

Detection of Cyclization with DSC Method

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The tertier-amino effect is used in an effective version of the production of polycyclic pyridazine compounds. As part of the examinations associated with the tertiary amino effect, the range of the used compounds was widened by the SE Department of Organic Chemistry. The variability of structural elements important with respect to the reaction was studied, and in the case of several analogs they failed to form the necessary target compound with cyclisation based on the tertiary amino effect. The amino groups of the pyridazine ring in the vinylic and orthopositions take place in the reaction. The rate of the cyclisation reaction was found to depend markedly on the substituent of the vinylic group

One of the examined spiro compounds is the MM-4 label. In the curve of the corresponding vinylic compound (SA-99/7 label) a double exothermic peak can be observed beside the endothermic sign of the melting point between 180 and 200 °C. If the heating process is stopped after this double peak, then the sample is heated again to 300°C after cooling, a ring-closed product behaving entirely in the same manner as the material labelled MM-4 is obtained. This is also confirmed by the NMR examinations, the spectrum of which was the same as that of the already ring-closed spiro compound.

The DSC examination of the EO-143 vinylic derivative revealed particularly interesting and important results. The ring-closed pair of this compound could not be produced in a preparative way. Thermoanalytical examinations showed that the EO-143 vinylic derivative melted at 275°C and soon after cyclisation took place, which was indicated by the DSC curve after cooling and was also confirmed by the C13 NMR examinations. The two-pillar carbon atom signs of the vinylic double bond can be observed in the spectrum at 120 ppm and 70 ppm lower shift values in the case of the ring-closed product, which is in harmony with the finding that the carbon atoms originally in the sp² hybrid state are transformed into the sp³ hybrid state in the product resulting in the DSC examination, which is proper proof for cyclisation.

Both spirocyclisation and the energetic description of the following transformation is of extremely great importance for international literature as the energetic description of this process has not been made yet, and as the mechanism of the tertiary amino effect, serving as the basis of cyclisation, has not been completely elucidated, either. The thermic examination of materials which could not be cyclised in a preparative way but the existence of which could be confirmed during the DSC measurement is especially exciting. Therefore our aim is to study this phenomenon thoroughly and to find the explanation which may help to reveal whether the cyclisation process takes place with 1,5 hydrogen migration.

Reference

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