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DSC Assisted Organic Thermolysis Reactions

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General Aspects

Differential Scanning Calorimetry (DSC) has been shown to provide useful information in organic synthesis in the stage of planning thermolytical reactions [1]. This information can be obtained before the reaction itself is performed and include the temperature range of the planned reaction, hints on subsequent rearrangement and decomposition reactions, choice of suitable solvents and safety precautions in exothermic processes.

Another point of interest is that also reactions with two reaction partners and the influence of solvents at the reaction temperature can be studied.

In this contribution three applications of DSC [2] in organic synthesis are presented

- Thermolytic cyclization of 4-azidocoumarin-3-carboxylate to an isoxazol and subsequent rearrangement by migration of the ethoxy group from the isoxazolo to the pyrano ring system
- Thermolytic ring closure of 4-azido-3-nitroquinoline - study on the influence of solvents
- Reaction of a furoxanes (oxadiazolo-N-oxide) with triphenylphosphane to a furazan (oxadiazole) by deoxygenation.

Aromatic azides are known to give in some cases strong exothermic reactions. To overcome these safety aspects we compared the reactions heat values of several azides obtained from the DSC diagrams in order to get safety informations for the synthetic reactions. We found that most of the ortho substituted azidohetarenes of our research field showed values ranging between 200-300 mcal/mg; only in some cases (depending rather on the structure of the basic hetarene than on the orthosubstituent) values up to 500-600 mcal/mg could be observed [3], which promped us to be cautious in these reactions in order to avoid explosions.

Thermolysis and Rearrangement of *ortho*-Azidoesters

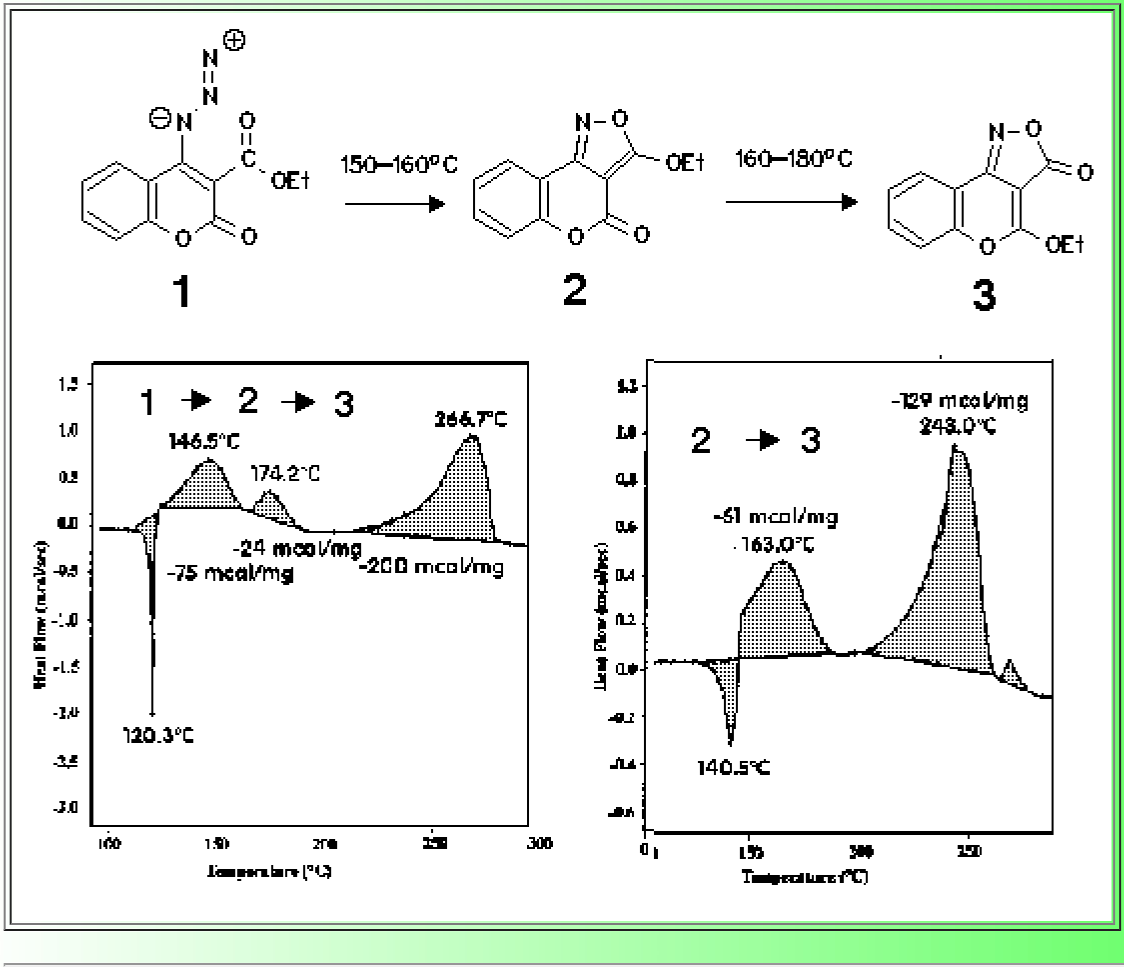
We found many heterocyclic azides with ortho-ester groups to give on thermolysis two exothermic reaction steps, which often could not be separated without DSC hints. Experimentally it could be proved that the first thermolytic reaction step gave, as a ring closure product, the isoxazols with the alkoxy group in the isoxazole ring, whereas at slightly higher temperatures a rearrangement to isoxazolones took place.

As an example, ethyl 4-azido-coumarin-3-carboxylate (**1**) gave a DSC plot with well separated signals:

- The reaction peak of the ring closure of the azide with the ester group to the isoxazole **2** at 146^{o}C,
- followed by the next reaction step, the migration of the ethoxy group from the isoxazole ring to the pyrane ring with a reaction peak at 174^{o}C to give the isoxazolone **3**.
- A decomposition area started at about 210^{o}C

The synthetic experiments were performed by thermolysis of **1** in chlorobenzene (b.p. 132 ^{o}C) in order to obtain **2** and in 1,2-dichlorobenzene. (b.p. 180 ^{o}C) to obtain **3**, both in good yields. Moreover, the isoxazole **2** could be rearranged to the isoxazolone **3** by thermolysis in 1,2-dichlorobenzene.

The methylester of the azidocoumarin did not show the two reaction signals well separated, and also the synthetic findings revealed that in this case the preparation of both isomers was much more difficult, however, the DSC data gave valuable information to perform the reaction in order to obtain both isomers in moderate yields.



Thermolysis of *ortho*-Nitroazides in the Solid State and in Solution

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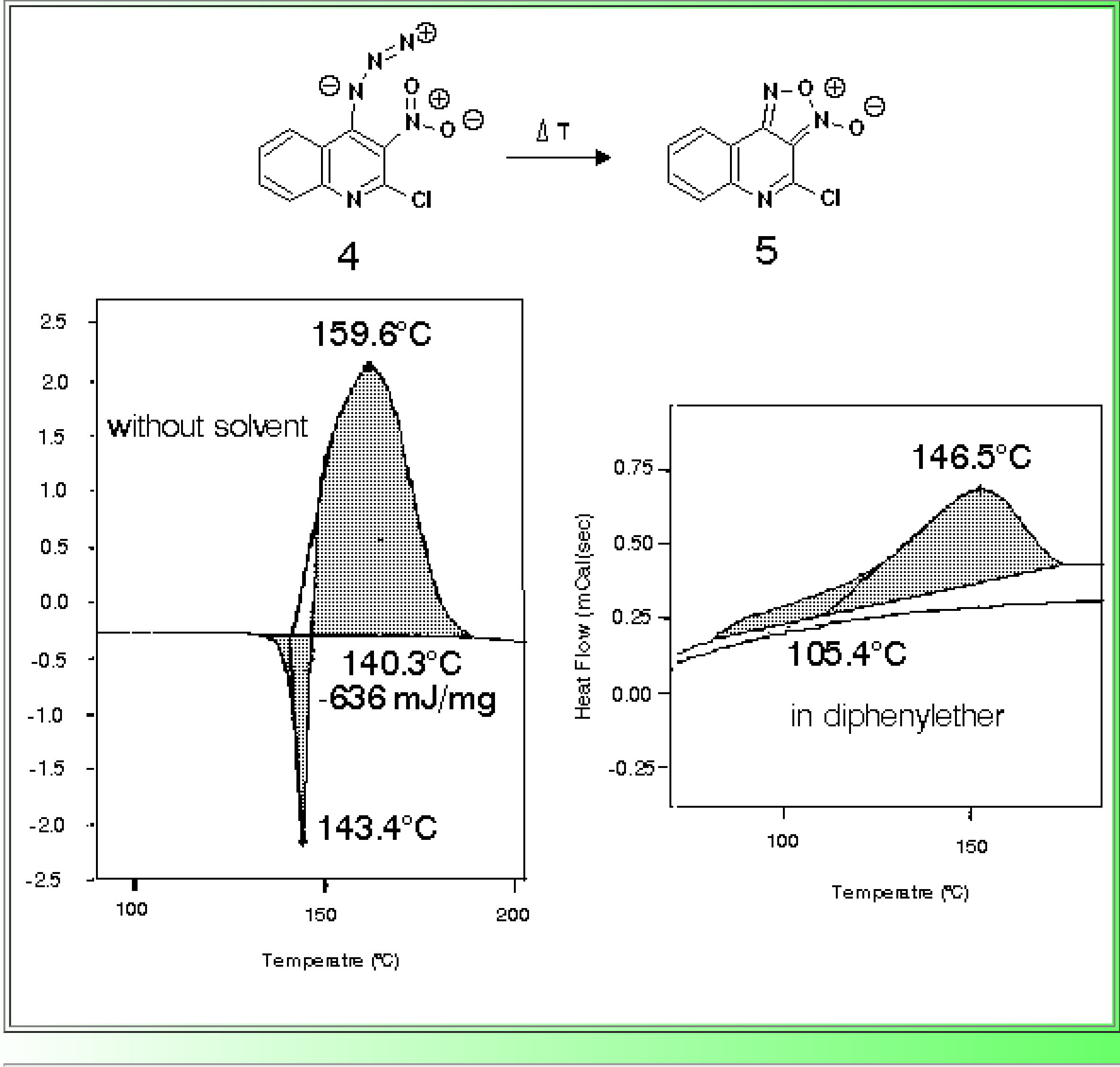
The influence of the solvent during a reaction caused by solvatation or catalytic effects is an important factor which must not be neglected. Therefore DSC measurements offer an additional help for planning and performing of synthesis reaction. For comparison we studied many thermolysis reactions in the solid state and in different solvents in order to obtain hints on effects of the solvents which could lower the reaction temperature to obtain milder conditions.

- As an example 4-azido-2-chloro-3-nitroquinoline **4** was thermolyzed in the solid state and in diphenyl ether solution to study the reaction to the furoxane **5**.

- The thermolysis in the solid state showed an onset temperature of about 140°C which contains the cyclization to the furoxane; beginning from 250°C a slow decomposition could be detected.
- In the second diagram the influence of the solvent is visible: in solution the onset point for the degradation of the azide was lowered to 106°C (nearly 40°C) and the rearrangement or cyclization area which followed the cyclization can be observed much better in solution than in the solid sample; the decomposition peak was moved to 270 °C.

In synthetic experiments the reaction was performed in refluxing toluene to obtain 4-chloro-1,2,5-oxadiazolo[3,4-cquinolin-3-oxide **5** in good yields. It is obvious that immediately and without long lasting and material intensive experiments it is possible to determine the ideal solvent for the particular reaction.

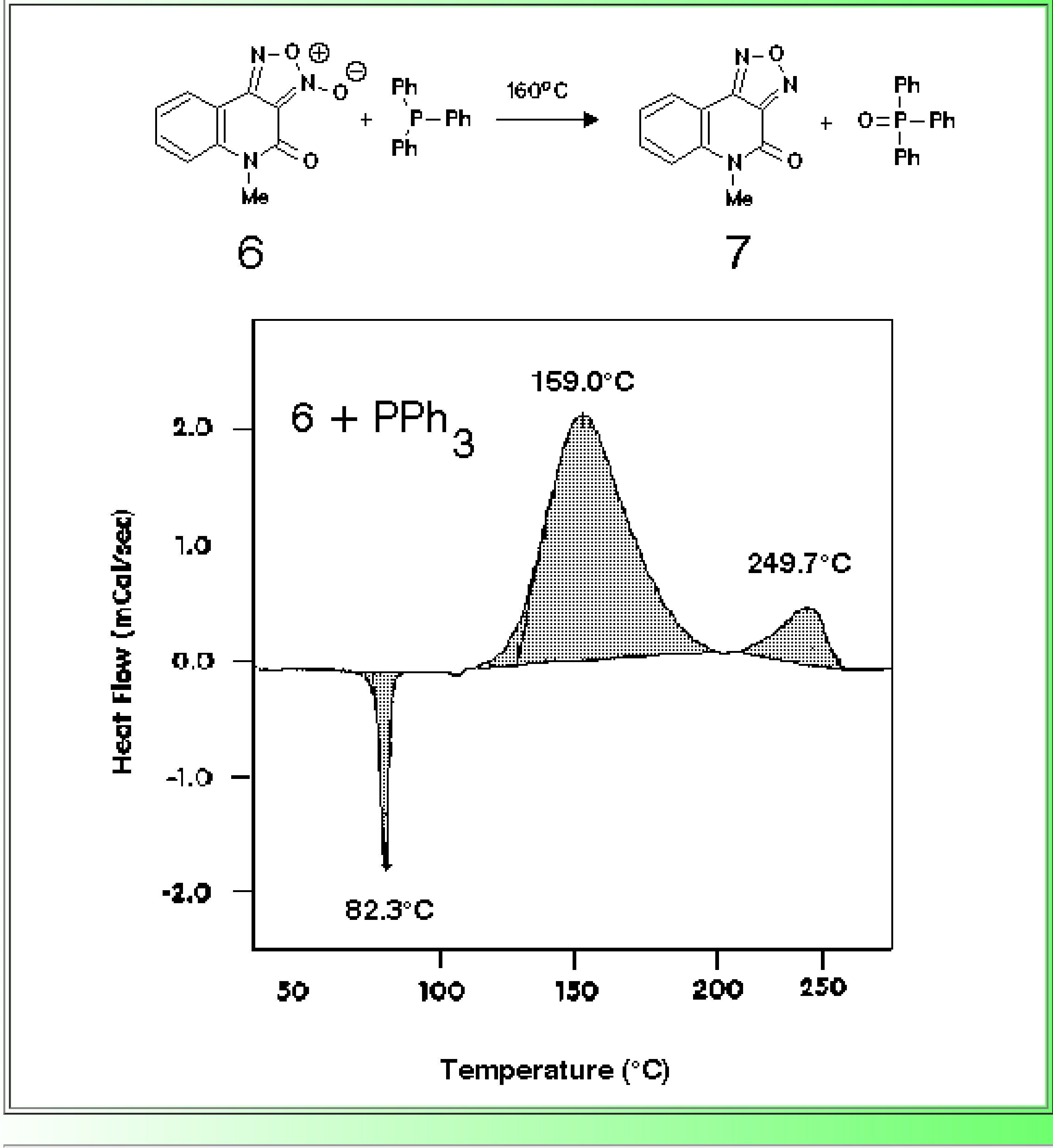


Reaction of Furoxanes with Triphenylphosphane

Furoxanes (oxadiazolo-N-oxides) are reported to react with phosphanes and phosphites to oxadiazoles by deoxygenation. Since the reported reaction temperatures are varying within a broad temperature range, we wanted to determine the suitable reaction temperature by DSC.

This query involves - in opposite to the *intramolecular* reactions of ortho-substituted azides as shown above - the observation of the *intermolecular* reaction of two reaction partners by DSC. We found that DSC can also give answers in these intermolecular reactions with more reaction partners - an application which we have not found till now in DSC experiments described in the literature.

A 1:1 mixture of 4-oxo-oxadiazolo[3,4-c]quinoline-3-oxide **6** and triphenylphosphane showed in the DSC-diagram, that after the melting point of triphenylphosphane (at 82 ^{o}C) a strong exothermic reaction started at about 120^{o}C. This reaction could be carried out in good yields in a preparative scale in chlorobenzene as solvent to obtain 4-oxo-oxadiazolo[3,4-c]quinoline **7**. In some other furoxanes the temperature must be raised up to 200^{o}C, which can easily be determined by DSC.



Acknowledgement:

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References

[1] Th. Kappe, W. Stadlbauer, *Molecules* **1** (1996) 255-263
[2] DSC data were obtained on a Rheometric Scientific DSC-Plus instrument with the DSC software V 5.42. The DSC plots were recorded between 25-500°C, the heating rate was 2-10°C/min, using 1.5-3 mg of substance in sealed aluminium crucibles.
[3] Dang V. T., W. Stadlbauer, *Molecules* **1** (1996), 201-206.

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Comments

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