



UNIVERSITY OF ALBERTA

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Dissertation assessment

Development of a method for the synthesis of *meta*-(aryloxy)phenols from cyclohexane-1,3-dione by Amankulova Dinara Yerkinovna

The first part of the dissertation consists of a review of the literature on the formation of *meta*-(aryloxy)phenols by classical approaches and by more modern, especially metal-mediated, reactions. This review, in a modified form, has been published as a 19-page article in a refereed journal (Amankulova *et al. Molecules* **2023**, 28, 2657). The dissertation review explains the importance and application areas of *meta*-substituted phenols and the difficulties inherent in substitution of phenols at the *meta* position because of the *ortho/para* directing effect of oxygen. The review shows how these difficulties can be overcome; numerous methods are described and the literature coverage is good. The review shows that many of the existing methods use harsh conditions.

Dinara's research was on the development of a new and mild method for making *meta*-(aryloxy)phenols and the second part of the dissertation explains the basis of the new approach and describes the types of spectroscopic information used to identify the structures of all the compounds. Assignments are made to most of the signals in both the infrared and nuclear magnetic resonance spectra. The route involves converting cyclohexane-1,3-dione into 2-chlorocyclohex-2-en-1-one, displacing the chlorine substituent with a phenoxide and then introducing bromine at carbon 2. The last step calls for treatment of the resulting 2-bromo-3-(aryloxy)cyclohex-2-en-1-one with DBU to effect aromatization. Overall, the method represents a mild alternative to the classical Ullmann reaction. In appropriate places some mechanistic information is included as is a discussion of experiments used to optimize the conditions for a number of the experiments. There then follows a section in which some suggestions are made as to how the method might be developed for industrial scale work.

The next section is the normal description of the individual experiments with full instructions to enable an organic chemist to repeat the work. Finally, copies of the NMR spectra are included as evidence not only of structure assignment but also of compound purity.

Dinara gained experience in modern standard experimental techniques of organic synthesis, in running high field NMR spectra and interpreting the results. Her work here has been published in a refereed journal [A Mild Alternative to the Classical Ullmann Coupling for Preparation of 3-Aryloxy Phenols. Duvvuru, B.; Dinara Amankulova, D.; Gauden, S.; Haffemayer, T.; Clive, D.L.J. *Tetrahedron* **2023**, *133*, 133264 (1–13)].

Yours sincerely,



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