Journal of Medicinal Chemistry

Extended Abstract
Vol. 5, Iss. 3
2018

Chemistry Congress : 2016 Willgerodt-Kindler Reaction's Microwave-Enhanced Synthesis of Thiobenzamides Derivatives in Heterogeneous Acid Catalysis with Montmorillonite K-10- Hyacinthe F. Agnimonhan

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One of the most widely used synthetic methods of accession thioamides is the Willgerodt-Kindler reaction (WK). This reaction is more attractive in catalytic synthesis methods. The acid catalyze reaction mixture and has been recycled at least twice (02) without any loss of activity. Operational simplicity, court reaction times, productive events and benign environmental conditions are among the advantages of this protocol, thus respecting the principles of green chemistry. Among the thioamides synthesized, 4- (morpholine-4-carbonothioyl) benzoic acid (h) is a new molecule which, to our knowledge, has never been synthesized before. 68% of the yield we received. In summary, We can conclude that the catalyze to acidic conditions with heterogeneous montmorillonite K-10 are favorable for the Willgerodt-Kindler reaction for carbonyl compounds. The structures of the synthesized thioamides were characterized and confirmed by high resolution mass spectrometry (HRMS) and 1D and 2D nuclear magnetic resonance (NMR) (COZY, HSQC, HMBC). has never been synthesized before. 68% of the yield we received. In summary, we can conclude that the carbonyl compounds for the Willgerodt-Kindler reaction are montmorillonite K-10 with the heterogeneous to catalyze the acid conditions. The structures of the synthesized thioamides were characterized and confirmed by high resolution mass spectrometry (HRMS) and 1D and 2D nuclear magnetic resonance (NMR) (COZY, HSQC, HMBC). has never been synthesized before. 68% of the yield we received. In summary, we can conclude that the carbonyl compounds for the Willgerodt-Kindler reaction are montmorillonite K-10 with the heterogeneous to catalyze the acid conditions. The structures of the synthesized thioamides were characterized and confirmed by high resolution mass spectrometry (HRMS) and 1D and 2D nuclear magnetic resonance (NMR) (COZY, HSQC, HMBC).

In recent years, thioamides have often been found in the literature on intermediaries such as medicinal and biological chemistry, but also in sulfur containing heterocycles of preparation for organic synthesis. The synthesis of thioamide derivatives has attracted so much attention that many researchers and many synthetic methods have developed the validated The Willgerodt-Kindler (WK) reaction. The Willgerodt-Kindler reaction is a well-known method for the synthesis of thioamides. The presence of sulfur in an amine with the carbonyl compound of condensation. This WK reaction has a bad reputation, with a long reaction time, difficult reaction conditions and the formation of hydrogen sulfide (gas) which is toxic to humans and the environment.

The application of the montmorillonite catalyst K-10 to this reaction in the synthesis of 1-morpholino-2- (naphthalene-1-yl) ethanethione, concludes that the acid-base catalysis of the conditions improves the reaction of WK of ketone compounds. Our working group uses this K-10 catalyst in a Willgerodt-Kindler reaction under microwave assisted arylaldehyde compounds. We have recently reported a study on the synthesis of the Willgerodt-Kindler reaction with acid catalysis in K-10 and DMF as solvent for phenyl (morpholino) methanethione and dimethylaminophenyl (morpholino) methane. It should be noted that the use of an aprotic polar solvent such as DMF optimizes this reaction by using microwaves to reduce the reaction time of hydrogen sulfide and reduction of the reactions obtained from phenyl (morpholino) methathione.

The synthesis was carried out under a microwave irradiation of a domestic microwave oven with "Brandt type MB 18 T (940 W, 2450 MHz)" without any modification. The evolution of the reagents into products using evaluated thin layer chromatography (TLC). This TLC was carried out on silica plates (silica gel 60 F254 Merck TCL) with a mixture of hexane and ethyl acetate in proportion (v / v, 6/4) and then wavelength with ultraviolet (UV) light. □ = 254 nm. All the compounds reported here were purified by chromatography on a silica column (63–160 µm). The synthesized and purified thioamides of the melting point are carried out on a fusion apparatus of 1A 9000 electrothermal type before characterization and confirmation of their structure by spectral analysis methods (MS, 1 D NMR).

Catalyst K-10: Montmorillonite K-10 Also Known As Terre de Sommières Montmorillonite K-10 is a commercial clay obtained from the acidification of the natural montmorillonite belonging to the phylosilicates family of formula, 3 (Al, Mg) 2 Si4 O10 (OH) 2 • nH2 O. It is obtained from Sigma Chemical Corporation.

Method A: Catalysis without: A mixture (5 mmol) of aldehyde and morpholine (0.63 ml, 7.5 mmol), stirring, 15 ml of DMF (the solvent) are added. To the mixture with stirring, sulfur (0.26 g, 8 mmol) is added. The microwave oven is then irradiated to a turntable until the aggregate is brown. After cooling to room temperature, the mixture is then poured into an ethyl acetate solution to allow the removal of the sulfur by simple filtration. The filtrate obtained was treated with 100 ml of hydrochloric acid (0.1 M) to protonate the excess amine, then with 100 ml of saturated NH4Cl solution and finally washed with 2 x 100 ml of distilled water. MgSO4 is concentrated by evaporation over drying after the organic phase. MgSO4 is concentrated by evaporation over drying after the organic phase. The crystals were formed from recrystallized ethyl alcohol at 95 °. To remove all traces of sulfur in the product, rather than recrystallization, the thioamide is washed with hexane if this thioamide is insoluble; Otherwise, a chromatography column is carried out.

The mobile phase is used in a mixture of hexane and ethyl acetate (v / v, 6/4) to yield 18-26% of yields. a chromatography column is carried out. Method B: Catalysis with K-10: For a mixture (5 mmol) of

This work is partly presented 2nd European Organic Chemistry Congress on March 02-03, 2017, 2016 held at Amsterdam, Nehterlands

aldehyde and morpholine (0.63 mL, 7.5 mmol) stirred, 15 mL of DMF (the solvent), then 0.35 g of K-10 and sulfur (0.26 g). , 8 mmol) are added. The microwave oven is then irradiated to a turntable until the aggregate is brown. After cooling to room temperature, the mixture is then poured into a solution of ethyl acetate to allow the removal of sulfur and simple filtration by K-10. The same treatment procedure followed by purification as described in Procedure A provides 34 to 68% of the yields with pursuit products.

The reaction mixture of methods A and B in a microwave oven was irradiated for 10-15 minutes at 940 W according to the following scheme: 10 or 15 irradiations of 1 min spaced 20 seconds apart for agitation, possibly cooling and returning oven, to better control a boiling too marked. Method B is described by a similar method by Agnimonhan et al. [8]. The reaction mixture of the temperature is between 138 and 143 ° C.

The methods of catalytic synthesis are bioactive molecules for search in a quest. These methods should reflect the new requirements of environmental legislation. The Green Chemistry of meeting this requirement by benzaldehyde derivatives from thiobenzamides of the synthesis of montmorillonite K-10, a solid acid catalyst with microwave irradiation under the Willgerodt-Kindler reaction. The solid catalyst K-10 is not only optimized for this reaction, but can be recyclable at least two (02) without losing its reactivity.