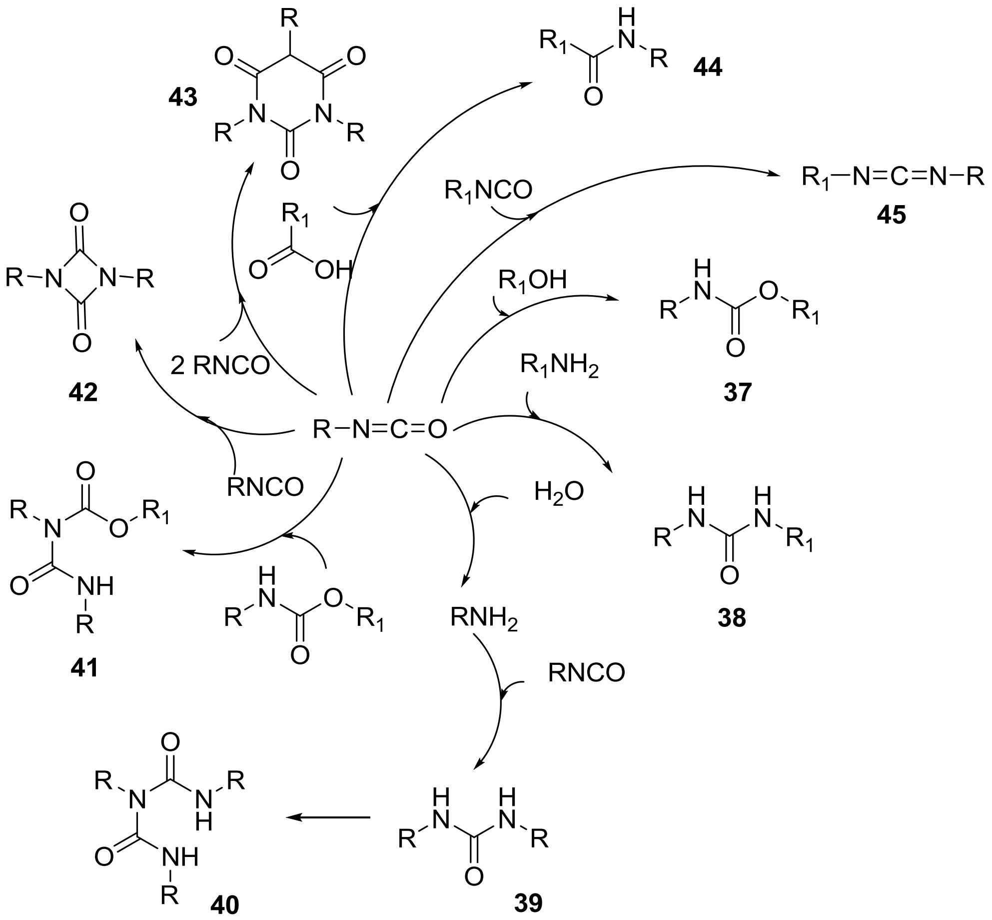
$$\downarrow$$

$$\text{-(O-CO-NH-BABAB-NH-CO-O-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2)_n$$

**Equation 3**

It is also possible to synthesise polyurethanes in a single stage process. The molar ratios for diisocyanate, polyol and extender should be carefully selected in order to reach the chain structure.[42] In the interest of a better understanding of PU formation reaction, we have to observe the reactivity of starting materials in particular the isocyanate and diols/polyols.

Isocyanates are highly reactive chemicals and create several chemically different products when combined with –OH and –NH functional substances. Desired products and side products are formed in different amounts. The basic reactions of isocyanate with different reagents are shown in Scheme 12.



**Scheme 12:** Basic reaction of isocyanates with different reagents.

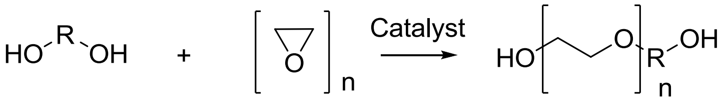
The high reactivity of isocyanate groups toward nucleophilic reagents is mainly due to the pronounced positive character of the carbon atom in the cumulative double bond sequence consisting of nitrogen, carbon and oxygen, especially in aromatic systems. The electronegativity of the oxygen and nitrogen imparts a large electrophilic character to the carbon in the isocyanate group. The common reactions of isocyanates can be divided into main classes:

- Reaction of isocyanates with compounds, containing reactive hydrogen, to give addition products;
- Polymerization of isocyanates, i.e. self addition reaction

Isocyanates react with hydroxyl compounds to give urethanes **37** and with amines to give ureas **38**. For primary and secondary alcohols, the uncatalysed reaction proceeds readily at 50-100°C, tertiary alcohols and phenols react slower. Typical primary and secondary aliphatic amines and primary aromatic amines rapidly react with isocyanate at 0-25°C to form urea functional substances. Similarly, water reacts with a diisocyanate and initially forms of an unstable carbamic acid, which decomposes and produces an amine freely carbon dioxide. Amine is a nucleophilc reagent and further reacts with an isocyanate function to produces urea linkage **39**. The availability of a lone pair of electrons on the nitrogen atom of urea group makes them nucleophilic centers, which upon reaction and fruitful collision with one molecule of isocyanates produces biuret **40.** Similarly, isocyanates react with urethanes and produce allophanates **41**. Different secondary reactions shown in Scheme 12 occur to a lesser extent than the primary reactions. Reactions leading to the formation of allophanates and biurets are influenced by reaction conditions such as temperature, humidity level and the type of isocyanate used. The self-condensation of isocyanate results in uretidione rings **42,** isocyanurate **43** or carbodiimide **45**. The formation of carbodiimide is not usually considered a polymerization reaction, but it could be classified as a condensation polymerization between isocyanate molecules with elimination of $CO_2$.[43] This is due to degradation of isocyanates taking place at high temperature.[44] When isocyanate reacts with carboxylic acids, the mixed anhydrides break down and form amide groups **44**. The trimer isocyanurate rings **43**, unlike uretidione rings **42**, are exceptionally stable. The high reactivity of isocyanates may cause detrimental secondary reactions and uncontrolled condensation leading to the formation of unworkable crosslinked materials that are difficult to process.[45] The polyfunctional isocyanate used to prepare PU coatings can be aromatic, aliphatic, cycloaliphatic or polycyclic in structure. The commonly used isocyanates in the manufacture of PUs are TDI, MDI (as seen in chapter 1), 4-4'-dicyclohexylmethane diisocyanate ($H_{12}$MDI), xylene diisocyanate (XDI), tetramethylxylylene diisocyanate (TMXDI), hydrogenated xylene diisocyanate (HXDI), naphthalene 1,5-diisocyanate (NDI), *p*-phenylene diisocyanate (PPDI), 3,3'-dimethyldiphenyl-4, 4'-diisocyanate (DDDI), hexamethylene diisocyanate (HDI), 2,2,4-trimethylhexamethylene diisocyanate (TMDI), isophorone diisocyanate (IPDI), norbornane diisocyanate (NDI), 4,4'-dibenzyl diisocyanate (DBDI), *etc*. (Figure 13)

Aromatic isocyanates have higher reactivity than aliphatic or cycloaliphatic diisocyanates. Different diisocyanates contribute to PU properties in different ways. For example, aromatic diisocyanate gives more rigid PUs than do aliphatic ones.[46]

The polyol component of the PUs can be a polyfunctional polyether, polyester polyol (PEPO), acrylic polyol (ACPO), polycarbonate polyol, castor oil or a mixture of these. A wide variety of branched or crosslinked polymers can be formed since the functionality of the hydroxyl containing reactant or isocyanate can be adjusted. The simplest polyols are glycols, such as ethylene glycol, 1-4 butane diol (BDO) and 1,6-hexane diol. The low molecular weight reactants result in hard and stiff polymers because of a high concentration of urethane groups. On the other hand, the use of high molecular weight polyols produce polymeric chains with fewer urethane groups and more flexible alkyl chains. Long chain polyols with low functionality give soft elastomeric PU while, chain polyols of high functionality give more rigid, crosslinked product. Polyether polyols **48** are produced by the addition of ethylene oxide **47** to a polyhydroxy "starter" **46** molecule in the presence of a catalyst (Figure 13)



**46** **47** **48**

**Figure 13:** Synthesis polyether polyols.

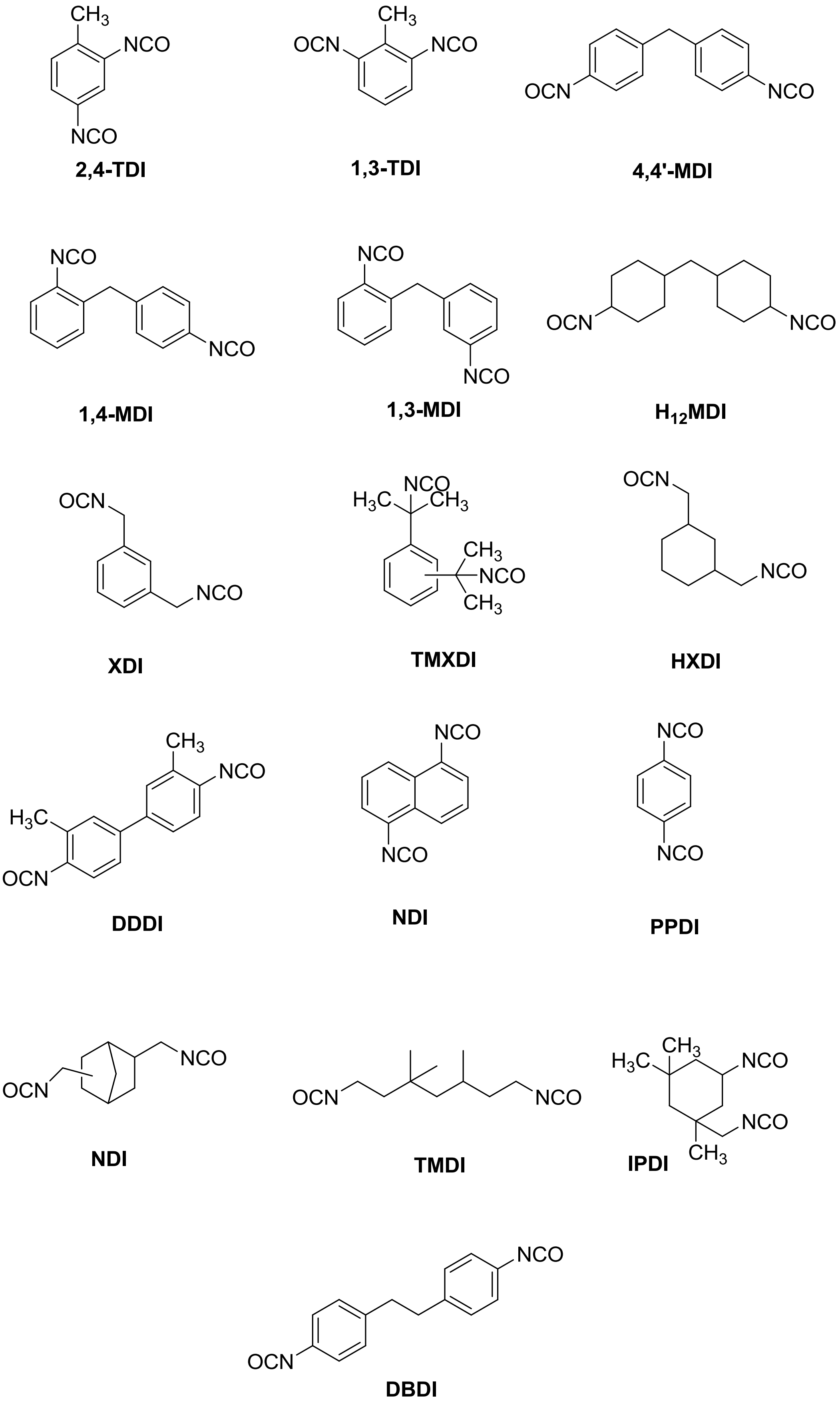
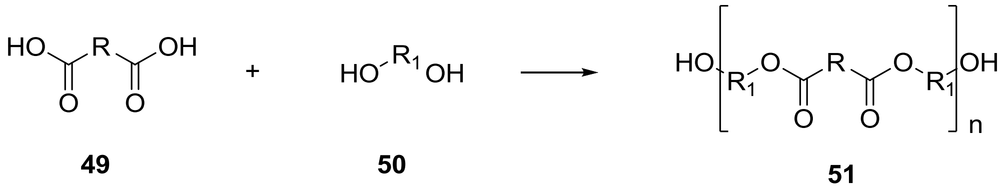


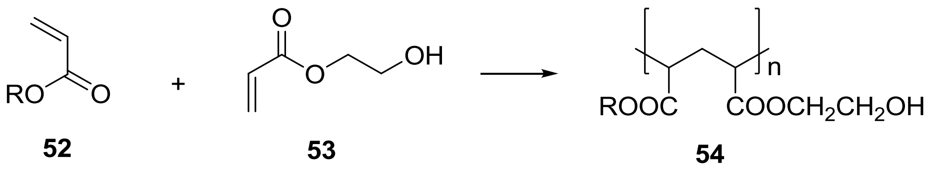
**Figure 14:** Different isocyanate structure, used to prepare PUs coatings.

Typical starting molecules include glycerol, ethylene glycol, propylene glycol and trimethylolpropane. PEPOs **51** are produced by the condensation reaction of polyfunctional carboxylic acid **49** with polyfunctional alcohols **50** (Scheme 14).



**Scheme 14:** Synthesis of PEPOs.

ACPOs **54** are produced by free radical polymerization of hydroxyethyl acrylate (HEA) **53** with other acrylic precursor (e.g alkylacrylate **52**) (Scheme 15).[47]



**Scheme 15:** Synthesis of ACPOs.

Depending on the field of application, PEPO, ACPO or polyether polyols have generally been chosen. In commercial applications, it is common to find polyesters prepared from a mixture of two or more diacids reacted with two or more glycols, which gives ample scope for a range of very complex products.[48,49] PEPO and ACPO based PUs are vulnerable to the gradual hydrolysis of the ester group but they are sufficiently stable against natural weithering. To slow down the hydrolysis of polyester groups, polycarboimides can be added to poly(ester urethanes) that act as acid scavengers.[50]

## 3.2 POLYURETHANES CATALYST

Catalysis is an important field for polyurethane chemistry and many improvements have been accomplished in recent years. Catalysis in the urethane formation is often complicated by the fact that urethane formation is subject to multiple side reactions. Further, the presence as well as the choice of catalyst may have considerable influence on the ultimate properties of the resulting polymers. As showed previously, the most important reactions in PUs preparation are those between isocyanate and the hydroxyl group (chain propagation reaction) and the reaction between isocyanate and water (foaming reaction). The functions of catalyst generally employed in urethane formation generally lie in:

- Speeding up reaction rates;
- Establishing a proper balance between the chain propagation reaction and the foaming reaction;
- Bringing about completation of the reactions, hence resulting in an adequate “cure” of the respective polymer.[51]

The most commonly used catalyst are tertiary amines, metal catalyst particularly tin catalysts and organic acids. Catalysts for the reaction between isocyanates and active hydrogens containing compounds (in practice alcohols, amines and water) fall into two general categories: amine and organotin compounds. The effectiveness of these two broad classes of catalyst can be seen in Table 1.[52]

**Table 1:** Relative reactivity of different catalyst classes [a]

| Catalyst | Relative reactivity |
|---|---|
| None | - |
| DABCO (0,1%) | 130 |
| DBTL (0,1%) | 210 |
| DABCO + DBTL (01 + 0,2%) | 1000 |

[a] DABCO: 1,4-diaza[2.2.2]bicyclooctane; BBTL: dibutyltindilaurate

The effectiveness of amine catalysts generally increases with increasing basicity; also steric hindrance of amino nitrogen plays a significant role. Generally the activity of amines increas with their basicity and with less steric hindrance of the nitrogen atom, for example the activity of 1,4-diaza[2.2.2]bicyclooctane (DABCO) is eight times higher comparated to triethylamine (Figure 15).

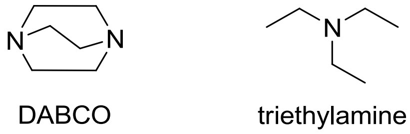
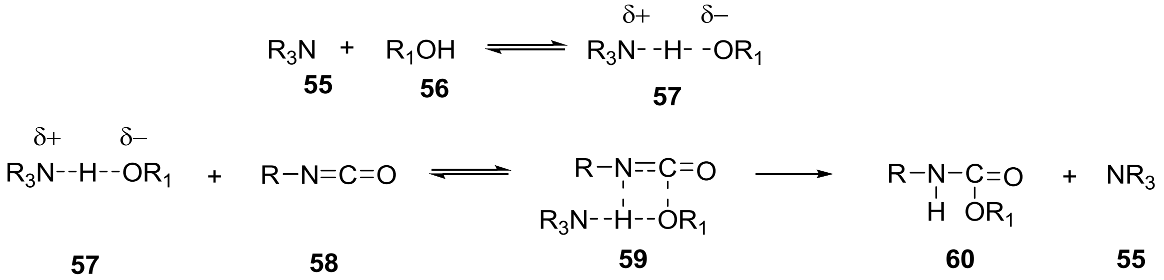


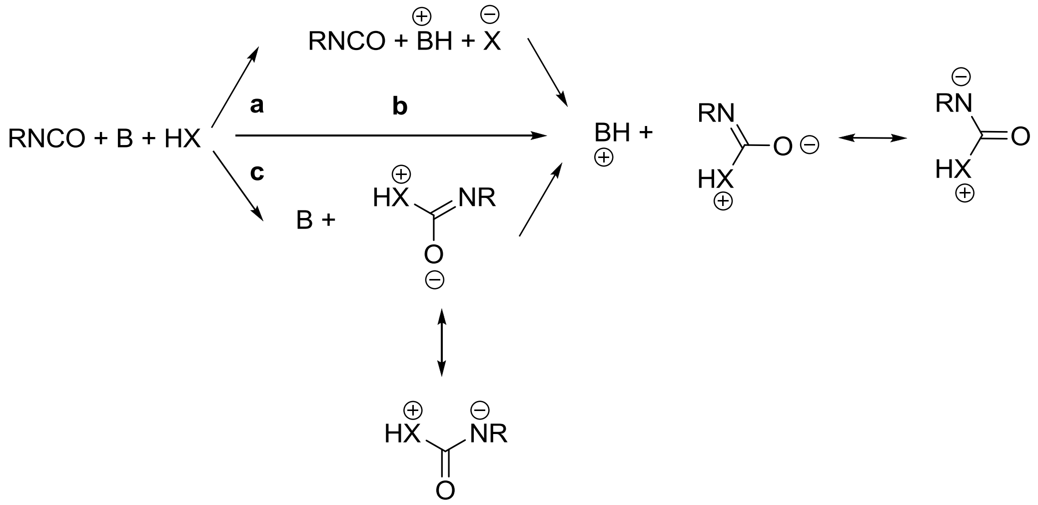
**Figure 15:** DABCO and triethylamine structures.

Moreover, the tertiary amines are able to lower the reaction enthalpy and to increase the reaction speed by opening a new pathway for hydrogen transport. One plausible mechanism has been proposed to describe the amine catalyzed urethane formation in the last five decades.[53] The complexation of the isocyanate **58** with the tertiary amine **55** is followed by the attack of the nucleophilic agent **57** and the formation of a hydrogen bonded complex **59** which attacks the isocyanate in the second step to give **60**, and releasing the amine **55** used as catalyst. (Scheme 16).



**Scheme 16:** Mechanism of the amine catalyzed urethane formation

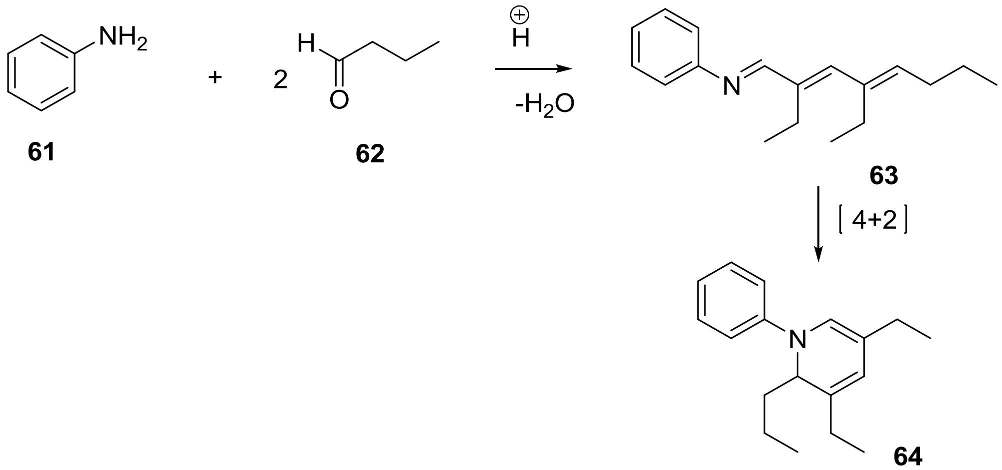
The exact mechanism depends on the electrophilicity of the isocyanate, the relative nucleophilicity of the polyol macro structure, and the basicity of the catalyst (Scheme 17).



**Scheme 17:** Different routes of the amine-catalyzed urethane formation.

Hydrogen containing compounds (HX) of high acidity and low nucleophilicity like phenol should lead to the protonation of the catalytic compound B followed by the nucleophilic addition of anionic species ($X^-$) to the isocyanate compound (Scheme 17, route a). HX compounds with low acidity and high nucleophilicity like aromatic amines directly added to the isocyanate lead to the formation of the new X-C bond (Scheme 17, route c). Proton transfer and X-C bond formation take place in a single step, if HX has moderate acidity and nucleophilicity (Scheme 17, route b).[54]

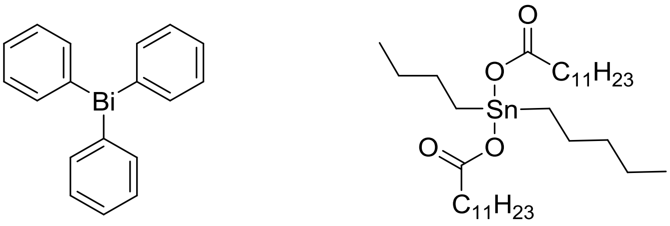
Among amine catalyst, DABCO has become a standard in polyurethane industry. Further, amine compounds have been preferentially tailored to catalyze the isocyanate/$H_2O$ reaction. This reaction has special significance in PU chemistry because generates $CO_2$ and this is a fundamental part of the “foam forming” step, in rigid PU and flexible foams. Catalysts that are particularly effective in promoting this reaction are referred to “blowing” catalysts. An interesting aminic catalyst was introduced in 1970s. This is an aldimine, coming from a condensation reaction between butyraldehyde **62** and aniline **61**. In particular, the catalytic effect (see Scheme 16) is due to the presence of one of the plenty condensation products , the 1,2-dihydropyridine **64** which act as a tertiary amine. This 1,2-dihydropiridine is a product of a [4+2] pericyclic reaction of the intermediate **63** (Scheme 18).



**Scheme 18:** Condensation of butyraldehyde and aniline.

Additionally to its catalytic effect, the aldimine crosslinks with isocyanates forming, at lower temperature, splittable bonds. This leads to products with very low solder times.[55]

Organometallic compounds, and especially organotin compounds, are generally more active than amines (see Table 1) and are particularly effective in catalyzing reactions between isocyanates and alcohols, but the use of organotin compounds present a huge problem in the PUs manufacturing. Infact their removal from PUs is often exceedingly difficult, resulting in deterious residual catalyst being left behind.[56] Several attempts have been made to replace tin with more environmentally benign organometallic catalysts, featuring bismuth, aluminium or zirconium.[57] Especially in the last year triphenyl bismuth (TPB), has found increasing use in the PUs preparation (Figure 16).

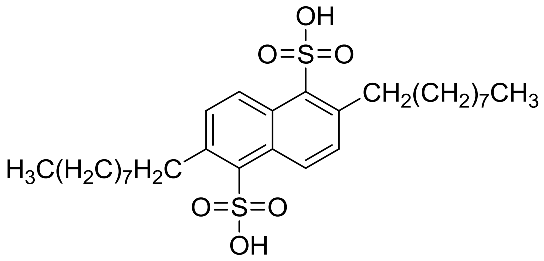


TPB DBTDL

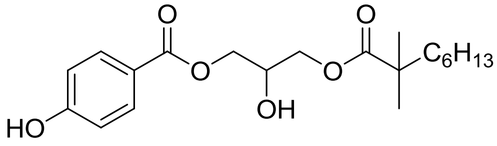
**Figure 16:** TPB and DBTDL structures.

It has experimentally been found that TPB was relatively low in catalytic activity, while DBTDL resulted in erratic cures, sometimes producing grains with tacky surfaces, and that both catalysts caused unacceptable gassing. A combination of TPB with dibutyltin dilaurate (DBTDL see Figure 15) is usually preferred instead of TPB alone. When the two catalysts are simultaneously used, DBTDL appeared to provide the major driving force for the curing reaction and activate the TPB for catalytic purpose, whereas TPB tends to moderate the reaction and produce consistent and complete curing process. The curing rates and pot life can be easily varied and controlled by adjusting the ratio and level of the two catalysts. It seems that the combination of these two catalysts strongly promoted the isocyanate-hydroxyl reaction.[58]

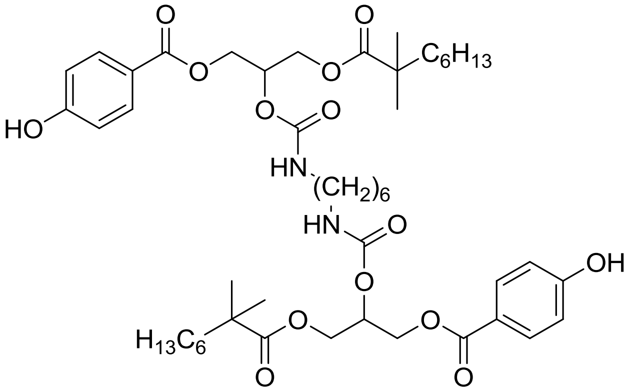
More recent studies, report the use of organic acid as catalyst in PU polymerization, but the obtained results have generally been inferior to those achieved by metallic catalysts. An interesting result was obtained by Yezrielev *et al.* who shows that 2,6-dinonylnaphthalene-1,5-disulfonic acid affectively catalyzes addition of phenolic ester alcohol (PHEA) with aliphatic isocyanate to form a aliphatic urethane (Figure 17).[59]



**2,6-dinonylnaphthalene-1,5-disulfonic acid**



**PHEA**



**aliphatic urethane**

**Figure 17:** Molecules used by Yezrielev *at al.*

# CHAPTER 4.
# IMINE SYNTHESIS

Imines or “Schiff bases” represent one of the most important organic compound family used as synthetic starting materials, coordination compounds and it is fundamental constituents in biological and polymeric compounds. From a structural point of view they are the nitrogen derivatives of aldehydes or ketones. In fact, the carbonylic group C=O is substituted by a C=N system type. Moreover, iminic functionalities show very large potentialities which are exploited in a huge number of synthetic processes. The first example of imines preparation was reported in 1864 by Hugo Schiff, organic chemistry professor at University of Pisa and after at University of Florence. During him studies, Schiff notices that mixing, in the same reaction system, aniline and an aldehyde the result was a new class of organic compounds called “bases”. Actually, after base definition by Lewis, this definition could be perfectly associated to iminic functionalities.[60]

Imines present a carbon-heteroatom double bond and a trigonal planar structure, where both atoms involved in the multiple bond are hybridized $sp^2$. Either carbon and nitrogen atom combine a $sp^2$ orbital and an atomic orbital p to form respectively a $\sigma$ and a $\pi$ bonds.[61] The carbon atom use both remaining $sp^2$ orbital to form a new bond with own substituents. On the contrary the nitrogen uses only one $sp^2$ orbital to form a C-N bond, but there is a remaining pair of electrons, lone pair, free in the double bond plan (Figure 18).

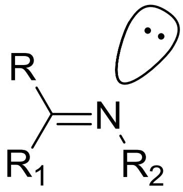


**Figure 18:** Schiff base general structure.

To better understand this functional reactivity, a good method is the explanation of involving molecular orbitals, in particular the localization of boundary molecular orbitals (HOMO and LUMO) which define the principal electronic properties of the imine system. In the Schiff base, the highest occupied molecular orbital (HOMO) can be identified as non-bonding molecular orbital *n*, and this correspond to the $sp^2$ orbital in which there is the Lone Pair. On the contrary, the lowest unoccupied molecular orbital (LUMO) it is represent by antibonding OM $\pi^*$. This kind of orbital has a very high energy (Figure 19).

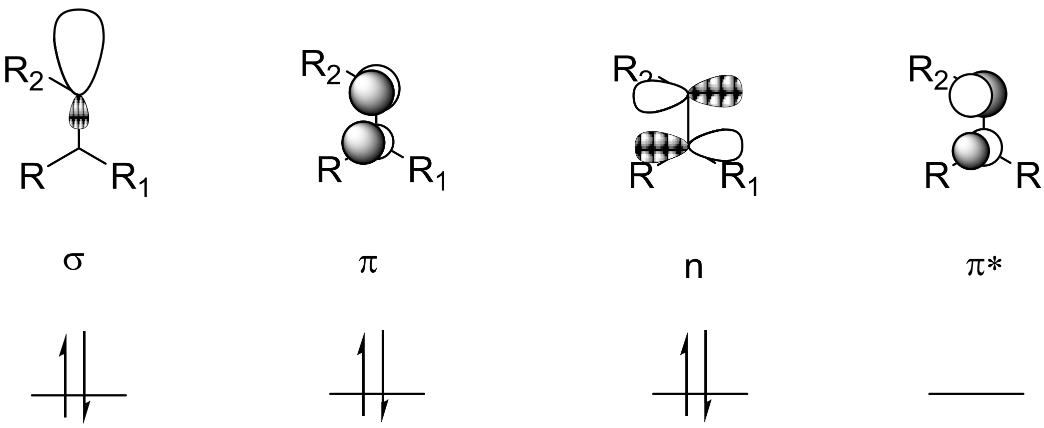
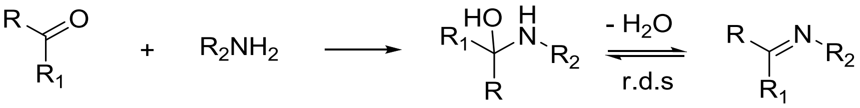


**Figure 19:** MO schematic representation of Schiff base.

Imines can act as Lewis base, if they react with a chemical specie which has a low energy LUMO, or as electrophilic system, if they react with a nucleophilic system. The Lewis base behaviour is showed in the reaction with metallic cation. In literature, there are a lot of examples of complex generated, starting from iminic functionalities.[62] When the imine is in the presence of a specie with low energy HOMO it can undergo to a nucleophilic addition process. The iminic functionalities can undergo to different types of nucleophilic additions, but their reactivity is more limited than carbonilic compounds. This is due to the less double bond C=N polarizability than C=O ($\chi_N < \chi_O$). Another very important aspect, related to imines chemical properties is their changing on stability when substituent groups on carbon and nitrogen atoms are modified.[63] Usually a primary imine (see Figure 18 $R_2$ = H) is extremely instable. In fact in solution an equilibrium takes place with starting materials and in this way its isolation is a pretty difficult task. When $R_2$, on the contrary, is an alkylic or arylic group, the system results more stabilize and the imine can be easily isolate and purified. In particular, the stability increases when $R_2$ is an aromatic group, because the imine is stabilize by the delocalization of π electrons.

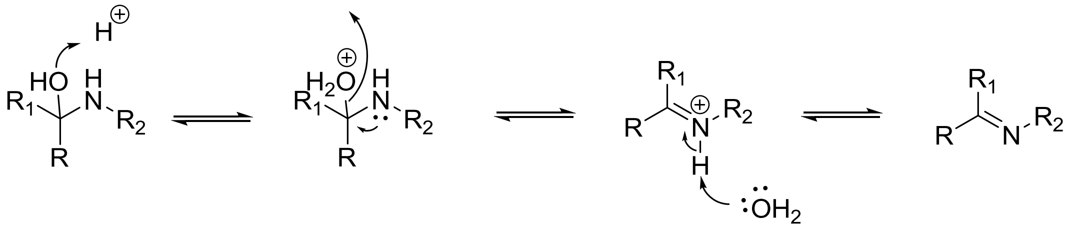
## 4.1 SYNTHETIC METHODOLOGIES

The classical synthesis reported by Schiff is a condensation between a carbonilic compound with a primary amine, using an azeotropic distillation.[64] The simple mechanism of this reaction is based on the nucleophilic attack of the amine to the carbonilic compound with the formation of a carbinolamine. This reactive intermediate undergoes to a dehydration (rate determining step). The azeotropic distillation it is used to remove the water and so shift the equilibrium towards the imine formation (Scheme 19)



**Scheme 19:** General reaction mechanism between carbonilic compound and amine.

In the last year, research was focused in the improvements of this condensation, using more and more efficient methods with a minimal environmental impact. To remove the water from the reactive system were used different strategies such as the use of molecular sieves or dehydrating solvents such as tetramethylorthosilicate or trimethylorthoformiate.[65] Moreover, water elimination from carbinolamine can be favoured by an acidic catalysis which permits the alcohol protonation and the subsequent dehydratation (Scheme 20).

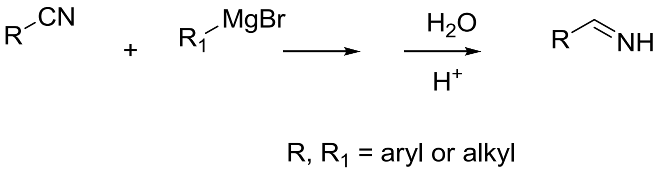


**Scheme 20:** Acidic catalysis in imine formation.

The presence of acid favour the dehydratation process but it can also inhibit the first step of condensation between ammine and carbonilic compound. If pH is very low the amine will be protonated and the reaction rate considerably decreases.[61] For this reason the acidic catalysis requires a careful pH control. It has experimentally been seen that the imine formation is faster in the pH range 4-6, on the contrary above this range the dehydratation occurs and beneath this range the nucleophilic addition occurs. The efficiency of these synthetic methodologies strongly depends to the type of substituents present on the starting materials and good yields can be obtained using very electrophilic carbonilic compounds and very nucleophilic amines. In the last years, in order to improve the efficiency of the synthetic methodologies and yields of reactions, Lewis acid have been employed as reaction promoters to activate the carbonilic compound. Moreover, they can act also as dehydrating agents ( e.g, $ZnCl_2$, $TiCl_4$, $Er(OTf)_3$ or $Mg(ClO_4)_2$.[66] Among all innovative techniques, microwaves irradiation presents several advantages thanks to its simply use, its good yields and its reaction rate. This technique was introduced by Rousell and Majetich research groups work. Microwave irradiation is less problematic and more efficient than other methods because the reaction are performed in very short time and with high yields, so the costs are considerably decreased. It presents advantages from an environmental point of view because there are no solvent or reactive excesses. A very high number of imine synthetic methodologies was studied by from the discovery of Schiff bases to nowadays. In this chapter will be mentioned the most used methodologies.[67]

- *Reaction of nitriles with organometallic compounds*

Moureau and Mignonac were the first who added an aryl or alkyl Grignard to an aryl cyanide to obtain, after careful hydrolysis at -15°C, treatment with hydrogen chloride, and finally with ammonia, the ketamine in 70% yield (Scheme 21).[68]

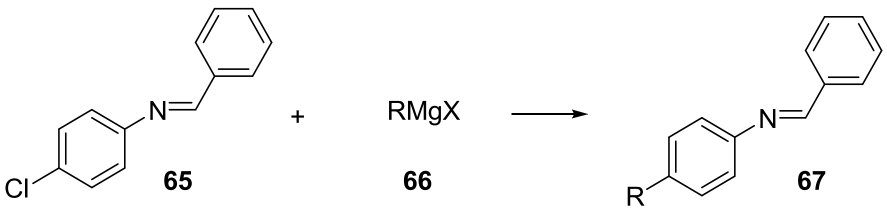


**Scheme 21:** Reaction between a Grignard and a aryl cyanide.

For example 2,2,6-trimethylcyclohexyl cyanide and phenylmagnesium bromide give a ketimine which is rather stable toward hydrolysis. These demonstrate the steric stabilization of certain imines to hydrolysis.[69]

- *Reaction of carbon-nitrogen double bond compounds with organometallics*

Busch found that the chlorine atom in C-chloro-N-benzylideneanilines **65** could be replaced by the alkyl or aryl groups of a Grignard reagent **66** in very good yields to give the corresponding imines **67** (Scheme 22).[70]

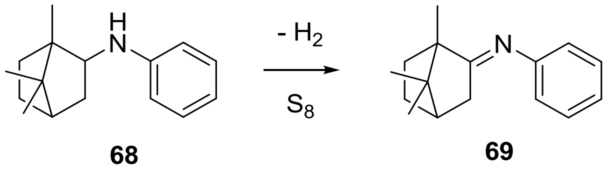


**Scheme 22:** Imines formation from carbon-nitrogen double bond compound and a Grignard.

Montagne later found that found that anilides, which may be regarded as C-hydroxyimines, react with alkyl or aryl Grignards to give the corresponding imine in about 40% yield.[71] Grammatickis, has also found that oximes of aromatic aldehydes react with Grignards to give as predominant product the benzylamine of the Grignard with the ketimine as secondary product.[72]

- *Dehydrogenation of amines*

Ritter was the first who carried out the dehydrogenation reaction of amines to achieve imines. He found that isobornylaniline **68** is readily dehydrogenated to the corresponding imine **69,** with sulphur at 220° to give an 89% of yield (Scheme 23).

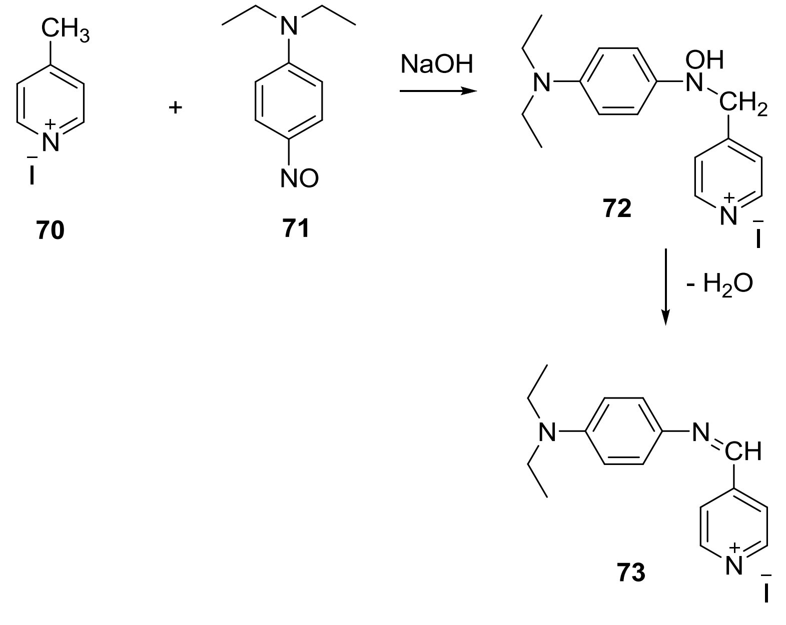


**Scheme 23:** Deidrogenation reaction.

Later it was found that this method is also effective for dehydrogenating benzhydrylamine, *N,N'*-diiospropylaniline, and *N-N'*-phenylpropylaniline. Isobornylaniline is also dehydrogenated with amyl disulphide. Numerous side reactions, such as addition of hydrogen sulphide to imine, reduction of the imin and others occur under these reaction conditions. Selenium methodologies are also reported for the dehydrogenation of amines to imines. Catalytic dehydrogenation of secondary amines over nickel, platinum or chromium catalyst at 180°C gives the imines, but more work in this area would be useful. Secondary amines, are readily dehydrogenated to imine by heating to reflux with acetic acid.[73]

- *Reaction of nitroso compound with active hydrogen compounds*

Early workers reported the reaction of active hydrogen compounds with nitroso compounds formed imines. After few years, some other researchers showed that nitrones were the reaction products rather than the expected imines. More recently it has been found that certain active hydrogen compounds give imines rather than nitrones so that both materials are formed.[74] Azzam in the reaction of benzyl cyanide and *p*-nitroso-*N,N*-dimethylaniline, has found that imine formation is favoured when a strongly basic catalyst, such as sodium hydroxide, and high reaction temperatures are used. The nitrone is favoured when a weak base, as piperidine, is used as the catalyst.[75] Kronke has more recently studied the reaction of 2- and 4-picoline ammonium salt **70** and *p*-nitroso-*N,N*-diethylaniline **71**. He has found that a ratio of two moles of nitroso compound to one mole of picoline ammonium salt gives the highest yield of crude product when catalyzed with 2N sodium hydroxide(Scheme 24). However, the imine to nitronate ratio is higher when the reactant ratio is one to one.[76]



**Scheme 24:** Imine from ammonium salt and nitroso compound.

## 4.2 IMPORTANCE OF IMINES IN POLYMER FIELD

The biological importance of Schiff bases as key intermediate in several enzymatic transformations is well know. In recent years, the imines were used as building block in the formation of different polymers that find applications in different fields. An important class of polymer is represented by poly(azomethine)s, known as polyamines or Schiff base polymers. This polymer class were first reported by Adams *et al.* in 1923.[77] The interesting for this class of polymers renewed in the last years because aromatic poly(azomethine)s are isoelectronic with poly(*p*-phenylene vinylene)s which are most known electroluminescent polymers, while polyazines are nitrogen containing analogues of polyacetylene, the most conducting polymer. Poly(azomethine)s exhibit interesting properties which are associated mainly with their conjugated back-bone and the presence of imine sites. Thus, they present good thermal stability, mechanical strength, non-linear optical properties, ability to form metal chelates, semiconducting properties, environmental stability and fiber-forming properties. Many of these polymers form mesophases on heating, but their high melting points and low solubilities make both their characterization and processing difficult. Their technical applications are strongly limited by their sensitivity to acidic hydrolysis and thermal exchange reactions between different azomethine groups. Therefore, many research efforts have been made to improve these characteristics by changing the nature of diamine or dialdehyde components or introduction into the main chain of bent, crankshaft-shaped, or laterally substituted and flexible substituents.[78]

The use of imine spacers is the base of conjugated oligomers. They are an important class of electro- and photoactive materials, investigated both in academic and industrial applicabilities. The great interest for conjugated oligomers emerges from their applications such as active components in organic electronic or electrochemical devices. The advantage of using small conjugated compounds is based on the possibility of tuning their photophysical properties by changing the chemical structure, e.g. by introduction of side substituents, end-capping groups, insertion of certain specific functional groups and by changing the oligomer length. Thus, conjugated oligomers are used as model compounds for conducting polymers since their monodisperse, defectless structure and better supramolecular organization in the solid state facilitate their experimental and theoretical investigations. An example of these conjugated olygomers is reported by Grigoras *et al.*, in particular conjugated arylamine oligomers containing two triphenylamine (TPA) or carbazole groups separated by imines which act as π-spacers.[79]

## 4.3 IMINES IN OUR WORK

In my thesis work we exploited the condensation between aniline and butyraldehyde, in order to optimize this synthetic methodologies. This interest is due to the industrial relevance of this reaction and especially the industrial use of this reactions products, because it was used as additive in the formulation of PU coatings which improves thermal properties and reduces the solder time. From a reactive point of view we observe that the condensation reaction brings to the formation not only of imine but also to secondary products which result very significant to describe the properties improvement in the final product.

# CHAPTER 5.

## EXPERIMENTAL SECTION

My thesis work was focused on the synthesis of an aldimine which acts as additive in PU formulations commercially used as copper wire coating. This additive is one of the products deriving from the condensation reaction between aniline and butyraldehyde. The condensation is an equilibrium reaction and the water released shift the equilibrium from the reagents to the products. Based on this fact, all the synthetic methodologies developed are based on the use of:

1. Formation of two immiscible phases (organic–water);
2. Dehydrating agents ($MgSO_4$ and molecular sivies 4Å);
3. Azeotropic distillation based on the Dean-Stark apparatus and acidic catalysis based on the use of weak acid (e.g, acetic acid) (Figure 20)

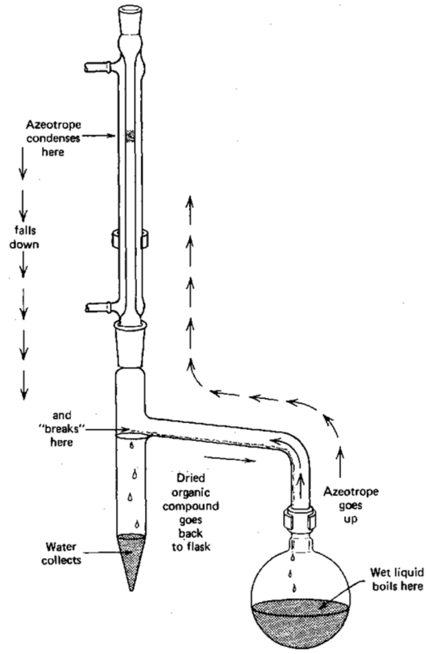
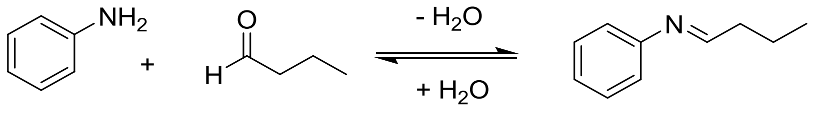


**Figure 20:** Dean-Stark apparatus.

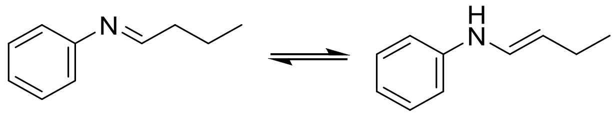
Moreover, in all the synthetic processes we used an excess of butyraldehyde with respect to the aniline (ratio 5:1 or 10:1), as reported in literature, and different types of weak organic acids, supported acid and Lewis acids. The general reaction between butanal and aniline is shown in the Scheme 25



**61** **62** **74**

**Scheme 25:** General mechanism of imine formation.

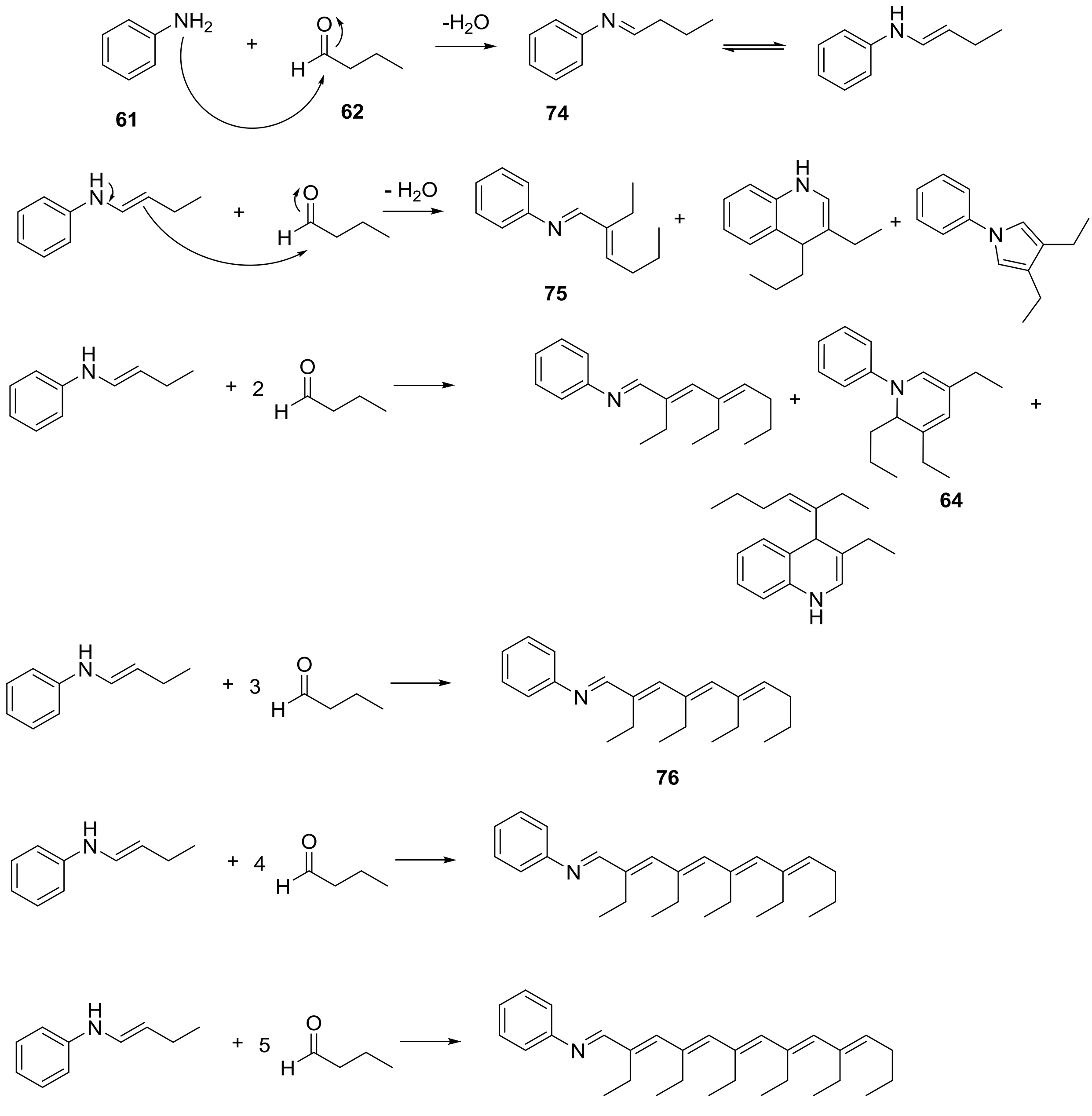
The produced imine presents an imine-enamine tautomerism. In this tautomerism a hydrogen atom switches its location between the heteroatom and the second carbon atom (Scheme 26).



**74**

**Scheme 26:** Tautomeric equilibrium imine-enamine.

This enamine is a good nucleophile agent, the reactivity of this enamine has to be taken into account due to the fact that an excess of butanal has been used, so side products are produced. The butanal in excess, in fact, reacts with the enamine thanks to a nucleophilic addition (Scheme 27), creating a series of polycondensation products (Figure 21).



**Scheme 27:** polycondesantion mechanism and resulting products.

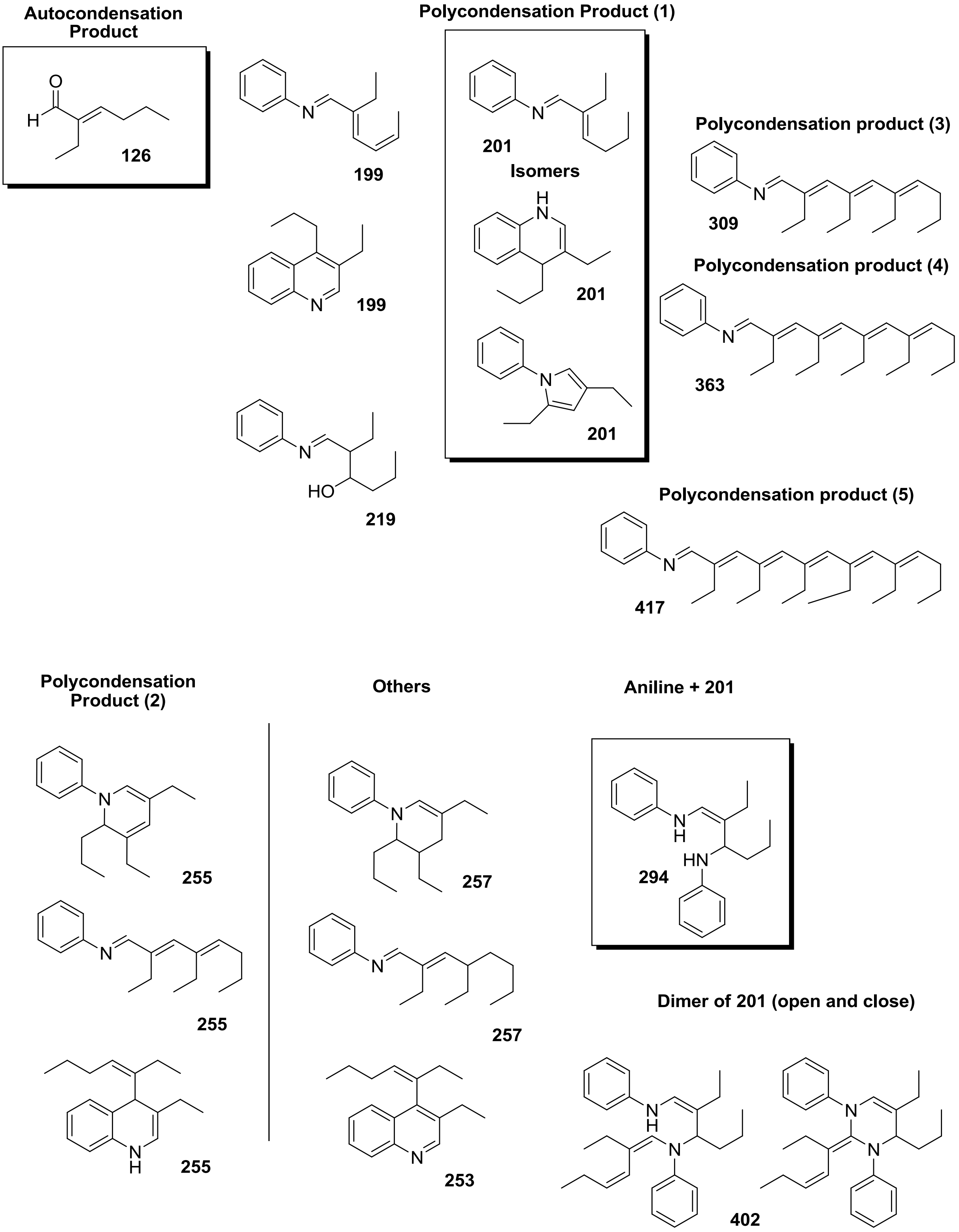
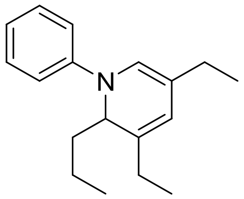


**Figure 21:** Condensation secondary products. All values reported represent m/z ratios

The study was focused on 6 different samples supplied by an Industry of polymer in Ascoli Piceno. The 6 samples sent by this company, came from different lots and the composition of them was performed using two different techniques. GC-MS and HPCL-MS instruments. From all these analysis it was found as major product a dihydropyridine of m/z = 255. At first, three possible structures were hypotisized of m/z = 255, then $^1$H-NMR, $^{13}$C-NMR, DEPT analysis were exploited to confirm the exact structure. The 3,5-diethyl-1-phenil-2-propyl-1,2 dihydropyridine was discovered as the exact structure of the major product defined in all samples we had it is the right structure (Figure 22).



**m/z = 255**

3,5-diethyl-1-phenyl-2-propyl-
1,2-dihydropyridine

**Figure 22:** Dihydropyridinic structure confermed by NMR-analysis.

The production of this dihydropyridine was studied and the optimization of the synthesis of this additive was carried out maintaining as much as possible the producing industrial conditions. With this purpose all chromatographic purifications or aqueous work up were avoided. The main scope was the development or the improvement of existing synthetic methodologies in order to obtain this 1,2-dihydropyridine (Figure 22) which is used to improve solder time and thermal resistance, fundamental characteristics of the final product (see Chapter 4.3). Moreover, it was tried to use different starting material (different amines) to generalize the reaction mechanism.

## 5.1 EXPERIMENTAL DATA

### 5.1.1 Strumentation

Nuclear magnetic resonance spectra were obtained using a Bruker AMX 400 MHz and DPX 250 MHz spectrometers.

Mass spectra were obtained using a coupling between gascromatograph and mass spectrophotometer Hewlett-Packard GC/MS 5970 with HP (30 x 0.25 mm) capillary column and working with electronic ionization method (70 eV). Gascromatograph Carlo Erba Fractovap 4160 with capillary column (0.32 x 25 mm) with stazionary phase OVI 0.4-0.45 μm to monitor the reaction trend.

### 5.1.2 Industrial Sample

Below, there are reported the GC spectrum of the industrial sample analyzed by Marcantoni's research group. Moreover, there are reported the MS spectra of the main products find in this sample. The same products was found also in our test reaction with the fragmentation pattern.

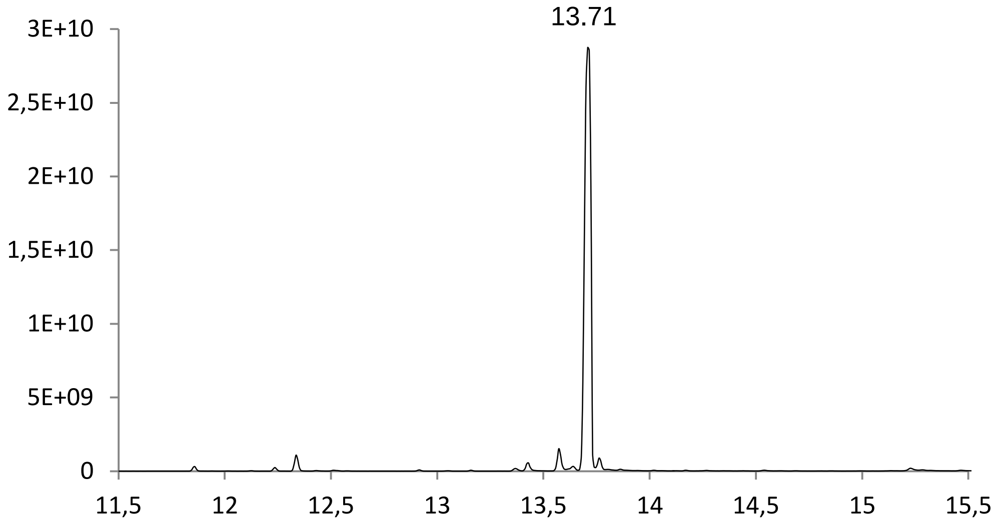


**Figure 23:** GC spectrum industrial sample.

The 3,5-diethyl-1-phenil-2-propyl-1,2 dihydropyridine has a retention time of 13.71 min. The other peaks are due to the presence of secondary products.

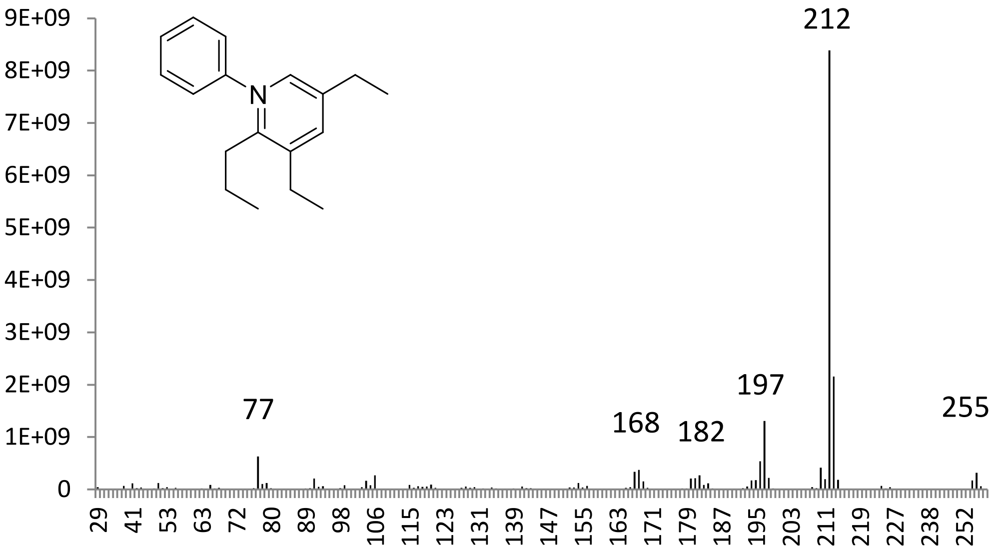


**Figure 24:** MS spectrum of the product with m/z = 255.

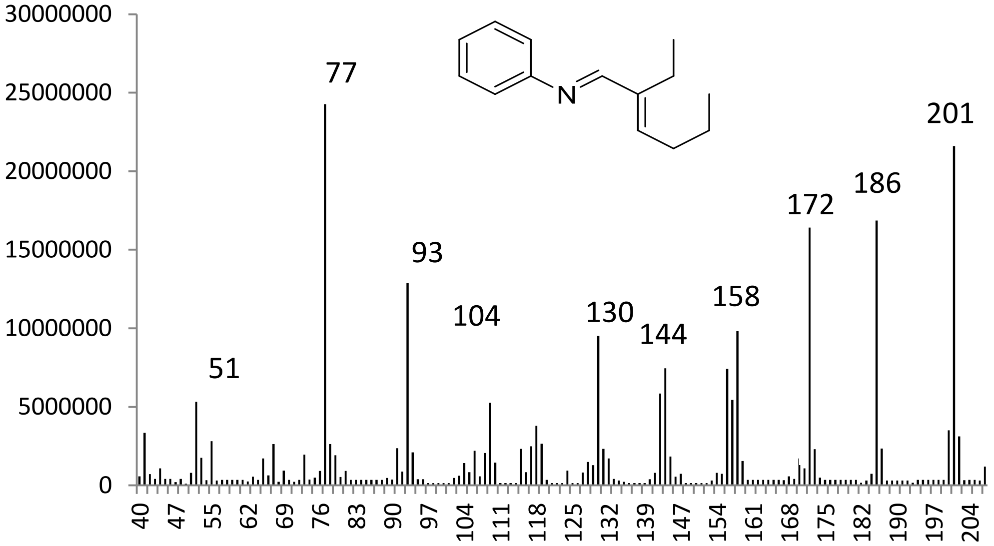


**Figure 25:** MS spectrum of the product with m/z = 201.

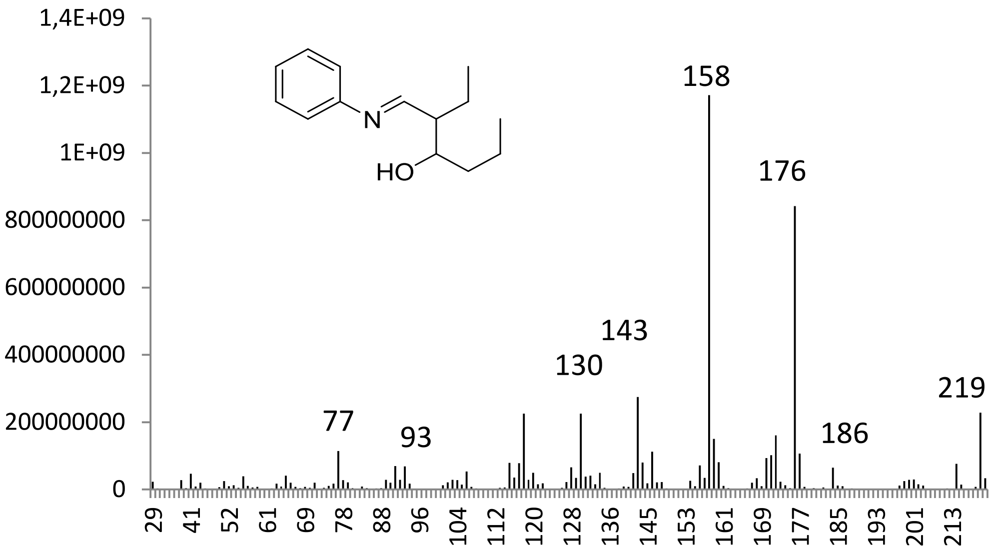


**Figure 26:** MS spectrum of the product with m/z = 219.

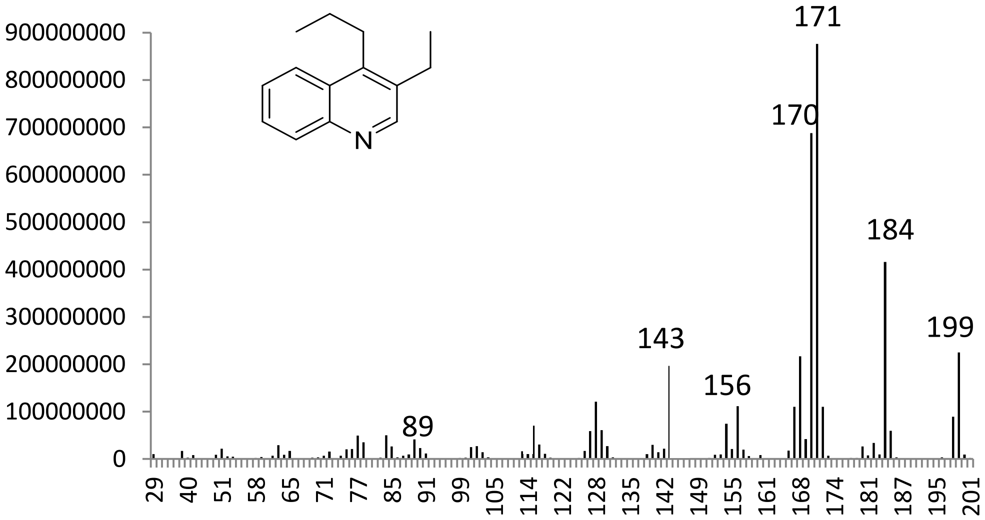


**Figure 27:** MS spectrum of the product with m/z = 199.

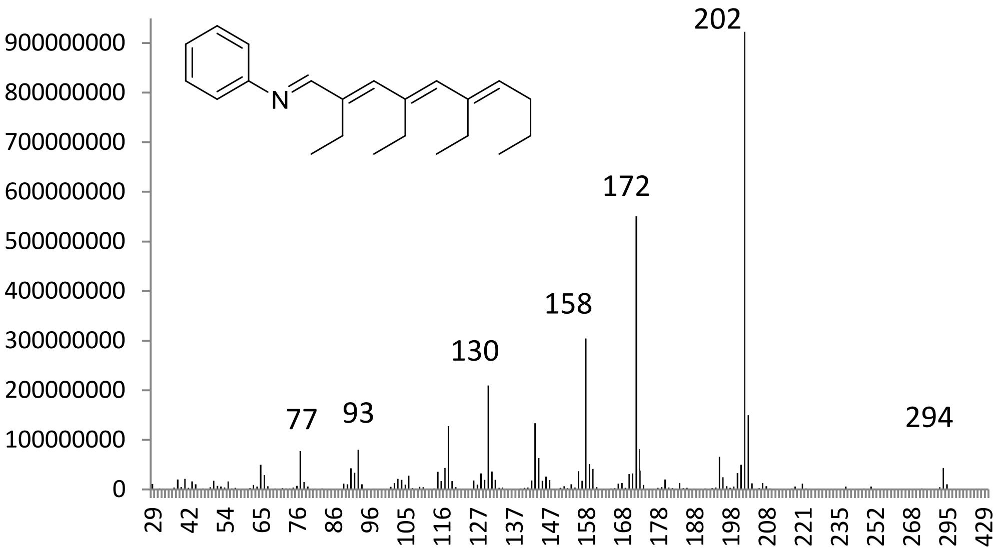


**Figure 28:** MS spectrum of the product with m/z = 294.

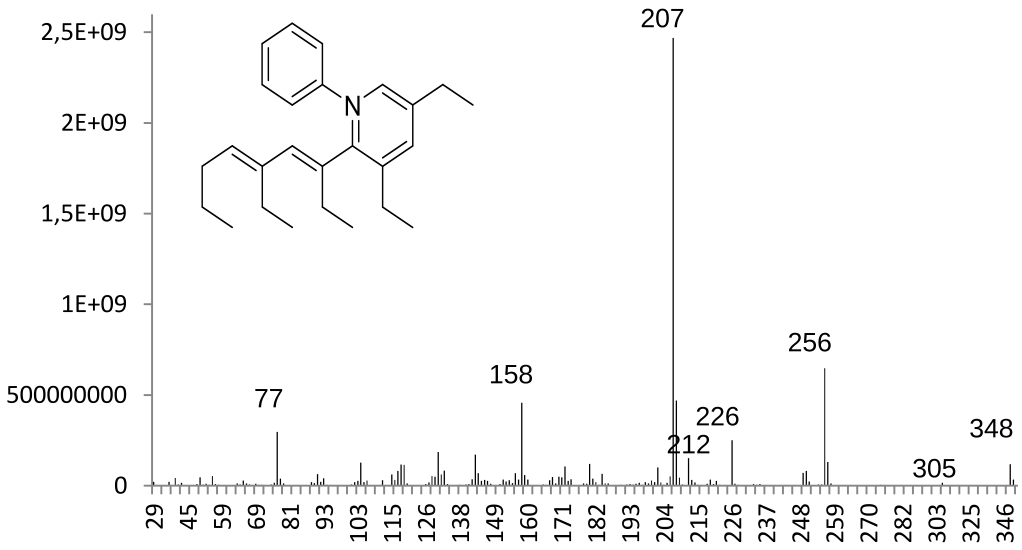


**Figure 29:** MS spectrum of the product with m/z = 348.

**Table 2:** Relative abundance of the products in the industrial sample.

| m/z | % |
|---|---|
| 199 | 5.6 |
| 219 | 8.3 |
| 255 | 86.1 |

The products with m/z = 201, 294, 348 are present in traces. This industrial sample is very pure and the 3,5-Diethyl-1-Phenil-2-Propyl-1,2 Dihydropyridine (m/z = 255) is present in 95.1%.

### 5.1.3 AD Samples Spectroscopic Data

The structure determination of our target molecule was possible thanks to GC-MS and NMR analysis. Especially, with GC-MS analysis, we were able to determine the composition of our additive and in this way, we discovered that the product with m/z= 255, was the majority product present in the industrial sample analyzed. The product with m/z= 255 presents three isomers, reported in Figure 30, so our aim was to determine the absolute structure of the product.

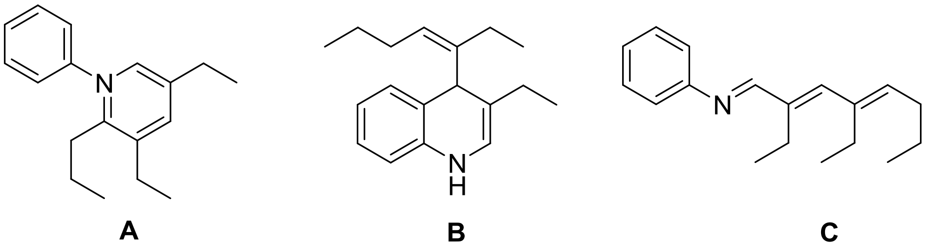


**Figure 30:** Structures with m/z= 255.

A first GC-MS analysis was performed in order to do a qualitative structural analysis. In fact, we saw that the base peak in the mass spectra had an m/z ratio equal to 212 (see Mass Spectra). In this way, we refused the structure **C**, is characterized by a base peak with m/z= 77 (due to $C_6H_5^+$) and this results as a diagnostic peak for this kind of molecules. Unfortunately mass spectrometry results ineffective to distinguish between **A** and **B**. Trying to solve this problem, we used a nuclear magnetic resonance analysis with the aim to define the structure of our target molecule. We did a $^1$H-NMR, $^{13}$C-NMR and DEPT. The results obtained with $^1$H-NMR and $^{13}$C-NMR didn't give us a clear difference between the isoquinolinic structure **B** and the dihydropidinic one **A**, but the presence of a triplet at 4.32 ppm in $^1$H-NMR and a signal at 60 ppm in $^{13}$C-NMR resulted very difficult to explain in the case of an isoquinolinic structure, so a dihydropiridinic structure was suspected. Below are reported the spectroscopic data (GC, $^1$H-NMR and $^{13}$C-NMR spectra reported in Figure 32-33).

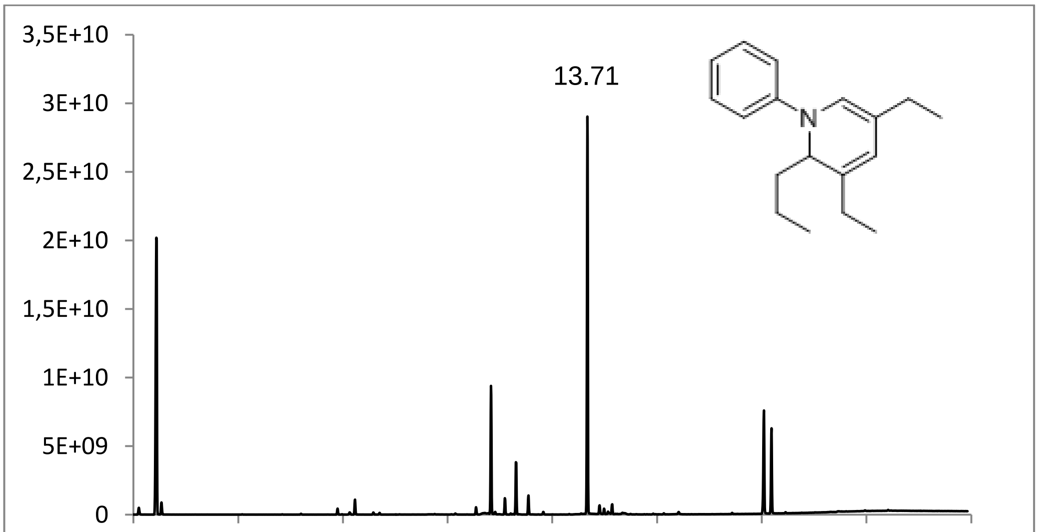


**Figure 31:** GC *3,5-diethyl-1-phenil-2-propyl-1,2 dihydropyridine* **64**.

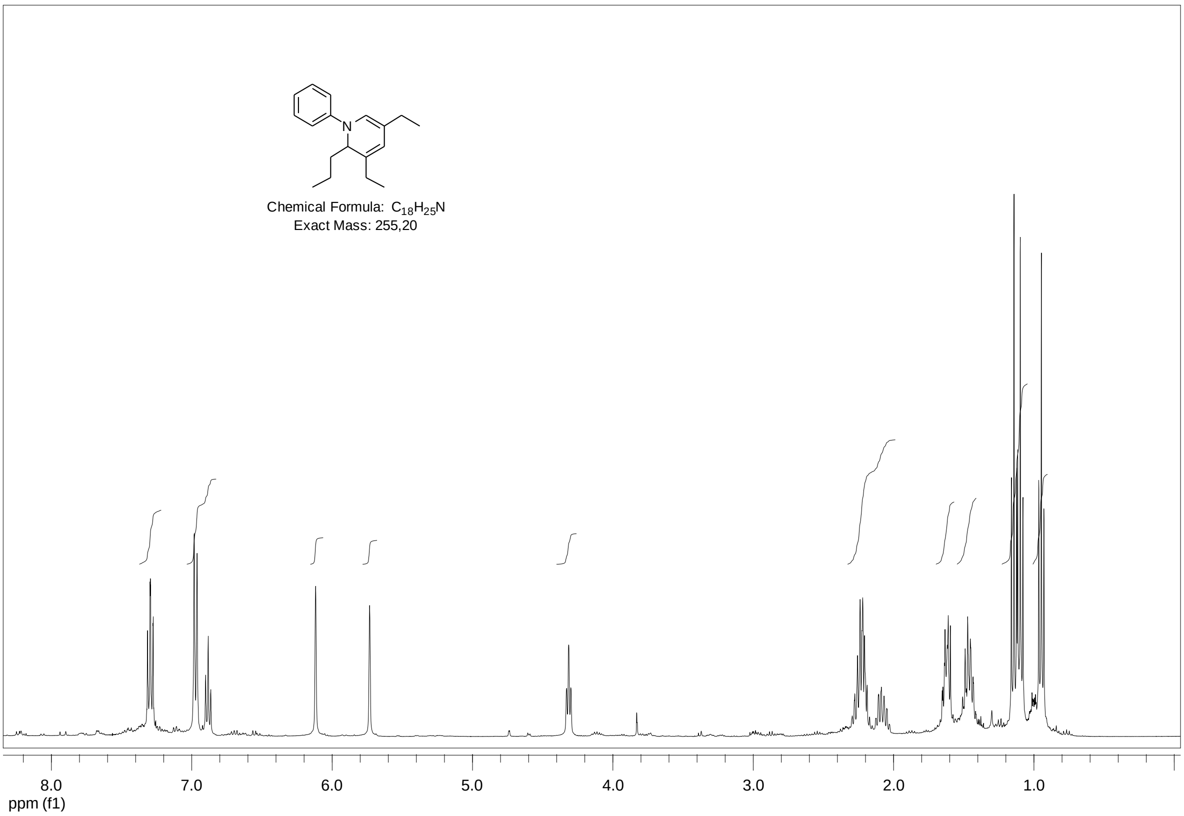


**Figure 32:** $^1$H-NMR 3*,5-diethyl-1-phenil-2-propyl-1,2 dihydropyridine* **64**

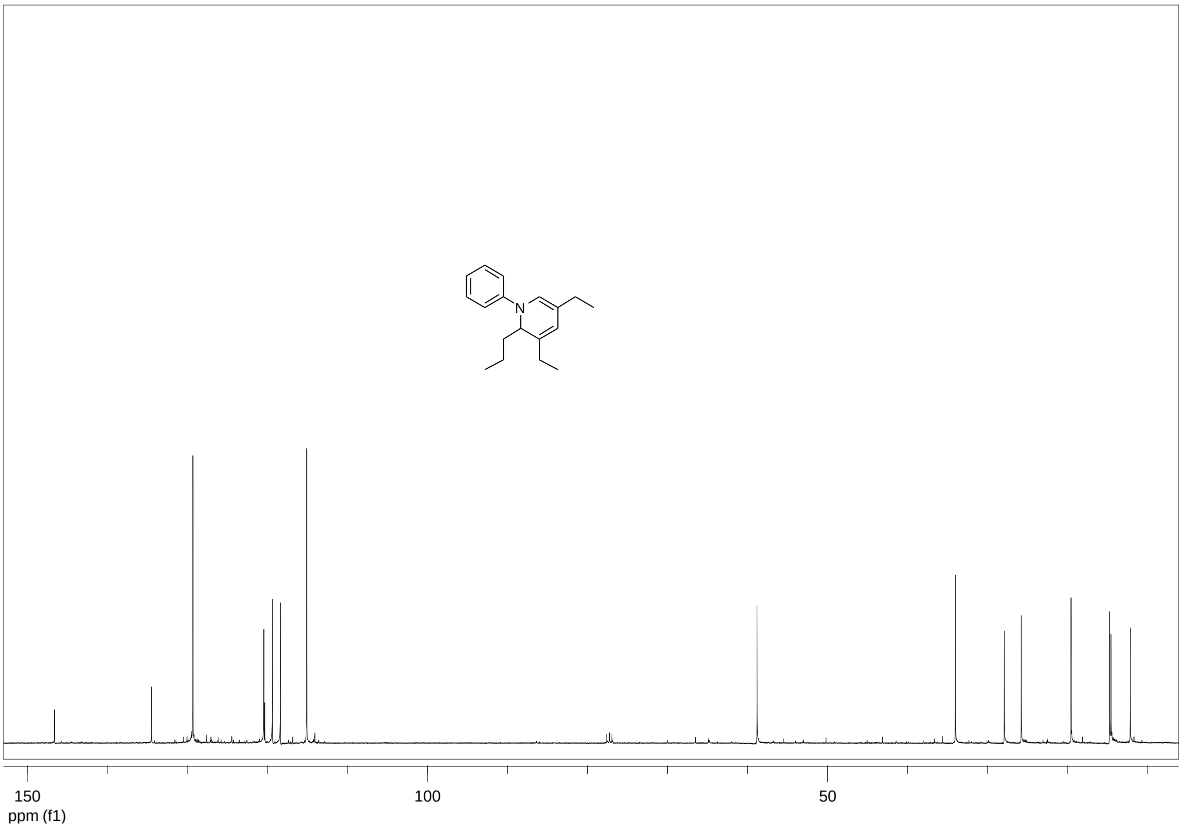
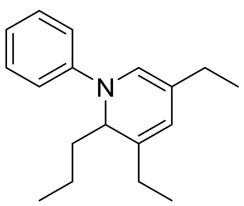


**Figure 33:** $^{13}$C-NMR *3,5-diethyl-1-phenil-2-propyl-1,2 dihydropyridine* **64** .



*3,5-diethyl-1-phenil-2-propyl-1,2 dihydropyridine* **64** Yellow oil. $^1$H-NMR ($CDCl_3$, 400 MHz) □: 0.95 (t, 3H, *J* = 7.3 Hz), 1.10 (t, 3H, *J* = 7.3 Hz), 1.15 (t, 3H, *J* = 7.3 Hz), 1.41-1.52 (m, 2H), 1.58-1.67 (m, 2H), 2.00-2.14 (m, 1H), 2.16-2.31 (m, 3H), 4.32 (t, 1H, *J* = 6.0 Hz), 5.73 (s, 1H), 6.73 (s, 1H), 6.85 (t, 1H, *J* = 7.7 Hz), 6.97 (d, 2H, *J* = 8.1 Hz), 7.27-7.32 (m, 2H). $^{13}$C-NMR ($CDCl_3$, 100 MHz) □: 12.3, 14.7, 14.9, 19.7, 25.9, 28.0, 34.1, 58.9, 115.1, 118.4, 119.4, 120.4, 120.5, 129.3, 134.5, 146.6. GC-MS (EI, 70eV): m/z: 255[M+], 212, 197, 182, 168, 77. Anal. Calcd. for $C_{13}H_{25}N$ (255.20): C, 84.65; H, 9.87; N, 5.48. Found: C, 84.53; H, 9.92; N, 5.30.

Finally, we made a DEPT analysis to confirm our hypothesis. Distortionless enhancement by polarization transfer analysis (DEPT) is based on a broadband proton decoupling which removes multiplicity in carbon resonances, allowing to establish the nature of the carbon atoms present in the molecule. This differentiation in the carbon atoms is possible making use of changes in signal intensities under differing experimental conditions.

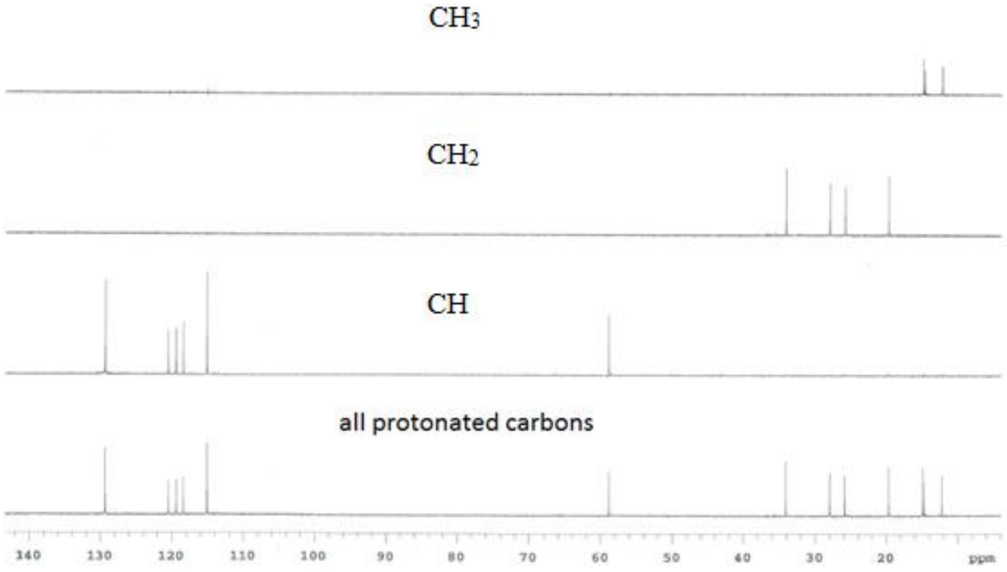


**Figure 34:** DEPT spectra.

In Figure 34, it can be seen that the analyzed compound are characterized by three different $CH_3$ groups, four $CH_2$ and six CH groups. Looking carefully at the structure of **A** and **B** in Figure 30, the only difference is the number of primary carbons: the isoquinolinic structure is characterized by a disubstituted aromatic ring and there is a total of seven different kinds of CH, whereas in the dihydropiridinic structure there is a monosubstituted aromatic ring and so there are eight CH signals. The difference is just in the signal related to the aromatic ring, but it is enough to say without doubts that the real structure of the main component of the industrial sample analyzed, with molar mass 255, is the 3,5-diethyl-1,2-dihydro-1-phenyl-2-propylpyridine **64,** as suspected from mass spectrum considerations.

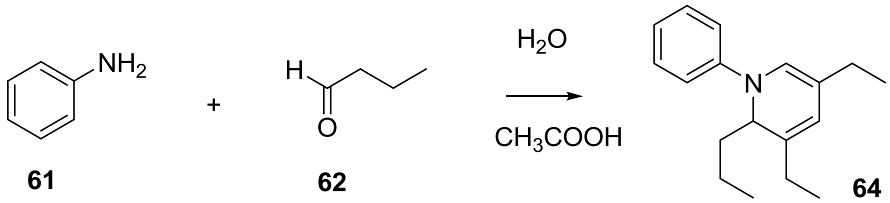
## 5.2 Results and discussions: the synthesis of 3,5-diethyl-1-phenil-2-propyl-1,2 dihydropyridine

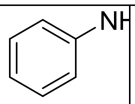
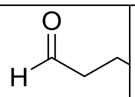
During the optimization of the reaction a starting point was related to the literature, about the 3,5-diethyl-1-phenil-2-propyl-1,2 dihydropyridine synthesis. At first the reaction was carried out dissolving aniline in the solvent, at room temperature, and then adding the butyraldehyde dropwise.

### 1. *Formation of two immiscible phases*

The first attempt of carrying out this condensation reaction was based on a synthetic procedure reported by Martin *et al* (Table 3)[80]

**Table 3:** Reaction conditions.



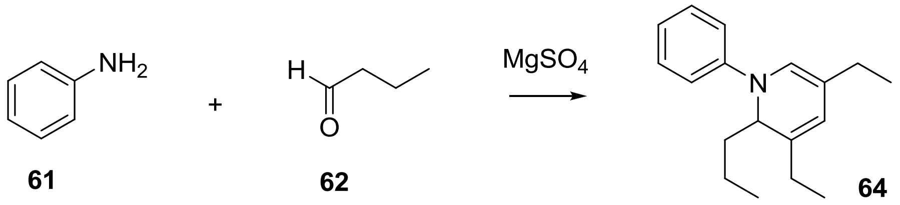
|  |  | **$H_2O$ (mL)** | **Time (t)** | **$CH_3COOH$ 37% (mL)** | **Reaction Name** |
|---|---|---|---|---|---|
| 10 mmol | 50 mmol | 1,08 | 24h | 0,087 | **AD 1** |

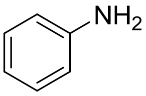
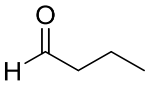
*General procedure*→ 50 mmol of butyraldehyde and 1,08 mL of water was added into a round bottom flask at 0 °C. Then 10 mmol of aniline was dropped inside the flask maintaining the temperature in a range of 0-10°C. After one hour the reaction mixture temperature was increased at 110°C (reflux temperature) and left for 5 hours. Finally, the reaction was allowed to reach room temperature was and stirred overnight. In this case the percentage of the 1,2 dihydropiridine **64** in the mixture was 56.9%. In order to obtain an higher percentage of the dihydropyridinic system we distilled the crude. Before the distillation the water and the acid traces were removed with a solvent extraction, using 15 mL of a saturated solution of sodium carbonate ($Na_2CO_3$) and dichloromethane (3 x 15 mL). The organic layer was collected and treated with anhydrous sodium sulphate ($Na_2SO_4$). The solvent was removed at reduced pressure, in order to get the crude of the reaction. Finally, the crude was purified through distillation as reported in literature at 1-3 mm Hg at 80°C to remove the 2-ethyll-hexenal (see Figure 21, m/z= 126) and then the pressure was decrease at 0,5-1 mm Hg at 145°C.

### 2. *Condensation reaction with the use of dehydrating agent*

In order to exploit different methodologies to remove water from the reaction mixture, avoiding aqueous works up, we used a dehydrating agent, in particular we use $MgSO_4$ trying different quantities of this one and reaction times. Moreover, in these synthetic procedure we avoided the use of acetic acid because, the butyraldehyde contains a certain unknown percentage of butyric acid, which is a butanal oxidation product. In this way the reproducibility fails (Table 4).

**Table 4:** Reaction conditions.



|  |  | **$MgSO_4$ (g)** | **Time (t)** | **Reaction Name** |
|---|---|---|---|---|
| 10 mmol | 100 mmol | 1 | 72h | **AD 2** |
| 10 mmol | 50 mmol | 1,5 | 72h | **AD 3** |
| 10 mmol | 50 mmol | 1 | 72h | **AD 4** |
| 10 mmol | 50 mmol | 1,5 | 96h | **AD 5** |
| 1 mol | 5 mol | 200 | 72h | **AD 6** |

*General procedure* → From AD 2 to AD 6 was used the same synthetic procedure: the aniline was added in a round bottom flask, the butyraldehyde was added dropwise and finally, the $MgSO_4$ was added to the reaction mixture. The reaction mixture was stirred for a certain time and then the dehydrating agent was removed with a simple filtration with dichloromethane (20 mL) using a Florisil® pad. Finally the solvent was removed at reduced pressure, in order to get the crude of the reaction.

AD 2 procedure: 10 mmol of aniline, 100 mmol of butyraldehyde and 1g of $MgSO_4$ and the reaction was stirred for 72h, obtaining a percentage of the 1,2 dihydropyridine **64** of 53.8%. With the aim to improve the percentage of our target molecule, we changed the reaction conditions.

AD 3 procedure: an aniline-butyraldehyde ratio of 1:5 (10 mmol : 50 mmol)was used, adding 1,5g of $MgSO_4$, maintaining the same reaction time (72h). A slightly lower percentage of the 1,2 dihydropyridine **64** was obtained (49.2%).

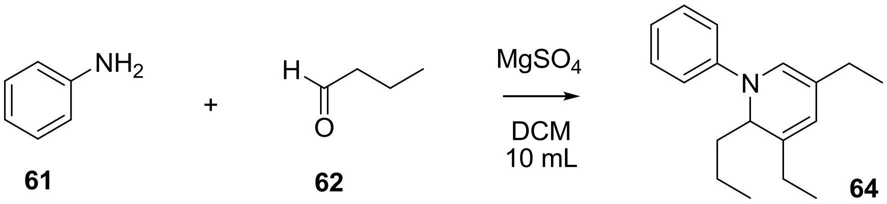
AD 4 procedure: the same aniline-butyraldehyde ratio was employed (1:5), but using a 1g of $MgSO_4$ and maintaining the same reaction time (72h), obtaining also in this case a slightly lower percentage of the 1,2 dihydropiridine **64** (46.8%).

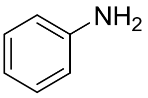
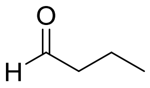
AD 5 procedure: was maintained the same aniline-butyraldehyde ratio (1:5) and the same quantity of $MgSO_4$ (1,5g) stirring the reaction mixture for 96h, obtaining a percentage of the 1,2 dihydropyridine **64** of 59.1%.

Then we tried the scale up of the reaction, using a 1 mol of aniline, 5 mol of butyraldehyde and 200g of $MgSO_4$ stirring the reaction for 72h, but unfortunately the percentage of the dihydropyridinic system was pretty low (16.9%).

A problem related to this kind of synthetic methodology was the formation of a very dense reaction mixture (formation of lumps due to the powdery dehydrating agent and the liquid reactants), so we tried to overcame this problem adding dichloromethane (10 mL) as solvent in order to avoid the lumps formation (Table 5). Unfortunately the percentage of our target molecule **64** was quite low (25.8%)

**Table 5:** Reaction conditions



|  |  | **$MgSO_4$ (g)** | **Time (t)** | **Reaction Name** |
|---|---|---|---|---|
| 10 mmol | 50 mmol | 1,5 | 24h | **AD 7** |

To see better the results obtained using this synthetic methodologies, the percentages of the product **64** was reported in the Table 6.

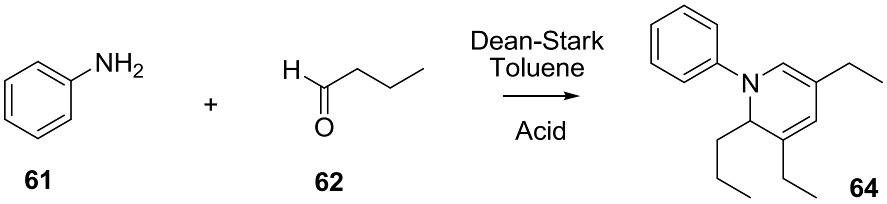
**Table 6:** Percentages of the product **64** (m/z = 255) of the reactions AD 2 to AD 7.

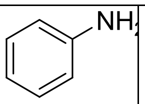
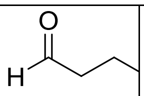
| **64 %** | **Reaction Name** |
|---|---|
| 53.8 | **AD 2** |
| 49.2 | **AD 3** |
| 46.8 | **AD 4** |
| 59.1 | **AD 5** |
| 16.9 | **AD 6** |
| 25.8 | **AD 7** |

### 3. *Azeotropic Distillation (Dean-Stark apparatus and acidic catalysis)*

We saw that, using dehydrating agent we obtained the dihydropiridinic system **64** in good percentage (e.g, AD 5), but the problem related to the lumps formation and the poor results obtained adding DCM, in order to overcome this problem, it drove us to improve a synthetic method which can fit with our conditions and which can give us a good percentage of **64.** For this reason we tested this condensation reaction using an azeotropic distillation to remove water (based on the Dean-Stark apparatus shown in Figure 20) and acidic catalyst to promote the imine formation and the subsequent reactions which lead to the formation of our target molecule **64** (see Scheme 26). In Table 7 are showed the conditions of the performed reactions.

**Table 7:** Reaction conditions.



|  |  | **Toluene (mL)** | **Time (t)** | **Acid** | **Reaction Name** |
|---|---|---|---|---|---|
| 10 mmol | 50 mmol | 30 | 24h | - | **AD 8** |
| 10 mmol | 50 mmol | 30 | 24h | *p*-TSA 7,5 mmol | **AD 9** |
| 10 mmol | 100 mmol | 10 | 24h | - | **AD 10** |
| 10 mmol | 50 mmol | 10 | 24h | $CH_3COO$ H 37% 10 mmol | **AD 11** |

*General procedure*→ From AD 8 to AD 11 we use the same synthetic procedure: the aniline and toluene was added to a round bottom flask, then the butyraldehyde was added dropwise. Finally the reaction mixture was stirred for 24h at reflux temperature (115°C). Then to remove the water and acid residues the crude of reaction was washed with 15 mL of a saturated solution of sodium carbonate ($Na_2CO_3$) and dichloromethane (3 x 15 mL). The organic layer was collected and treated with anhydrous sodium sulphate ($Na_2SO_4$). The solvent was removed at reduced pressure, in order to get the crude of the reaction.

AD 8 procedure: 10 mmol of aniline and 50mmol of butyraldheyde (1:5 ratio) and 30 mL of toluene were used, but we did not added the acid because, butyraldehyde containing a certain unknown percentage of butyric acid, but we obtained a very poor percentage of **64** (2.4%).

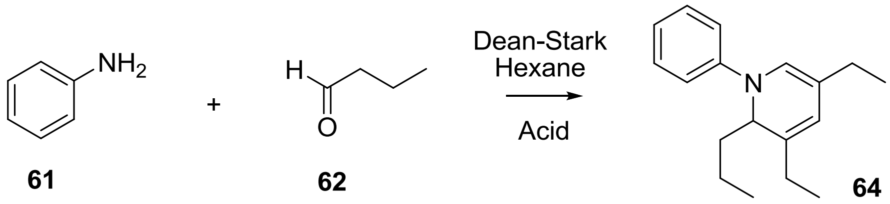
AD 9 procedure: 7,5 mmol of *p*-toluenesulfonic acid (*p*-TSA) were added, maintaining the same conditions of AD 8, but also in this case we obtained very poor percentage of **64** (>1%), maybe due to the decomposition of the target product (*p*-TSA is a quite strong acid, *pKa* = -1.74).

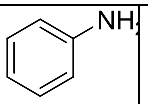
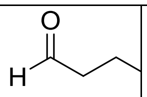
AD 10 procedure: aniline-butyraldehyde ratio of 10 mmol : 100 mmol (1:10) were added, in order to avoid the leak of the butyraldehyde (b.p. =74.8°C, while reflux temperature = 115°C). Moreover, we used a decreased toluene quantity (10 mL instead of 30 mL) and no acidic system. Unfortunately, also in this case we obtained a low percentage of **64** (5.3%).

AD 11 procedure: acetic acid (37% 10 mmol),an aniline-butyraldehyde ratio 10 mmol : 50 mmol (1 : 5) and 10 mL of toluene were used. In this case we obtained 49.8%of **64**.

The good result given by AD 11 procedure drove us to improve this procedure in particular, trying to avoid the leak of butiraldehyde (b.p. =74.8°C) using a low boiling point azeotrope, so we changed toluene with hexane (Table 8)

**Table 8:** Reaction conditions.



|  |  | **Hexane (mL)** | **Time (t)** | **Acid** | **Reaction Name** |
|---|---|---|---|---|---|
| 10 mmol | 50 mmol | 10 | 24h | $CH_3COOH$ 37% 10 mmol | **AD 12** |

Unfortunately the percentage of **64** was quite low (28.4%). This result can be explained because our product it is more soluble in toluene than in hexane.

To see better the results obtained using this synthetic methodologies, the percentages of the product **64** was reported in the Table 9.

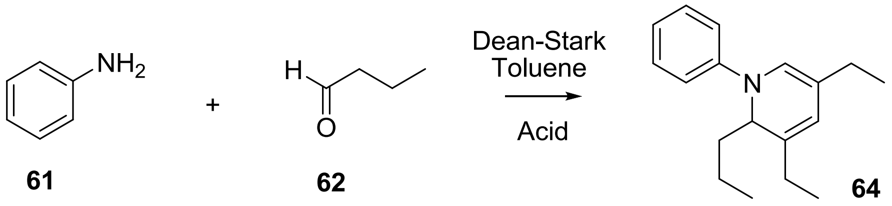
**Table 9:** Percentages of the product **64** (m/z = 255) of the reactions AD 8 to AD 12.

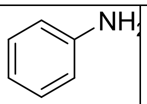
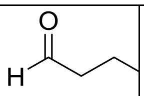
| **64 %** | **Reaction Name** |
|---|---|
| 2.4 | **AD 8** |
| >1 | **AD 9** |
| 5.3 | **AD 10** |
| 49.2 | **AD 11** |
| 28.4 | **AD 12** |

## 4. *Azeotropic Distillation Optimization*

Based on all the evidence from AD 1 to AD 12 we optimized our synthetic method. In particular, it was based on azeotropic distillation shown in AD 11 combined with conditions of AD 1 (Table 10).

**Table 10:** Reaction conditions.

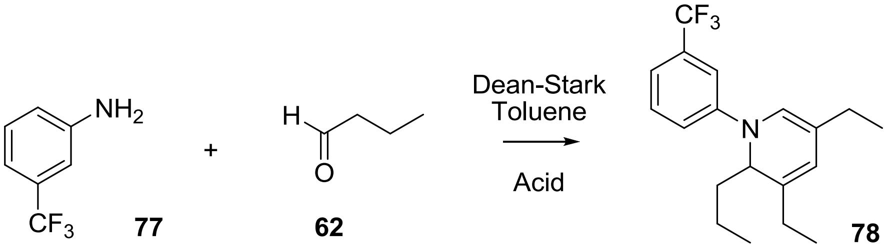


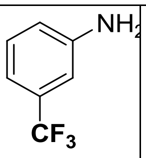
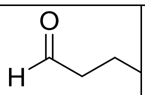
|  |  | **Toluene (mL)** | **Time (t)** | **Acid** | **Reaction Name** |
|---|---|---|---|---|---|
| 10 mmol | 50 mmol | 10 | 12h | $CH_3COOH$ 37%<br>10 mmol | **AD 13** |

*General procedure*→50 mmol butyraldehyde and 10 mL toluene was added to a round bottom flask maintaining the temperature at 0°C. Then 10 mmol of aniline was dropped inside the flask maintaining the temperature in a range of 0-10°C. After 1h the reaction mixture temperature was increased at 115°C (reflux temperature using Dean-Stark apparatus) and left for 8 hours. Finally 10 mmol of acetic acid was added and the reaction mixture was stirred for 3h. Then to remove the water and acid residues the crude of reaction was washed with 15 mL of a saturated solution of sodium carbonate ($Na_2CO_3$) and dichloromethane (3 x 15 mL). The organic layer was collected and treated with anhydrous sodium sulphate ($Na_2SO_4$). The solvent was removed at reduced pressure, in order to get the crude of the reaction. With this procedure we reach 61.2% of **64**. This is the best percentage obtained in our synthesis.

In order to verify the generality of the method it was tried the same procedure but with a different anline : 3-(trifluoromethylaniline) **77** (Table 11).

**Table 11:** Reaction conditions.



|  |  | **Toluene (mL)** | **Time (t)** | **Acid** | **Reaction Name** |
|---|---|---|---|---|---|
| 10 mmol | 50 mmol | 10 | 8h | $CH_3COOH$ 37% 10 mmol | **AD 14** |
| 10 mmol | 50 mmol | 10 | 8h | $CH_3COOH$ 37% 15 mmol | **AD 15** |
| 10 mmol | 50 mmol | 10 | 24h | $CH_3COOH$ 37% 10 mmol | **AD 16** |

We did a screening of acetic acid amounts (10-15 mmol) and a time screening (8–24h), but we obtained poor results (Table 12).

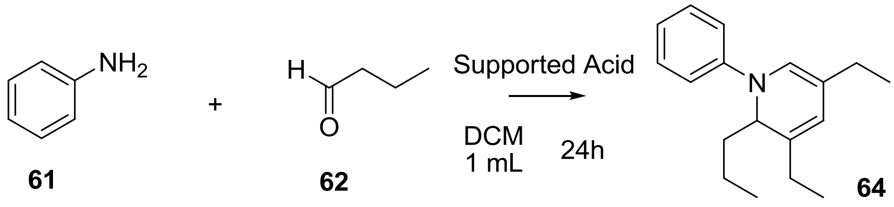
**Table 12:** Percentages of the product **78** (m/z = 280) of the reactions AD 14 to AD 16.

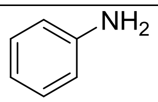
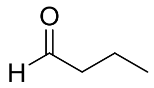
| **78 %** | **Reaction Name** |
|---|---|
| 24.8 | **AD 14** |
| 25.3 | **AD 15** |
| 8.3 | **AD 16** |

### 5. *Condensation with solid supported acids*

In the last year, the use of solid supported acids in organic synthesis was very exploited, due to the advantages that these solid supported reagent present: easily removal from reaction mixture by a filtration, recycling of recovered reagents is economical and environmental efficient, easy and safety handle. Based on the these advantages we try to perform this condensation using solid supported acids as catalysts (Table 13).

**Table 13:** Reaction conditions.



|  |  | **Supported Acid (g)** | **Reaction Name** |
|---|---|---|---|
| 1 mmol | 5 mmol | Hydrotalcite 0,5 | **AD 17** |
| 1 mmol | 5 mmol | HSZ-30 0,5 | **AD 18** |
| 1 mmol | 5 mmol | Montmorillonite 0,5 | **AD 19** |
| 1 mmol | 5 mmol | $Al_2OSO_3H$ 0,5 | **AD 20** |
| 1 mmol | 5 mmol | $Al_2O_3$ 0,5 | **AD 21** |

*General procedure*→ From AD 17 to AD 21 we used the same synthetic procedure: 1 mmol aniline and 1 mL dichloromethane were added in a round bottom flask, then 5 mmol butyrladehyde was added dropwise: Finally 500 mg solid supported acid was added and the reaction was stirred at room temperature for 24h.

We did a screening of different types of solid supported acids (from Hydrotalcite to $Al_2O_3$) but unfortunately we obtained very poor percentages of **64** (Table 14).

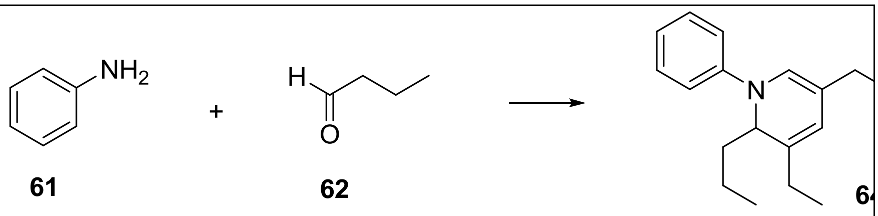
**Table 14:** Percentages of the product **64**(m/z = 255) of the reactions AD 17 to AD 21.

| **64 %** | **Reaction Name** |
|---|---|
| >1 | **AD 17** |
| 11.1 | **AD 18** |
| >1 | **AD 19** |
| >1 | **AD 20** |
| >1 | **AD 21** |

## 5.3 CONCLUSION

In conclusion we exploited different synthetic methodologies for the condensation between butyrladehyde and aniline and in this way we were able to understand different conditions which affect this reaction. The amount and the strength of the acid used was very important, in particular the use of a weak acid as acetic acid favors the formation of the desired product. On the contrary stronger acid (as *p*-TSA or supported acids used) favor the formation of other secondary products despite of the dihydropiridinic system, in this it can be explained the low relative abundances of the reaction based on the use of different acids than acetic acid. Moreover, the acid have to be removed if we want purify the product, in fact during the distillation process, at high temperature in presence of acid the dihydropiridinic product decomposes. Also different solvents were tested, infact, the solvent is important for this kind of reaction, it was see that the best solvent for this synthetic methodology is toluene and the dichloromethane, on the contrary the use of hexane bring to very low relative abundance of the dihydropiridine. The best synthetic methodologies, for this condensation reaction, herein are reported in Table 15.

**Table 15**: Best synthetic methodologies results.

<table>
<tr><td colspan="2"><br>61<br>62<br>6</td></tr>
<tr><td><b>Azeotropic distillation</b></td><td>61.2%</td></tr>
<tr><td><b>Dehydrating agent</b></td><td>59.2%</td></tr>
</table>

The second procedure brings to a low relative abundance than the other one but it can be considered as one of the possible procedure, but the procedure associated to this process is linked to the fact that the first attempt was performed in small quantities. Ones we tried to scale up the reaction we weren’t able to reproduce the same result. Instead, our methodology, based on azeotropic distillation, allowed a better result than the previous procedure moreover, we saw that the reproducibility was enhanced and also in this way this procedure can be reproduce also from an industrial point of view.

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