

**POLYANILINE AS A NEW SOLID BASE
CATALYST IN MICROWAVE ASSISTED
ORGANIC CHEMISTRY**

**Natalia Gospodinova^{*}, Stéphane Frère, Valérie Thiéry,
Thierry Besson^{*}**

*Groupe de Chimie Organique, Laboratoire de Génie Protéique et
Cellulaire, EA3169, U.F.R. Sciences Fondamentales et Sciences
pour l'Ingénieur, Bâtiment Marie Curie, Université de La
Rochelle, F-17042 La Rochelle cedex 1, France.
Fax: (33) (0)5 46 45 82 47; e-mail: tbesson@univ-lr.fr,
ngospodi@univ-lr.fr*

ABSTRACT: A new solid base catalyst in microwave assisted organic chemistry is proposed. Successful replacement of sodium hydride by environmentally friendly polyaniline based catalyst is achieved to convert iminodithiazoles into aryl isothiocyanates and quinazolines under microwaves. The simple handling, reusability and possibility of "dry media" microwave processes represent the main advantages of polyaniline based catalyst.

KEYWORDS: *Microwave irradiation, polyaniline, dry media reactions, green chemistry*

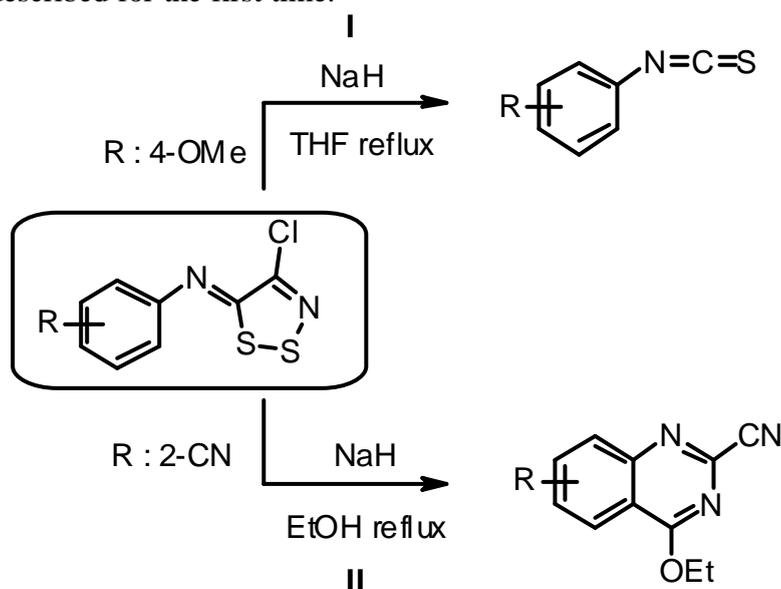
RESUME: L'idée d'un nouveau catalyseur est proposée en chimie assistée par les micro-ondes. Les iminodithiazoles sont converties en aryl isothiocyanates et quinazolines sous micro-ondes en remplaçant l'hydruide de sodium par de la polyaniline qui sert alors de catalyseur basique. Le fait de pouvoir réutiliser la polyaniline au sein de réaction réalisées sans solvants est un atout majeur pour son développement.

INTRODUCTION

A variety of organic reactions (isomerisation of alkenes, reactions of alkynes, methylations, addition reaction, etc....) are catalysed by solid base catalysts [1]. These catalytic materials include zeolites, alkaline oxides, $\text{KNH}_2/\text{Al}_2\text{O}_3$, $\text{KF}/\text{Al}_2\text{O}_3$, and Si_2NO_2 . The replacement of liquid base by solid base catalysts would have the advantages to decrease corrosion and environmental problems, accompanied by easier separation and recovery of the catalysts. Among experimental procedures, the microwave irradiation exhibits an interesting possibility and it has been employed for some organic reactions catalysed by inorganic solids [2].

It is now well established that conducting polymers such as the polyaniline (PANI) are of great interest as microwave absorbing materials. The high conductivity at microwave frequency makes it possible to be used for developing microwave components like filters [3]. Taking into account this property of PANI in combination with recently confirmed catalytic activity of conducting PANI in the esterification of carboxylic acids with alcohols [4], it is reasonable to suppose that the PANI would have promising perspectives as solid base catalyst in microwave assisted organic chemistry.

The chemistry and microwave chemistry of *N*-arylimino-1,2,3 dithiazoles is one of the major axes of our researches. These imines are highly versatile intermediates in heterocyclic synthesis. For example, they can be converted into *N*-arylisothiocyanates (reaction I) or quinazolines (reaction II) in basic conditions (Scheme1) [5,6]. In the present work we investigate these reactions by replacement of traditional sodium hydride by an environmentally friendly PANI catalyst. The simple handling, reusability and possibility of "dry media" microwave synthesis represent the main advantages of PANI catalyst. An efficient use of PANI as organic solid base catalyst in microwave chemistry is described for the first time.



Scheme 1.

MATERIAL AND METHODS

PANI-P was synthesised in 1M HCl by oxydation of aniline using ammonium peroxidisufate (1 equiv.) at 0°C. Reaction was continued for 3h. The metallic-apparent precipitate was washed with aqueous HCl and with acetone until the washings were colourless. It was dried in air at 60°C for 48h and then powdered. PANI-I was obtained by treatment of PANI-P by aqueous 1.25M NaOH. It was washed and dried as above.

Focused microwave experiments were carried out at atmospheric pressure with a Synthwave S402 Prolabo microwave reactor (300 W, monomode system), which has quartz reactors, visual control, irradiation monitored by PC computer, infrared measurement and continuous feedback temperature control (by PC).

The Time-Temperature profiles for different solid supports (graphite, PANI-P, PANI-I and PANI-P/PANI-I mixture) were obtained upon microwave irradiation (power 150W).

Synthesis of 4-methoxyphenyl isothiocyanate (reaction I)

A stirred mixture of 4-methoxy-*N*-(4-chloro-5*H*-1,2,3-dithiazole-5-ylidenyl)aniline and PANI was placed under in a quartz vial (10ml) inside the oven. The irradiation was programmed to obtain a constant temperature (120 and 150 °C) with a maximal power output of 12 W. After cooling and addition of ethyl acetate, the mixture was filtered and solid PANI catalyst was washed with ethyl acetate. After solvent evaporation, the crude product was purified by column chromatography with light petroleum-dichloromethane as the eluent.

Synthesis of 4-Ethoxy-quinazoline-2-carbonitrile (reaction II)

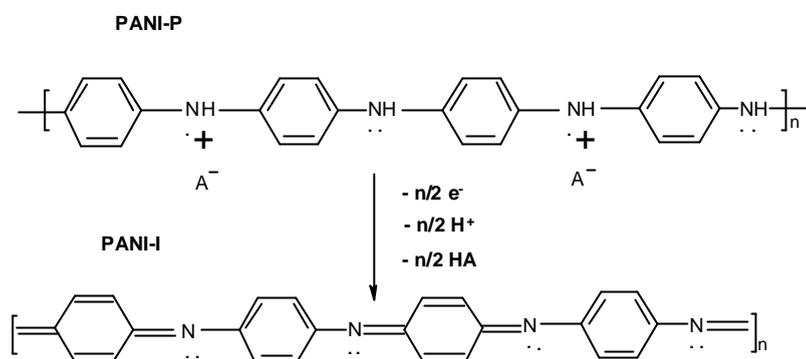
A stirred mixture of *N*-(4-chloro-5*H*-1,2,3-dithiazole-5-ylidenyl)-2-cyanoaniline and PANI in ethanol was placed under in a quartz vial (10ml) inside the oven. The irradiation was programmed to obtain the reflux with a maximal power output of 12 W. The separation of solid PANI catalyst and the purification of the product were realised as above.

¹H and ¹³C NMR spectra of products were recorded on JEOL 5410 LV spectrometer. Spectral data for 4-methoxyphenyl isothiocyanate and 4-ethoxyquinazoline-2-carbonitrile are consistent with those previously described.^{5,6}

RESULTS AND DISCUSSION

PANI exists in $m/2$ oxidation states (m - number of aniline units) characterised by the ratio of amine and imine nitrogen atoms (Scheme 2) [7]. Not only conductivity, but also basicity of PANI depends on oxidation state. The conducting form of PANI is the protonated form (PANI-P) in which the emeraldine oxidation state (number of amine and imine nitrogen atoms is the same) is stable. The deprotonation of PANI-P is accompanied by its oxidation by residual oxidant or atmospheric oxygen. The oxidation state depend on pH of the medium: increase of pH leads to increase the oxidation state of PANI, accompanied by regularly decreasing conductivity and increasing basicity up to fully oxidised (all the nitrogen atoms are imine) form. This electrically insulating form of PANI (PANI-I) is characterised by the highest basicity. Thus, conducting

PANI (PANI-P) should manifest the highest microwave heating capacity, whereas insulating PANI (PANI-I) should have the highest basic catalytic strength.



Scheme 2. Legends: m - number of aniline units, $n = 4m$; A^- - counter anion; PANI-P- conducting form of polyaniline, PANI-I – insulating form of polyaniline

We investigated the effect of microwave irradiation on heating capacity of PANI-P and PANI-I. Upon the same conditions, we have also irradiated graphite, which is one of the solids most efficiently heated by microwaves and widely used in microwave chemistry as solid support [8]. The Time-Temperature profiles of graphite, PANI-P, PANI-I and PANI-P/PANI-I mixture are shown in Fig.1. We observed that, in the temperature range studied (up to 160°C), heating velocity of PANI-P and graphite is almost the same. As expected, PANI-I is absolutely inactive in respect to microwave heating, but, by addition of only 10% by weight of PANI-P, high heating capacity can be achieved.

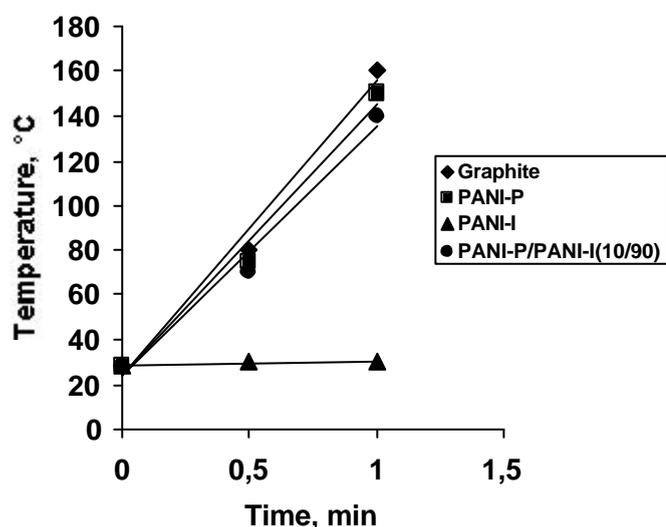


Figure 1. Time-Temperature profiles of different solid supports under microwave irradiation.

Table 1. Synthesis of 4-methoxyphenyl isothiocyanate (reaction I) and 4-ethoxy-quinazoline-2-carbonitrile (reaction II)

Reaction	Conditions	Yield, %	Reference
I	NaH (2.2 equiv.), THF, reflux, 18h, conventional heating ^a	57	5
I	PANI-P (1.1 equiv.), 120°C, 50 min, microwaves ^b	25	Present work
I	PANI-P/PANI-I (10/90) ^c (1.1 equiv.), 120°C, 50 min, microwaves ^b	50	Present work
II	NaH (1.1 equiv.), EtOH, reflux, 40h, conventional heating	29	6
II	NaH (1.1 equiv.), EtOH, reflux, 2h, microwaves ^b	80	6
II	PANI-I (1.1 equiv.), EtOH, reflux, 1h, microwaves ^b	70	Present work
II	PANI-P/PANI-I (10/90) ^c (1.1 equiv.), EtOH, reflux, 1h, microwaves ^b	68	Present work

^a oil bath; ^b 12W; ^c by weight

Consequently, the use of PANI-P/PANI-I mixture should represent a successful compromise between heating capacity and basic strength of PANI based catalyst.

In order to estimate the activity of PANI as catalyst we investigated synthesis of 4-methoxyphenyl isothiocyanate (reaction I, Scheme 1) and 4-ethoxy-quinazoline-2-carbonitrile (reaction II, Scheme 1) using corresponding iminodithiazoles in the presence of PANI-P, PANI-I and their mixture. Some selected results, as well as those described earlier [5,6] are summarised in Table 1. Replacement of sodium hydride by the PANI based catalyst allows to perform reaction I in "dry media" microwave conditions. We observed that the mixture PANI-P/PANI-I, containing of 90% of PANI-I, manifest much higher activity in the synthesis of 4-methoxyphenyl isothiocyanate than PANI-P, which is in accordance with higher basic strength of insulating PANI form. In an attempt to accelerate this reaction we irradiated up to 120°C. In order to check the hypotheses of 4-methoxyphenyl isothiocyanate formation due to high temperature employed, we have examined the possibility to realise this synthesis on graphite. No formation of 4-methoxyphenyl isothiocyanate was observed. No increasing of yield was achieved by growth of temperature up to 150°C or by increase of the quantity of PANI catalyst (up to 3 equiv.).

Successful replacement of sodium hydride by PANI based catalyst was also observed in 4-ethoxyquinazoline-2-carbonitrile synthesis. Because ethanol, a polar liquid used in this case, is a good candidate in microwave heating, testing of pure isolating form of PANI (PANI-I) was possible. No significant effect on 4-ethoxyquinazoline-2-carbonitrile yield was observed when PANI-I instead of PANI-P/PANI-I mixture was used. This result confirms our idea of the use of PANI-P/PANI-I mixture as a successful compromise between heating capacity and basic strength of PANI based catalyst.

All polyaniline based catalysts here described were recovered and reused several times (3-4) in the same reaction conditions. The same yields of products were obtained.

CONCLUSION

In conclusion, we present here for the first time successful use of polyaniline as solid base catalyst in microwave organic chemistry. This environmentally friendly catalyst can be easily prepared, recovered and reused.

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