First International Electronic Conference on Synthetic Organic Chemistry (ECSOC-1), www.mdpi.org/ecsoc/, September 1-30, 1997

[A0031]

MICROWAVES APPLICATION IN ORGANIC SYNTHESIS. Microwave-Assisted Preparation of Diphenylamines in 'Dry Media'

Sorin V. Filip,* Gabriela NAGY, Emanoil SURDUCAN, and Vasile SURDUCAN

Institute for Isotopic and Molecular Technology, P.O.Box 700, Cluj-Napoca 5, RO-3400, ROMANIA
tel. +40-64-184037, fax. +40-64-420042, e-mail svfilip@L30.itim-cj.ro
http://www.itim-cj.ro/~micro/ecsoc.htm

Received: 8 August 1997 / Uploaded: 8 August

Abstract: The application of microwaves in organic chemistry has experienced exponential growth within the last eight years. Rate enhancements varied from 10 to 1500 times compared with those of conventionally heated samples. We propose here a new technology for preparation of diphenylamine by microwave-activation, using an inorganic solid support, namely bentonite. This method offers the following advantages over conventional synthesis of this compound: high efficiency, safety, the experimental procedure is much simpler and environmental friendly.

Keywords: Microwave, organic synthesis, dyphenilamine, solid support, bentonite, environment.

Introduction

In the past few years there has been a growing attention in the use of microwave heating in organic synthesis since the first contributions by Gedye [1] and Giguere [2] in 1986. Microwave-assisted organic synthesis have several advantages over conventional technology: remarkable decreases in the times necessary to carry out reactions (up to 3 orders of magnitude), improved isolated yields of products (when thermal decomposition is associated with the conventionally heated reactions) and, sometimes effects on chemo-, regio- and stereoselectivity, are also achieved. On the other hand, it was shown that microwaves have a specific catalytic effect, named "microwave effect", lowering the activation energy of a reaction [3]. Other investigators have observed similar microwave effects (i.e. reduced processing temperatures and times) in glasses and polymers, and these results have created much interest and controversy in the microwave processing community [4]. At present, there is a little doubt that measured processing temperatures and times are reduced when conventional heating is replaced with microwave energy. At issue are the underlying causes/mechanisms responsible for this effect. Specifically, is there a nonthermal effect, or are the measured temperatures not representative of the true temperatures due to inaccuracies in the temperature probe or the presence of temperature gradients? As we mentioned above, the issue of microwave effects is very controversial. Unfortunately, many of the expected results from microwave processing such as rapid and uniform heating, inverse temperature profiles, and selective heating are included in the general microwave effects [5]. However, it is affirmed that only those anomalies that cannot be predicted or easily explained based on our present understanding between thermal and microwave heating should be called "microwave effects" [6]. Enhancements in the rates of activated processes involving material transport (i.e. sintering, ion exchange, and chemical reactions) are considered microwave effects because a reduction in the activation energy appears to be required, and investigators have been unable to provide a scientific basis for this behavior. In addition to enhanced rates, differences in reaction pathways and reaction products due to microwave processing also should be considered microwave effects [7]. Enhanced rates have been attributed to poor temperature measurements in a microwave field and localized temperature variations. To date, neither has been proven to be responsible for the observed enhancements. Many of the investigations reporting enhancements in processing rates and lower processing temperatures have paid close attention to temperature measurements; sheathed thermocuples, optical fibers [8] and non-contact measurements devices have been used. However, accurate temperature measurements are difficult in the presence of thermal gradients, which most certainly occur during microwave processing of bulk samples. Therefore, more emphasis should be placed on reporting the method of temperature measurement, the accuracy, and where the measurements are made (i.e. on the sample surface or in the interior). The simplest method for conducting microwave-assisted reactions involves irradiation of reactants only, in an open container made from quartz, Teflon or ceramic material. The scope for such processes is obviously limited, because of the reduced number of suitable organic compounds. Consequently, two other solvent-free techniques have been developed: reactions on solid mineral support in "dry media", and solid-liquid phase transfer catalysis. For "dry media" reactions, supports such as alumina, silica, bentonite, montmorillonite clays, and zeolites, have been investigated. Although this technique seems best suited to transformations involving a single organic species (e.g. as in deprotection, rearrangement, oxidation and dehydration), condensations have also been reported [9].

Experimental

We studied the microwave-assisted condensation reaction of aniline 1 to diphenylamine (DPA) 2.

Many methods for the synthesis of DPA were developed, see for example Floru et al. [10], and it is shown that the method involving the use of a solid inorganic support is the best choice. However, it needs high temperature (400-500 C) and pressure (15-40 atm), and required a considerable reaction time (5-10 hours) . Our experiments were done in "dry media" using bentonite and mixtures of alumina, silica, ferric oxide, calcium oxide, magnesium oxide and titanium oxide, as solid supports. The reagent, namely aniline, was absorbed on the support and than irradiated with microwaves in an opened quartz vessel, at 850 W power output and 2.45 G Hz. The

best ratio of aniline to solid support was proved to be 16 mmol / 5 g. The product was extracted with acetone and the solvent was evaporated at 30 C. The resulting mixture was added to a warm diluted HCl solution and stirred, when only aniline is dissolved. Melted raw DPA is collected and treated with a warm (over 53 C) NaOH solution and than with warm water. The solution is maintained above the melting point of DPA (53 C) and is separated by involving with superheated watery vapours (250-300 C). A pure product was obtained after crystallization. The identity of the product was checked-up by elemental analyses and confirmed by comparison of TLC (on "MERCK" silicagel 60 F 254 plates, toluene as eluent and a visualisation with a 254 nm UV lamp) of this compound with that of an authentic sample. Melting point is uncorrected. The bentonite is original from Gurasada (Romania) and has the following composition: SiO_2 (73.4 %), Al_2O_3 (14.35 %), Fe_2O_3 (1.72 %), CaO (0.52%), MgO (2.32%), K_2O (0.44 %), Na_2O (0.29 %), TiO_2 (0.24 %). For studying the effect of the solid support we use the same oxides (except Na_2O and K_2O that are unstable in watery atmosphere) for simulate the composition of bentonite. Immediately after the microwave treatment, the temperature of the sample was measured by a sheathed thermocouple, with an ± 5 C error. The presence of a specific "microwave effect" was shown by a classic simultaneous treatment in an electric heated oven, at the same temperature. Reaction time was 60 seconds in all cases. The results are presented in the Table.

TABLE. Diphenylamine prepared by microwave irradiation at 850 W (2.45 GHz) on a solid inorganic support.

Solid support	Yield of DPA	
	Conventional	Microwave
Bentonite	31	82
Alumina (Al_2O_3)	0	4
Silica (SiO_2)	0	0
Al_2O_3 + SiO_2	0	0
Al_2O_3 + SiO_2 + Fe_2O_3 + MgO	0	0
Al_2O_3 + SiO_2 + Fe_2O_3 + CaO	0	0
Al_2O_3 + SiO_2 + Fe_2O_3 + MgO + CaO	0	0
Al_2O_3 + SiO_2 + Fe_2O_3 + MgO+CaO+TiO_2	0	0
Al_2O_3 + SiO_2 + Fe_2O_3 + TiO_2	0	0
Al_2O_3 + SiO_2 + MgO	0	0
Al_2O_3 + SiO_2 + TiO_2	0	0
Al_2O_3 + SiO_2 + CaO	0	0
Al_2O_3 + SiO_2 + Fe_2O_3	0	0

The use of bentonite as support allows a very good yield when microwave treatment is carried out. This enhancement of the reaction rate could be explained by a specific "microwave effect", because all the conditions are identically. Bentonite has also a specific effect in this reaction, possibly because of its crystalline structure and very good absorptive capacity.

Conclusions

In conclusion, the above DPA preparation demonstrates once more that a great simplification of procedure can be achieved and the organic reactions take place more rapidly this way, safely, environmentally friendly and with higher yields. The study of "microwave effect" is a challenge for both physicists and chemists, and this is the next step of our research work.

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Comments

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