

Microwave photochemistry. Photoinitiated radical addition of tetrahydrofuran to perfluorohexylethene under microwave irradiation

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Abstract

Generation of UV radiation by microwave field has been applied to a photochemical reaction of perfluorohexylethene with tetrahydrofuran. Reactions were carried out under microwave and UV combined irradiation using a new simple photochemical reactor developed for organic synthetic reactions. Comparative experiments with conventional mercury lamps showed the higher efficiency of microwave electrodeless lamps providing high yield of product in shorter reaction time.

Keywords: Radical addition; Microwave irradiation; Photoinitiation; Electrodeless UV lamp

In recent years, the activation of chemical reactions by microwave (MW) energy has become a very attractive tool in synthetic organic chemistry because of its great ability to accelerate reactions and to improve yields and selectivity [1,2]. Microwaves are considered as a new method for activation of chemical reactions, in addition to UV irradiation and ultrasound, even though the microwave energy is substantially lower than that of UV irradiation ($E_{MW}=1.6\times 10^{-3}$ eV, $E_{UV}=4.1$ eV) and, therefore, is not sufficient to cleave chemical bonds.

Our idea was to apply microwave irradiation to photochemistry, i.e. to examine combination of MW and UV energy for activation of chemical reactions. This approach has not yet been applied. The above combination has so far been exploited only in such processes like sterilization [3], waste [4] and polymer [5] treatment. We have developed a new MW-UV system for the application in organic synthesis. The unique feature of our system is that UV irradiation is generated by microwaves, i.e. by wireless way. It provides very simple, economic and efficient design of results in simultaneous MW and UV radiation of the reagents.

We have used the fact that mercury lamps generate UV radiation when exposed to electromagnetic field [6]. We have found that a relatively low MW energy output (10–20 W) is sufficient to put the UV lamp in operation. This electrodeless mercury lamp was developed and made by TESLAMP company. The intensity of UV radiation has not been measured at this early stage because the necessary equipment was not available. The UV lamp is simply

immersed into the reaction mixture placed in a multimode cavity and exposed to MW irradiation under reflux.

In order to test the microwave photoreactor and simultaneous action of microwave and UV irradiation, the addition of tetrahydrofuran (THF) to perfluorohexylethene has been chosen as a model reaction. Neither microwave- nor photoinitiation of this reaction has been reported. It has only been known that this reaction when thermally initiated under reflux proceeds very slowly (reaction time 5–7 days) [7]. The reaction proceeds via a radical chain mechanism according to Scheme 1.

In the photochemical reaction, perfluorohexylethene (**1**) is excited by UV light absorption to a diradical-like triplet state **3** (initiation) that is able to abstract hydrogen atom from THF to generate the radicals **6** and **4**, in the initiation step, as shown in Scheme 1. The radical **6** starts a propagation cycle by addition to alkene **1** giving the adduct-radical **7** which is transformed to the final product **2**. The fluoroalkane **5** and 2,2'-bioxolane **8** may be formed as byproducts, however in very low yields [8]. In our reaction only formation of monoadduct **2** was observed.

In this study we have performed comparative experiments with mercury UV lamps of two types:

1. conventional medium-pressure UV lamps TESLA (RVK 125 W and RVK 400 W),
2. microwave electrodeless UV lamps TESLAMP (MWL₁ and MWL₂).¹

¹Electrodeless MWL₂ lamp corresponded to three times bigger MWL₁ lamp.

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When the MWL₂ lamp was used, the reaction time was reduced three times, affording the high yield of product **2** (91%, Table 1). Rate enhancement was most likely due to the higher intensity of UV irradiation generated by MWL₂ lamp. An additional effect of microwave irradiation on the reaction rate has not been observed.

In conclusion, the results demonstrate that microwave irradiation can provide UV radiation sufficient for initiation of chemical reactions. A microwave photoreactor with an electrodeless non-contact lamp of simple construction has been found convenient and efficient. Further applications of the microwave irradiation to photochemistry are under study.

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