

THE SUZUKI REACTION REVISED – SIMPLIFICATION AND SCALE UP IN THE MICROWAVE FIELD

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Metal-catalysed reactions are ubiquitous in organic chemistry and represent a modern research area. In the last years considerable progress was achieved in the field of palladium-catalysed C-C-coupling. A high number of publications as well as a great amount of reviews and books documented the progress and is reflected in reactions names after Heck, Sonogashira, Stille or Suzuki. Reactions of this type should reach high importance in case of technical und economical feasibility in the production of fine chemicals, pharmaceuticals and other high-level products. Also microwave irradiation was used for the activation of palladium-catalysed reactions. But only in a few cases deviations from the original composition of the reaction mixture are described.

These reaction mixtures are very complex in the most of the described experiments. Depending on the type of reaction the starting material (e.g. aryl halide) is reacted with a substituent-supplying educt (e. g. olefins, acetylenes, boronic acids, and siloxan derivates). However, further auxiliaries are necessary to adjust the reaction conditions. As a rule a base (e. g. triethyl amine, sodium carbonate), a metal compound (e. g. palladium acetate) and an additional complexing agent (e. g. triphenyl phosphine) are required beside a solvent (often DMF). The described reaction times are often very long, when the reaction is carried out at room temperature or slightly above. The resulting mixtures are worked up in the most cases by diluting with water and extraction a water immiscible organic solvent (MTBE, dichloromethane).

We discuss here two concepts for the simplification of the Suzuki reaction, in which the entry of microwave energy plays important role in the reaction processing. Scale-up is also taken into consideration. Preliminary results are represented her.

I. Reactions on solid support (dry reaction)

The in this context presented investigations are only fragmentary and not systematically. A mixture of alumina and potassium fluoride has been described as support and simultaneous as solid base.

The investigations presented here cover the variation of the experimental conditions, particularly the support composition, the reaction time and temperature as well as the educts. The palladium compound used reacts under the conditions very quickly to metallic palladium. A great part of the educts react now immediately in an exothermic conversion. Additional microwave irradiation is necessary for completion of the reaction. The experiments allow the synthesis of substituted biaryls in high yields and high selectivities. Scale-up of the dry reaction is also demonstrated.

II. Reactions with support fixed palladium using water as solvent

The use of water as solvent in organic reactions is a modern trend of sustainable chemistry. In most of reactions described up to now homogeneous reactions conditions are used and accepted the problems

connected with recycling or loss of catalyst at the end of the reaction. Scale-up of Suzuki reactions is described only in few cases for this reason.

By using an exact defined porous glass, a fixation of palladium on the surface is possible, so that the catalyst is reusable several times. We report here about our first experiments to prepare the catalyst in a microwave field as well as first data to the catalysts properties. A scale-up of the microwave-assisted catalyst preparation is also demonstrated. The efficiency of the catalyst is shown in the Suzuki reaction using water as solvent. The possibilities and limits of the new method are illustrated.