

Microwave Photochemistry in Organic Synthesis

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INTRODUCTION

It is known that organic reactions can be accelerated by different methods like ultrasound, high pressure, ultraviolet radiation and recently applied microwave radiation. The paper is focused on combination of UV and microwave radiation technique, i.e. on the combination of short- and long-waves to induce chemical reactions.

According to our knowledge this method has not been described in the literature up to now to be used for activation of chemical reactions. This idea is based on the possibility to take advantages of both methods. Some information have been found in patent literature which concern combinations of different methods [1-3] with principal aim of their practical utilization (e.g. for sterilizing various materials, waste water treatment, curing of coatings, synthesis of polymers, generation of electromagnetic radiation, and other applications).

It is known that the energy of microwaves is too low (1.2 J/mol) to be able to split off chemical bond. On the other hand UV radiation is able to do it because its short-wave energy is over several orders higher (300-665 kJ/mol).

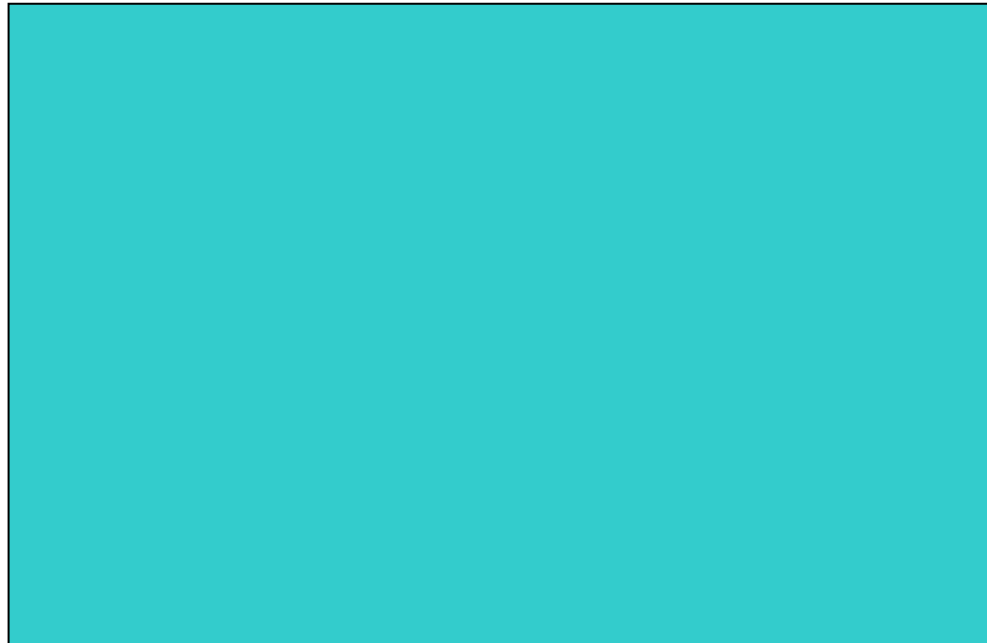
Conditions for photochemical transformations

Basic and important condition for photochemical transformation of molecules is the excitation of their valence electrons to the higher, so called antibonding orbital [4]. However, the excitation of molecules per time unit should be considered too (i.e. the efficiency of the radiation source) since theoretically, microwave energy ($E = 1.2 \text{ J/mol}$) is not high enough to induce even rotation excitation ($E_{\text{rot}} \approx 400 \text{ J/mol}$). The first condition, leading in practice to generation of energetically much higher excited states has been evidenced by several examples of excitations of atoms or molecules by lamps and by the existence of photochemical reactions from so called “hot“ state [4]. This phenomenon indicates that some reactions which can not proceed under conventional conditions could be initiated by this new way of activation.

The transfer of electron to excited state changes also the space structure of molecule [4, 5]: interatomic distances increase and molecular symmetry changes. Information concerning geometry of excited particles can be obtained from calculated dipole moments (obtained by analyses of absorption and emission spectra) which undergo significant changes. It is a case of microwave radiation which is absorbed by a molecule, depending on its dielectric polarization. This second condition concerns the potential ability of selective heating-up of different excited states, and invokes the reevaluation of theorem of temperature effects on photochemical reaction [4].

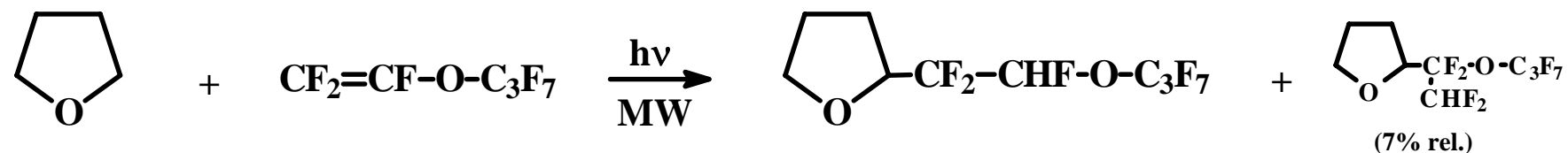
DEVICE

LAVIS 1000 Basic (MILESTONE, Italy)



Instrument with 1000W power output and equiped with PC temperature control via IR thermometer and specially made UV lamp (low pressure).

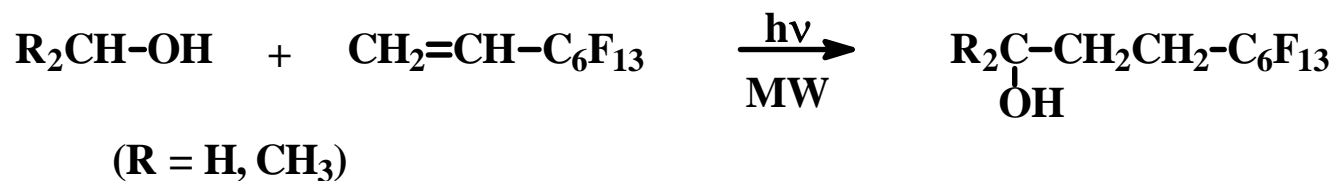
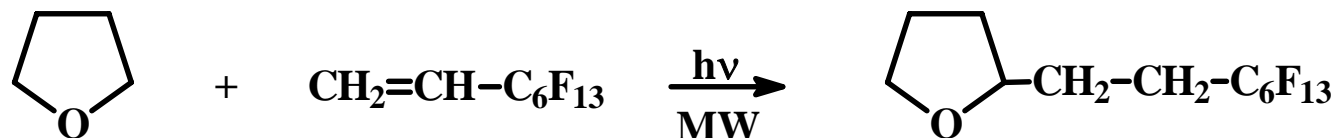
Photochemical radical addition of THF to perfluoropropyl vinyl ether



Our proposed original idea of combination of the microwaves with UV irradiation was tested on the reactions which proceed under photochemical conditions only. We have got sufficiency of experiences with such reactions (cf. our earlier studies of photochemically initiated additions to fluoroalkenes [6,7] and we have tried to examine the scope and limitation of this new method of activation.

Therefore the addition of cyclic ether, such as tetrahydrofuran (THF), to perfluoropropyl vinyl ether ($\text{C}_3\text{F}_7\text{O}-\text{CF}=\text{CF}_2$) was used as the model reaction.

Photochemical radical additions to perfluorohexyl ethylene



The classical method of photochemical initiation was not successful in the case of the radical additions of alcohols or tetrahydrofuran to perfluorohexyl ethylene. Therefore, acetone has to be used as an excellent triplet sensitizer [7]. However, the microwave-photochemical initiation of addition was successful without any sensitizers.

Comparison of the classical method of photochemical initiation with the microwave-photochemical initiation

Olefins ^a	Addendum	Initiation	Time [h]	Conversion of olefine [%]	Yield of products [%]
C₃F₇O-CF=CF₂	THF	hν	2	98	94
		hν+ MW	2	96	91
C₆F₁₃-CH=CH₂	THF	hν	3	0	0
		hν+ MW	3	92	88
C₆F₁₃-CH=CH₂	(CH₃)₂CHOH	hν	3	0	0
		hν+ MW	3	91	86
C₆F₁₃-CH=CH₂	CH₃CH₂OH	hν	3	0	0
		hν+ MW	3	91	86
C₆F₁₃-CH=CH₂	CH₃OH	hν	4	0	0
		hν+ MW	4	0	0

^a **0.02 mol of olefine, 0.10 mol of addendum**

CONCLUSIONS

1) Model reaction, the addition of THF to perfluoropropyl vinyl ether, was successfully performed by microwave-photochemical initiation.

a) Reaction was regioselective in addition of THF, it pass through the cleavage of the OCH-H bond only.

b) Reaction was non-regioselective on fluorinated alkene ($C_3F_7OCF=CF_2$), i.e. the addition proceeded to terminal and internal C=C bond.

2) Photochemically initiated additions of THF or alcohols to low reactive perfluorohexyl ethylene ($C_6F_{13}CH=CH_2$) did not proceed. However, microwave-photochemical initiation of additions of THF or alcohols to perfluorohexyl ethylene was successful.

a) Reactions were regioselective for THF and alcohols, and it passed through the cleavage of the C-H bond only.

b) Reactions were also regioselective on perfluorohexyl ethylene, i.e. the addition proceeded only to terminal C=C bond.

References

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