

Synthesis of 3-tosylcyclohex-2-enone from 2-cyclohexenone

© Anna N. Davydova,⁺ Bulat T. Sharipov, and Farid A. Valeev*
Ufa Institute of Chemistry – Subdivision of the Ufa Federal Research Centre
of the Russian Academy of Sciences. Prospect Oktyabrya, 71. Ufa, 450054.
Fax: +7 (3472) 35-60-66. E-mail: sinvmet@anrb.ru

*Supervising author; ⁺Corresponding author

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Abstract

In this paper, a regioselective two-stage synthesis of 3-tosylcyclohex-2-enone from a commercially available cyclohexenone through the α -bromocyclohexenone preparation step was developed. It is known the 3-arylsulfonyl-2-cyclohexenone can be a precursor of 2-cyclohexenone in the [4+2]-cycloaddition reaction. We tested the reaction of 3-tosylcyclohex-2-enone with cyclopentadiene.

In the first stage, cyclohexenone was brominated to α -bromoketone. It has been established the β -tosyl-2-enone and its α -regio isomer can be obtained by boiling α -bromoketone with sodium *p*-toluenesulfinate. The effect of solvent and temperature on the yield of the reaction was studied for the preparation of 3-tosyl-2-enone. It is shown that the optimal condition for regioselective interaction of α -bromocyclohexenone with sodium *p*-toluenesulfinate is boiling in ethanol or acetonitrile, leading to 3-tosyl-2-cyclohexenone. It was found that as the polarity of the solvent increases, the solubility of *p*-TsNa increases, which leads to an increase in the conversion and yield of the products. In the case of carrying out the reaction in water, α -bromoketone was insoluble, which affected the yield of products. In DMF or DMSO, the reaction proceeds much more quickly and is easily achievable at room temperature, but it does not have a high regioselectivity.

The Diels-Alder reaction of 3-tosyl-2-enone with cyclopentadiene was studied. [4+2]-Cycloaddition proceeds well without solvent at room temperature, where SiO₂ acts as the catalyst. As a result, a mixture of *endo*- and *exo*-adducts is formed in 72 hours with yields of 43% and 36%, respectively. When trying to carry out this reaction under thermal conditions in the absence of a catalyst, it was not possible to achieve complete conversion of the reaction. Thus, when boiling in toluene for 50 hours, the reaction proceeded with no more than 30% conversion.

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