MICROWAVE PHOTOREACTOR FOR ORGANIC SYNTHESIS

V. Církva , M. Hájek

Institute of Chemical Process Fundamentals, AS CR, Rozvojová 135, 165 02 Prague 6-Suchdol, Czech Republic, E-mail: cirkva@chem.wisc.edu

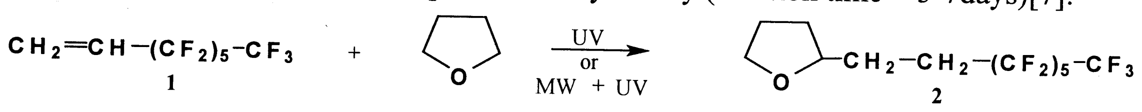
Activation of chemical reactions by microwave (MW) energy became a very attractive tool for organic synthesis in last years because of great possibilities to accelerate reactions and to improve yield and selectivity [1,2]. In addition to UV irradiation or ultrasound, microwaves are considered as a new method for activation of chemical reaction irrespective of the energy of microwave is substantially lower than UV irradiation (E_{MW} = $1.6.10^{-3}$ eV, E_{UV} = 4.1 eV) and not sufficient to split off chemical bond.

Our idea was to examine the combination of microwave irradiation (i.e. MW energy) with UV energy (i.e. in photochemistry) for activation of chemical reactions because this approach has not yet been examined. The above of combination has so far been reported only in such processes like sterilization [3], waste [4] and polymer treatment [5]. For its application in chemical synthesis we have developed a new photoreactor which is characterized by:

1. Direct activation of chemical reactions
2. Generation of UV radiation by microwaves, i.e. by a wireless way

It is known that mercury UV generates UV radiation when exposed to electromagnetic field [6]. In our MW photoreactor microwaves generate UV radiation and simultaneously irradiate the sample by combination of MW and UV energy. We have found that a rather low MW energy output (10-20 W) is sufficient to put UV lamp in operation.

In order to test our new microwave photoreactor, addition of tetrahydrofuran to perfluorohexylethylene has been chosen as a model reaction (microwave activation of this reaction has not yet been performed). It has been only known that this reaction when thermally initiated (under reflux) proceeds very slowly (reaction time = 5-7days)[7].



We have performed our comparative experiments with mercury lamps:

a) conventional medium-pressure UV lamp TESLA (RVK 125 W or RVK 400 W)
b) microwave electrodeless lamp (MWL)

In the case of a low-output lamp RVK 125 W, no reaction has been observed both at room temperature and under reflux (64 °C). In the case of a high-output lamp RVK 400 W the reaction proceeded readily under reflux with almost complete conversion of fluoroalkene **1** (93 %, yield 88 %) within 3 hours (run 5, table 1).

Photochemical reactions under microwave conditions have been carried out in a multimode oven (MILESTONE 1000 Lavis) under reflux at 77 °C [8]. One and three pieces of MWL UV lamp were used in test experiments. The results revealed the efficiency of MW lamp was approx. 10 times higher than that of conventional one because it consumed approx. 1/10 MW energy [10] to achieve similar results (conversion = 96 %,

Table 1
Photoinitiated radical addition of THF to $CF_3(CF_2)_5$-CH=CH_2[a] under MW irradiation

Run	Irradiation source [b]	Temperature (°C)	Time (h)	Conversion of **1**[c] (%)	Yield of **2**[d] (%)
	None	64	168	99	76[e]
1	UV (RVK 125W)	20	1	0	-
2		64	1	0	-
3	UV (RVK 400W)	20	1	61	55
4		64	1	63	58
5		64	3	93	88
6	MW	77	1	0	-
7		77	3	0	-
8	MW+UV(MWL 1x)	77	1	69	63
9		77	3	96	90
10	MW+UV(MWL 3x)	77	1	96	91

[a] THF (72.0 g, 1.00 mol), olefin (6.92 g, 0.02 mol). [b] RVK (middle-presure lamp), MW (microwave irradiation), MWL (microwave electrodeless lamp). [c] GC analyses with calibration. [d] Purity = 99%, Bp = 100-102 °C/10 torr (Ref. [7] , 93°C/20 torr). [e]Ref. [7].

yield = 90 %) in comparison with RVK 400 W conventional lamp (runs 9,10, table 1). When the intensity of MW radiation of MWL lamp was 3 times higher (3 pieces) the reaction time was reduced to 1/3 i.e. to 1 hour.

In conclusion, the MW photoreactor can be characterized as follows:

1. Very simple construction and convenient device for synthetic photochemistry
2. Reaction rate is higher and therefore reaction time can be significantly reduced
3. Energy consumption for UV generation is substantially lower compared to a conventional lamp.

Financial support of this work by the Grant Agency of the Czech Republic (Grant No. 203/97/1175) is gratefully acknowledged.

[1] G. Bram, A. Loupy, D. Villemin: Solid Supports and Catalysis in Organic Synthesis, ed. K. Smith, Horwood Ltd., New York, 1991, 302.
[2] S. Caddick: Tetrahedron, 1995, **51**, 10403.
[3] L. Vay, C. Thurston: US pat. appl. 5166528 (1992).
[4] J.M. Rumler: EP pat. appl. 0696259 (1994).
[5] S. Suzuki at al: EP pat. appl. 0283667 1988).
[6] W. Lautenschläger: Eur. Pat. Appl. EP 0429814 (1991).
[7] A. Chauvin, J. Greiner, R. Pastor, A. Cambon: *J. Fluorine Chem.*, 1985, **27**, 385.
[8] The higher boiling point of reactants was caused by superheating of the reaction mixture. From the theory of photochemical reactions it is known that the temperature has a slight effect on photochemical reactions [9].
[9] A. Gilbert, J. Baggot: Essentials of Molecular Photochemistry, pp. 168, 229.Blackwell, London, 1991.
[10] Most of MW energy was absorbed by the reaction mixture thus brought to boil.