

Additives in composite materials: synthesis and characterization of innovative promoters in polyurethane

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Abstract. Composite materials, namely materials made of two or more different components, recover a fundamental role both in everyday life and in industrial applications. In the last years the increasing development of electric industry has meant that there is a huge request of insulation materials, that have the function of recovered conductor materials, able to ensure high performances and excellent chemical physical properties. Among these insulation systems, a particular attention is placed on coatings for metallic wires, Polyurethane enamels appear to be widely used at industrial level because based on usage of cheap raw materials readily available. From a synthetic point of view, polyurethane synthesis it's been widely explored during the years, but the increasing necessity of more performing materials has meant that inorganic and organic additives find a fundamental role in the polyurethane compound formulation: promoters, catalysts, primers, UV-absorbents, flame retardant, plasticizer, ant-oxidants and disperdents bring an improvement in the material's mechanic and chemical physical 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 will be focused on the importance of these promoters, in particular way the condensation product between aniline and butyraldehyde, in the formulation of polyurethane blends, their synthesis and their characterization, in order to improve the solderability and the thermal resistance.

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

Introduction

In the early 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, 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.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. The general polyurethane formation reaction is based on a polycondensation between a di- or polyisocyanate and a hydroxyl containing compound (e.g, polyols).

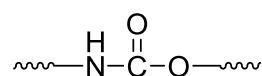


Figure 1: Urethane interunit linkage.

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 dicarboxylic 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 resistance. 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 naphtha.²

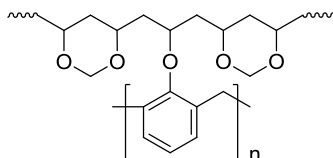


Figure 2: Poly (vinyl formal)-phenolic resin.

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 terephthalic acid polyesters and polyester imides as high thermal stability wire enamels by Dr. Beck & Co. GmbH (Figure 3).⁴

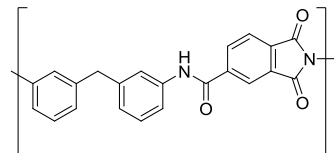


Figure 3: Polyester imides.

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.

In particular, a very important role in the polyurethane formulations is represented by additives. 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 DNP, technical grade technical grade glyceryl-monostearate 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.¹ 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.²

Experimental Section

This 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 sieves 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 3).

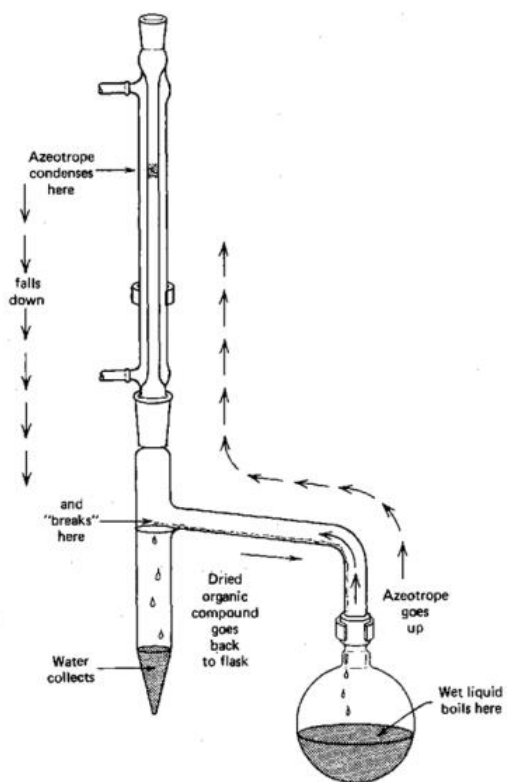
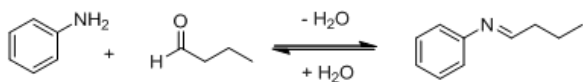


Figure 3: Dean-Stark apparatus.

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 1.



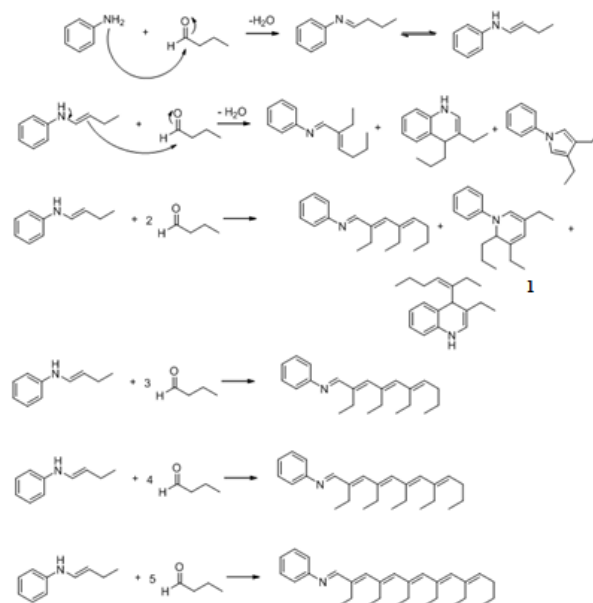
Scheme 1: General mechanism of imine formation.

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 2).



Scheme 2: 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 3), creating a series of polycondensation products.



Scheme 3: polycondensation mechanism and resulting products.

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 hypothesized of $m/z = 255$, then $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, DEPT analysis were exploited to confirm the exact structure. The 3,5-diethyl-1-phenyl-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 4).

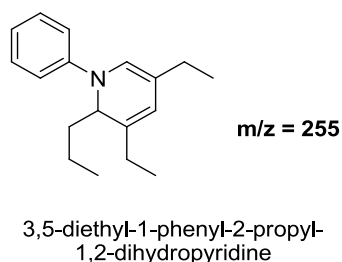


Figure 4: Dihydropyridinic structure conformed by NMR-analysis.

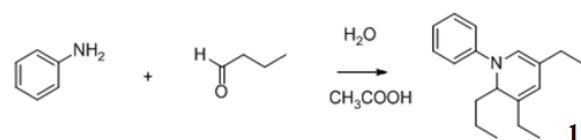
The production of this dihydropyridine was studied and the optimization of the synthesis of this additive was carried out maintaining as much as possible the producing industrial conditions. With this purpose all chromatographic purifications or aqueous work up were avoided. The main scope was the development or the improvement of existing synthetic methodologies in order to obtain this 1,2-dihydropyridine (Figure 4) which is used to improve solder time and thermal resistance, fundamental characteristics of the final product. Moreover, it was tried to use different starting material (different amines) to generalize the reaction mechanism.

The synthesis of 3,5-diethyl-1-phenyl-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-phenyl-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 (Scheme 4 AD 1) was based on a synthetic procedure reported by Martin *et al.*¹



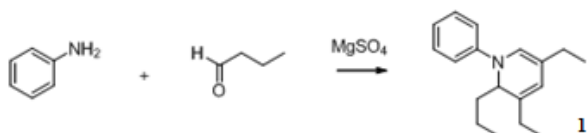
Scheme 4: Condensation reaction AD 1.

General procedure AD 1: 50mmol of butyraldehyde and 1,08mL of water was added into a round bottom flask at 0 °C. Then 10mmol 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 5h. Finally, the reaction was allowed to reach room temperature was and stirred overnight (the entire reaction time is 24h). In this case the percentage of the 1,2 dihydropyridine **1** 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 15mL of a saturated solution of sodium carbonate (Na₂CO₃) and dichloromethane (3 x 15mL). The organic layer was collected and treated with anhydrous sodium sulphate (Na₂SO₄). 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 1-3mmHg at 80°C to remove the 2-ethylhexenal (m/z= 126, condensation product of two butyraldehyde) and then the pressure was decrease at 0,5-1mmHg 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 MgSO₄ trying different quantities of this one and reaction times (Scheme 5 AD 2-6).

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.



Scheme 5: Condensation reaction AD 2-6.

General procedure AD 2-6: 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 MgSO₄ 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 (20mL) using a Florisil® pad. Finally the solvent was removed at reduced pressure, in order to get the crude of the reaction.

AD 2 procedure: 10mmol of aniline, 100mmol of butyraldehyde and 1g of MgSO₄ and the reaction was stirred for 72h, obtaining a percentage of the 1,2 dihydropyridine **1** of 53.8%. With the aim to improve the percentage of our target molecule, we changed the reaction conditions.

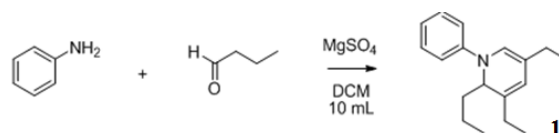
AD 3 procedure: an aniline-butyraldehyde ratio of 1:5 (10mmol : 50mmol) was used, adding 1,5g of MgSO₄, maintaining the same reaction time (72h). A slightly lower percentage of the 1,2 dihydropyridine **1** was obtained (49.2%).

AD 4 procedure: the same aniline-butyraldehyde ratio was employed (1:5), but using a 1g of MgSO₄ and maintaining the same reaction time (72h), obtaining also in this case a slightly lower percentage of the 1,2 dihydropyridine **1** (46.8%).

AD 5 procedure: was maintained the same aniline-butyraldehyde ratio (1:5) and the same quantity of MgSO₄ (1,5g) stirring the reaction mixture for 96h, obtaining a percentage of the 1,2 dihydropyridine **1** of 59.1%.

Then we tried the scale up of the reaction (AD 6), using a 1mol of aniline, 5mol of butyraldehyde and 200g of MgSO₄ 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 overcome this problem adding dichloromethane (10mL) as solvent in order to avoid the lumps formation (Scheme 6 AD 7). Unfortunately the percentage of our target molecule **1** was quite low (25.8%)



Scheme 6: Condensation reaction AD 7.

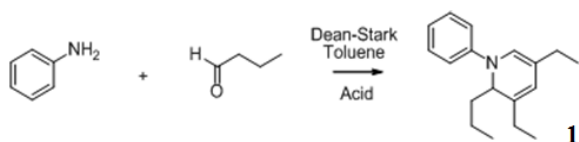
To see better the results obtained using this synthetic methodologies, the percentages of the product **1** was reported in the Table 1.

TABLE 1: PERCENTAGES OF THE PRODUCT 1 (M/Z = 255) OF THE REACTIONS AD 2 TO AD 7.

1 %	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 dihydropyridinic system **1** 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 **1**. For this reason we tested this condensation reaction using an azeotropic distillation to remove water (Scheme 7 AD 8-11) and acidic catalyst to promote the imine formation and the subsequent reactions which lead to the formation of our target molecule **1** (see Scheme 2).



Scheme 7: Condensation reaction AD 8-11.

General procedure AD 8-11: 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 15mL of a saturated solution of sodium carbonate (Na₂CO₃) and dichloromethane (3 x 15mL). The organic layer was collected and treated with anhydrous sodium sulphate (Na₂SO₄). The solvent was removed at reduced pressure, in order to get the crude of the reaction.

AD 8 procedure: 10mmol of aniline and 50mmol of butyraldehyde (1:5 ratio) and 30mL of toluene were used, but we did not added the acid because, butyraldehyde containing a certain unknown percentage of

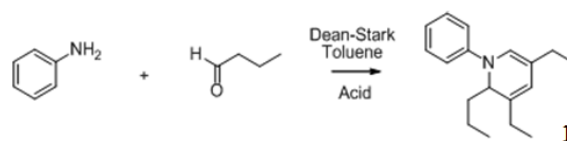
butyric acid, but we obtained a very poor percentage of **1** (2.4%).

AD 9 procedure: 7,5mmol 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 **1** (>1%), maybe due to the decomposition of the target product (*p*-TSA is a quite strong acid, *pKa* = -1.74).

AD 10 procedure: aniline-butyr-aldehyde ratio of 10mmol : 100mmol (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 (10mL instead of 30mL) and no acidic system. Unfortunately, also in this case we obtained a low percentage of **1** (5.3%).

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

The good result given by AD 11 procedure drove us to improve this procedure in particular, trying to avoid the leak of butyraldehyde (b.p. =74.8°C) using a low boiling point azeotrope, so we changed toluene with hexane (Scheme 8 AD 12).



Scheme 8: Condensation reaction AD 12.

Unfortunately, maintaining the best reaction conditions (AD 11) the percentage of **1** was quite low (28.4%). This result can be explained because our product it is more soluble in toluene than in hexane.

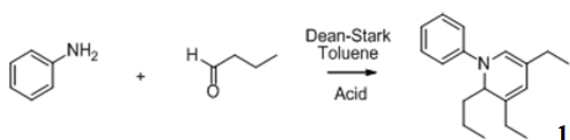
To see better the results obtained using this synthetic methodologies, the percentages of the product **1** was reported in the Table 2.

TABLE 2: PERCENTAGES OF THE PRODUCT 1 (M/Z = 255) OF THE REACTIONS AD 8 TO AD 12.

1 %	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

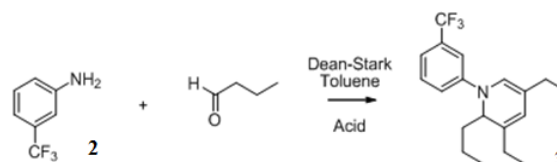
Based on all the evidence from AD 1 to AD 12 we optimized our synthetic method. In particular, it was based on azeotropic distillation shown in AD 11 combined with conditions of AD 1 (Scheme 9 AD 13).



Scheme 9: Condensation reaction AD 13.

General procedure AD 13: 50mmol butyraldehyde and 10mL toluene was added to a round bottom flask maintaining the temperature at 0°C. Then 10mmol 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 8h. Finally 10mmol 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 15mL of a saturated solution of sodium carbonate (Na₂CO₃) and dichloromethane (3 x 15mL). The organic layer was collected and treated with anhydrous sodium sulphate (Na₂SO₄). The solvent was removed at reduced pressure, in order to get the crude of the reaction. With

this procedure we reach 61.2% of **1**. 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 aniline : 3-(trifluoromethylaniline) **2** (Scheme 10 AD 14-16)



Scheme 10: Condensation reaction AD 14-16.

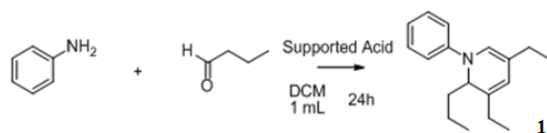
We use the same procedure of AD 11 with different reaction time (8h for AD 14-15 and 24h for AD 16) and different acetic acid amounts (10mmol for AD 14-16 and 15mmol for AD 15). We obtained poor results (Table 11)

TABLE 3: PERCENTAGES OF THE PRODUCT 3 (M/Z = 280) OF THE REACTIONS AD 14 TO AD 16.

3 %	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 (Scheme 11 AD 17-21).



Scheme 11: Condensation reaction AD 17-21.

General procedure AD 17-21: From AD 17 to AD 21 we used the same synthetic procedure: 1mmol aniline and 1mL dichloromethane were added in a round bottom flask, then 5mmol butyraldehyde was added dropwise: Finally 500mg 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 (Hydrotalcite 0,5g for AD17, HSZ-30 0,5g for AD 18, Montmorillonite 0,5g for AD 19, $\text{Al}_2\text{OSO}_3\text{H}$ 0,5g for AD 20 and Al_2O_3 0,5g for AD 21) but unfortunately we obtained very poor percentages of **1** (Table 4)

TABLE 4: PERCENTAGES OF THE PRODUCT 1 (M/z = 255) OF THE REACTIONS AD 17 TO AD 21.

1 %	Reaction Name
>1	AD 17
11.1	AD 18
>1	AD 19
>1	AD 20
>1	AD 21

Experimental data

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 stationary phase OVI 0.4-0.45 μm to monitor the reaction trend.

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.

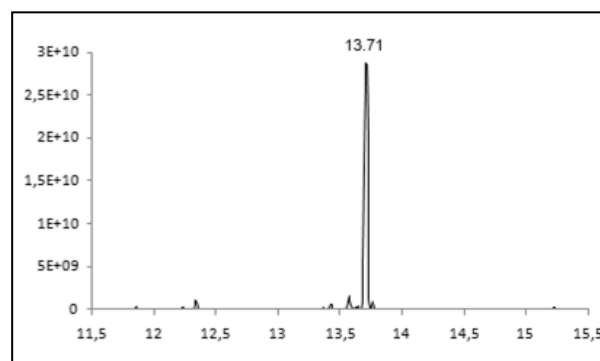


Figure 5: GC spectrum industrial sample.

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

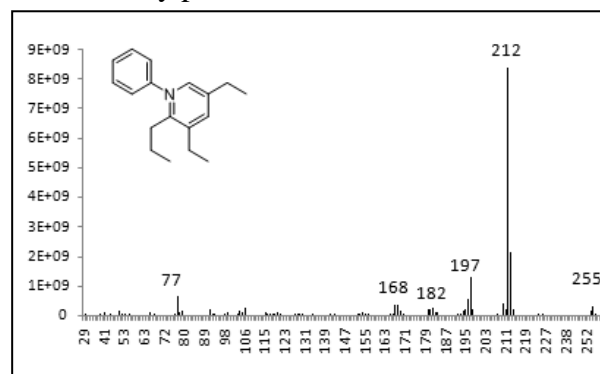


Figure 6: MS spectrum of the product with m/z = 255.

The industrial sample analyzed is very pure and the 3,5-Diethyl-1-Phenyl-2-Propyl-1,2-Dihydropyridine ($m/z = 255$) is present in 95.1%.

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 7, so our aim was to determine the absolute structure of the product.

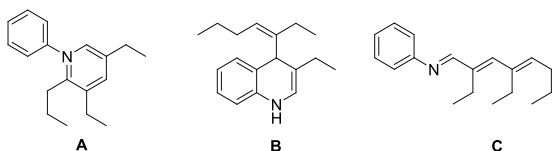


Figure 7: Structures with $m/z = 255$.

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 1H -NMR, ^{13}C -NMR and DEPT. The results obtained with 1H -NMR and ^{13}C -NMR didn't give us a clear difference between the isoquinolinic structure **B** and the dihydropyridinic one **A**, but the presence of a triplet at 4.32 ppm in 1H -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 dihydropyridinic structure was suspected. Below are reported the spectroscopic data (GC, 1H -NMR and ^{13}C -NMR spectra reported in Figure 8-9).

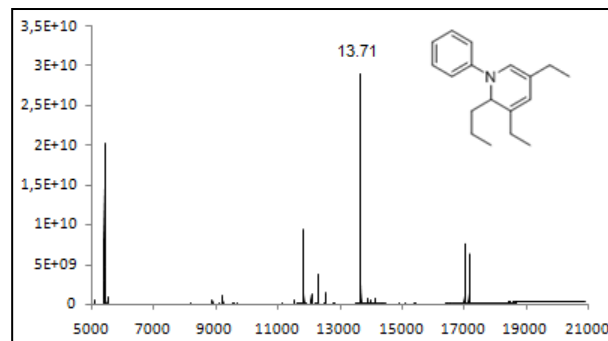


Figure 8: GC 3,5-diethyl-1-phenyl-2-propyl-1,2-dihydropyridine 1.

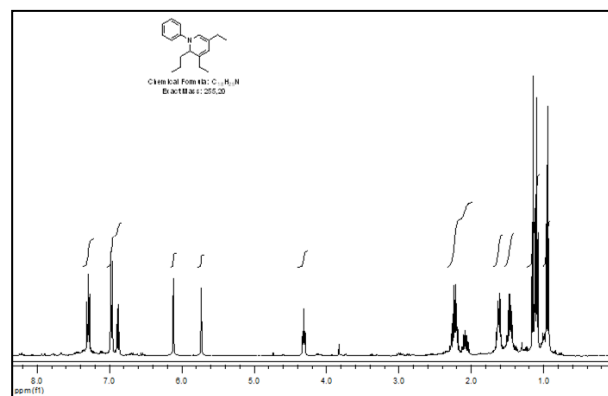


Figure 9: 1H -NMR 3,5-diethyl-1-phenyl-2-propyl-1,2-dihydropyridine 1.

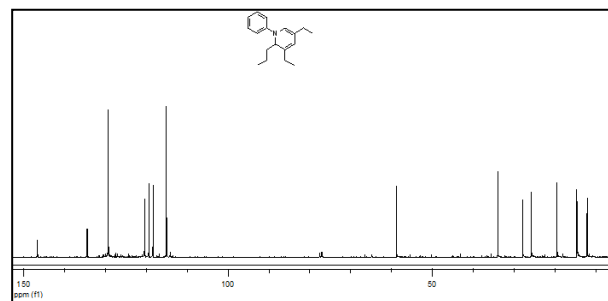
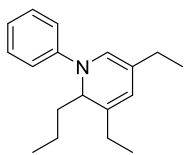


Figure 10: ^{13}C -NMR

3,5-diethyl-1-phenil-2-propyl-1,2 dihydropyridine 1.
3,5-diethyl-1-phenil-2-propyl-1,2 dihydropyridine 1



Yellow oil. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 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). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 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 $\text{C}_{13}\text{H}_{25}\text{N}$ (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.

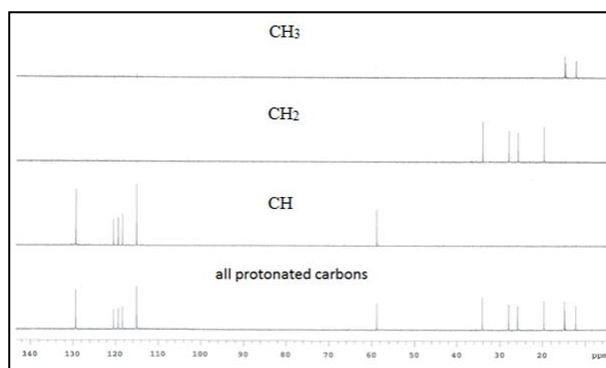


Figure 11: DEPT spectra.

In Figure 11, it can be seen that the analyzed compound are characterized by three different

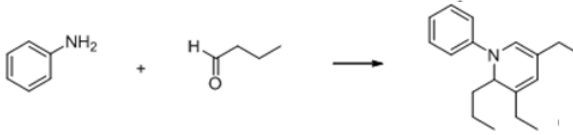
CH_3 groups, four CH_2 and six CH groups. Looking carefully at the structure of **A** and **B** in Figure 7, the only difference is the number of primary carbons: the isoquinolinic structure is characterized by a disubstituted aromatic ring and there is a total of seven different kinds of CH , whereas in the dihydropyridinic 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 **1**, as suspected from mass spectrum considerations.

Conclusion

In conclusion we exploited different synthetic methodologies for the condensation between butyraldehyde 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 favours the formation of the desired product. On the contrary stronger acid (as *p*-TSA or supported acids used) favour the formation of other secondary products despite of the dihydropyridinic 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 dihydropyridinic product decomposes. Also different solvents were tested, in fact, 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 dihydropyridine. The best synthetic methodologies, for this condensation reaction, herein are reported in Table 4.

TABLE 4: BEST SYNTHETIC METHODOLOGIES RESULTS.


Azeotropic distillation 61.2%
Dehydrating agent 59.2%

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. Once 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 reproduced also from an industrial point of view.

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