

**ABSTRACT.** The doctoral thesis presents thermal [4+2] cycloadditions between selected pyran-2-ones as diene systems and various dienophiles; the subsequent transformations of adducts obtained are also described. With the addition of a heterogeneous dehydrogenation catalyst (various carbon materials), the transformations of a plethora of 2*H*-pyran-2-ones with *N*-substituted maleimides can be selectively steered in the direction of the formation of isoindole derivatives. These transformations take place as a domino reactions consisting of a sequence of cycloaddition/elimination/dehydrogenation steps. The influence of the catalyst is most pronounced upon the dehydrogenation step, therefore its presence is crucial to avoid the formation of bicyclo[2.2.2]octene derivatives (that represent the other possible type of products). The detailed study of the effects of the dehydrogenation catalyst and reaction conditions has shown that the best combination to carry out such transformations is the application of activated carbon Darco KB as a low-price catalyst that does not contain precious metals, decalin as the solvent and the use of closed ACE thick-walled glass tubes. We have shown that the aromatization of the cyclohexadiene intermediate takes place predominantly with the transfer of the hydrogen onto the maleimide derivatives (thus transformed into the corresponding succinimides). This process is facilitated by the presence of heterogeneous catalysts with large active surface. Dehydrogenation system Darco KB/maleimide has shown its applicability also for the *in situ* oxidation of 9,10-dihydroanthracene into anthracene that subsequently enters into a Diels–Alder reaction with *N*-substituted maleimides yielding 13-substituted [3,4]epipyrroloanthracene-12,14-diones. In this case, however, the process of aromatization additionally includes the transfer of hydrogen to the molecular oxygen, albeit only in a minor amount. Under alkaline conditions it is possible to selectively hydrolyze only one of the ester groups of the dimethylphthalate substrates that are formed in a cycloaddition reaction between pyran-2-ones and dimethyl acetylenedicarboxylates. The observed phenomenon of the selective hydrolysis can be described as an intramolecular catalysis with the assistance of a secondary amide substituent at the *ortho* position of the aromatic ring. In the last part of the dissertation, the results of preliminary studies of desymmetrization reactions of prochiral bicyclo[2.2.2]octene systems are presented. In aqueous solutions of KHCO<sub>3</sub> it is possible to transform the dianhydride derivatives into corresponding di- and/or tetraacid products. Alkaline hydrolysis of dianhydride systems with an excess of pyridine under microwave irradiation yields unusual asymmetric polycyclic lactones with three carboxylic acid functional groups. With the asymmetric alcoholysis taking place in the presence of various organocatalysts, a controlled partial opening of anhydride rings can be achieved. With the application of enzymatic or organocatalysed reactions it is possible to transform tetraalcohol derivatives into mixtures of partially acylated asymmetric regioisomers.

**keywords:** cycloaddition, 2*H*-pyran-2-ones, dehydrogenation, heterogeneous catalysis, selective hydrolysis, desymmetrization.