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Microwave assisted transformation of compounds capable of internal reorientation

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### Abstract

The nature of microwave effects during organic syntheses is still a matter of discussion. The present study covers the unknown issue that is an influence of microwave irradiation on reactions, in which one of substrates is able to intramolecular reorientation under microwave conditions. The reactions of triphenylmethanol (i.e., dehydration and etherification), as an example of compound with active hydroxyl group, were investigated.

### Keywords

Microwave irradiation, intramolecular reorientation, relaxation time, triphenylmethanol

### Introduction

During last 20 years there is a growing interest to use microwave irradiation (2.45GHz) to carry out chemical reactions. Microwave synthesis is a popular and common laboratory technique because of simplicity associated with good results: shorter reaction time and higher yield. A number of papers describe applications of microwave irradiation to organic synthesis and explain obtained results using non-thermal (specific) microwave effect theory. However, more recently, a better reaction control (i.e. temperature measurement and thermal homogeneity) during the experiment makes the results comparable with those carried out under conventional condition. For these reasons, most of chemists agree about theory that microwave effect is only a thermal effect (fast volumetric heating, thermal runaway, hot spots) [1].

Browsing microwave related literature, one can see that in the most cases the authors run a reaction in microwave field without any knowledge about dielectric properties of reagents. Moreover, there is still a lack of information about

influence of microwave irradiation on a specific reaction, e.g. where one of substrates poses polar group capable to change orientation in microwave field.

## Theoretical background

Considering following conditions:

- there is a hypothetical reaction carried out in non-polar solvent (transparent to microwaves),
- one of substrates is able to internal reorientation [2]. It means that only a part of the molecule can change the orientation under influence of external electromagnetic field, in this case at range c.a. 1-20 GHz,
- under the reaction condition, the reorientation time  $\tau$  of the substrate is approximately equal to  $\frac{1}{2 \cdot \pi \cdot 2.45 \cdot 10^9} = 65 \text{ps}$ , in other words at 2.45GHz dielectric loss factor  $\epsilon''$  of the substance reaches maximum (keep in mind that is a function of temperature, viscosity and molecular structure of the solvent) [3],
- the group which can change the orientation is an active site of the reaction, e.g. transforms his structure during the reaction progress.

In this case, microwave energy should be transferred to the reaction mixture because of intermolecular motions of the part of substrate molecule localized close to reaction centre. Next the energy is dissipated (as heat) due to molecular collisions. Thus, an observation of specific (non-thermal) microwave effect seems to be possible if it exists. Triphenylmethanol (TPM) is one of substances that meets above criteria. TPM has a relative low relaxation time  $\tau = 10 \text{ps}$  which correspond to intramolecular rotation of hydroxyl groups [4](Table 1).

Table 1. Relaxation times of some substances [3, 4]

| Compound               | Relaxation time $\tau$ , [ps] |
|------------------------|-------------------------------|
| Water                  | 9                             |
| MeOH                   | 51                            |
| EtOH                   | 170                           |
| Hexan-1-ol             | 976                           |
| Benzyl alcohol         | 188                           |
| Triphenylmethanol      | 10                            |
| Triphenylchloromethane | 62                            |

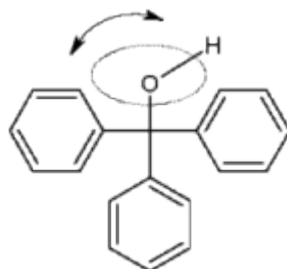


Figure 1. Molecular structure of triphenylmethanol. Relaxation process  $\tau = 10 \text{ps}$  is localized close to hydroxyl group.

## Results and discussion

We have evaluated our hypothesis in two ways: by carrying out reaction of TPM in non-polar medium and, for comparison, in polar solvent. We have selected two reactions, in which hydroxyl group undergo chemical transformation: dehydration of TPM catalysed by toluenesulphonic acid (TsOH) carried out in decane (Figure 2) and etherification of TPM by ethanol (also used as a solvent) catalysed by TsOH (Figure 3) [5]. Yields of the reactions are presented in [Table 2](#).

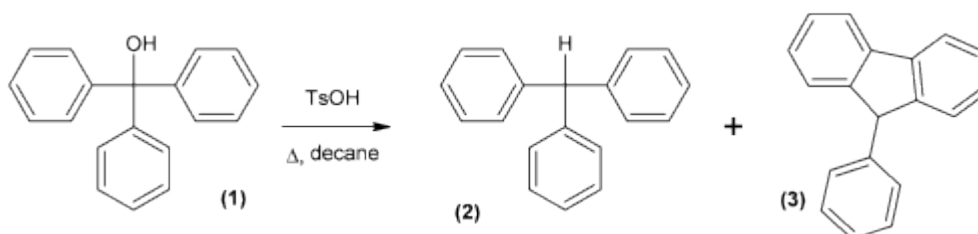


Figure 2. Reaction of dehydration of TFM catalysed by TsOH in non-polar solvent

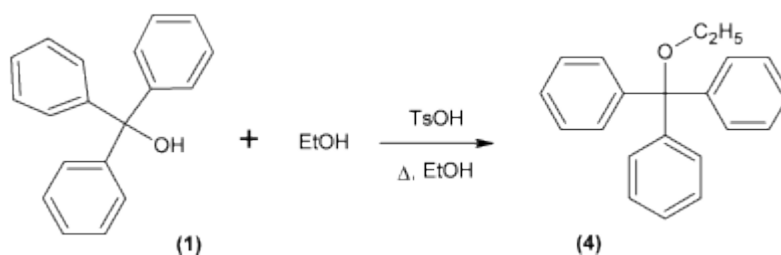


Figure 3. Reaction of etherification of TFM by ethanol catalysed by TsOH

As can be seen yields of reactions carried out in EtOH are comparable in both conventional and microwave condition, and the results were predictable. Polar molecules of the solvent shield reagents molecules – microwave energy is absorbed only by the solvent. Specific microwave effect, if any, is thus masked.

The results of dehydration reaction of TPM are more complex. In the case of microwave induced reaction, a very low rate of heating of the reaction mixture was observed. Even though dielectric loss factor of TPM reach maximum at microwave region, the value of dielectric loss factor  $\epsilon''$  is small (c.a.  $<1$ ) and thus absorption of microwave energy occurs in low level, in other words interaction of microwave irradiation is slight. Because of different heating profiles under microwave and conventional conditions, the results are hard to compare, nevertheless it is possible to observe that the yield of (2) is higher for microwave experiment.

Table 2. Yield of the reactions, [%].

|              | Dehydration    |     |     |
|--------------|----------------|-----|-----|
|              | (1)            | (2) | (3) |
| Conventional | 0              | 43  | 53  |
| MW           | 14             | 52  | 33  |
|              | Etherification |     |     |
|              | (1)            | (4) |     |

|              |    |    |
|--------------|----|----|
| Conventional | 43 | 57 |
| MW           | 42 | 58 |

## Conclusion

Our hypothesis about influence of microwave irradiation on reactions of TPM, a molecule capable to intramolecular reorientation, remains still not clarified. In the case of reaction carried out in polar solvent (EtOH) there is no differences between yields of reaction carried out both in microwave and conventional conditions. However, in non-polar medium, because of small TPM dielectric loss factor, the interaction of the molecule with microwaves is low and makes experimental setup difficult. There are a few ways to overcome the problem - improve the interaction: increase concentration of reagents, apply higher microwave power and use dual heating mode (heat reaction mixture by means of heating exchanger immerse in the mixture). This ways will be further evaluated.

## Experimental part

All chemicals were purchased from Aldrich and used as received. The reactions were carried out in an oil bath or a single-mode microwave reactor with a continuous power regulation (SynthWave 402, Prolabo). The inlet at the top of the reactor allowed the introduction of the fiber-optics thermometer (ReFlex, Neoptix), which was used to control the temperature during microwave experiments. Yields of the reactions were estimated by means of GC/MS (GC/MS 5890 SERIES II HEWLETT-PACKARD gas chromatograph equipped with Ultra2 column with HEWLETT-PACKARD 5971 Series Mass Detector).

### Dehydration

To 15ml of decane 0.26g (1mmol) TPM and 0.019g (0.1mmol) TsOH were put. The mixture was stirred and then placed in a) oil bath b) microwave reactor. The reactions were carried out at 170°C for 30min.

### Etherification

To 20ml of ethanol 0.26g (1mmol) TPM and 0.019g (0.1mmol) TsOH were put. The mixture was stirred and then placed in a) oil bath b) microwave reactor. The reactions were carried out at 78°C for 30min in flask equipped with reflux condenser.

## References

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