

## AUTOCONDENSATION OF CYCLIC KETONES ON CLAY CATALYSTS

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### Introduction

Aldol condensation reactions are useful in carbon carbon bond formations in organic synthesis. However, the harmful and highly corrosive nature of the acid and base catalysts used in these reactions and their difficult work-up procedures led scientists to find convenient and environmental friendly green catalysts. The objective of the present project was to study the self-condensation reaction of cyclic ketones, namely cyclohexanone, cyclopentanone and cycloheptanone in the presence of montmorillonite clay exchanged with  $H^+$ ,  $Al^{3+}$  and  $ZrO^{2+}$  cations in solvent free conditions. Apparently, self-condensed products of cyclohexanone can be used as a precursor for manufacturing 2-cyclohexylcyclohexanol (a fragrance) and in industrial synthesis of 2-phenylphenol (a bactericide) (Trakha-nov *et al.*, 2003).

### Materials and Methods

#### *Preparation and characterization of clay catalysts*

The Bentonite-Aldrich montmorillonite clay (10 g) was stirred overnight separately with 0.5 M (400 mL) solutions of aluminium nitrate, hydrochloric acid and zirconyl chloride to get  $Al^{3+}$ -montmorillonite,  $H^+$ -montmorillonite,  $ZrO^{2+}$ -montmorillonite clay catalysts, respectively. The clay catalysts were then centrifuged and washed with distilled

water repeatedly to remove nitrate ions or until washing showed negative test for chloride ions with aqueous  $AgNO_3$ . The clay samples were then allowed to dry under ambient air for a week and ground to get the fine particles. Clay catalysts prepared were then characterized with X-ray diffraction and thermogravimetric analysis.

#### *Self-condensation reaction of cycloalkanones with modified montmorillonite clay catalysts*

Cyclohexanone (29 mmol) and 0.15 g of the clay catalyst ( $H^+$ -MMT or  $Al^{3+}$ -MMT) were placed in a round-bottomed flask fitted with a drying tube. The mixture was then heated at 140-150 °C for different time intervals (1, 2, 3 and 6 h). After the reaction, the catalyst was separated by filtration. The effect of reaction time, amount of clay catalyst used (0.15 g, 0.50 g, 1.00 g),  $Al^{3+}$ -MMT clay activation (100 °C for 2 h prior to the reaction) and the usage of  $ZrO^{2+}$ -MMT catalyst on the percent conversion of cyclohexanone to the self-condensed product mixture was also investigated. The product mixture obtained with 0.15 g of  $Al^{3+}$ -MMT catalyst was distilled to remove the remaining reagent prior to NMR analysis.

The self-condensed product mixture of cyclohexanone which was obtained with 0.50 g of  $Al^{3+}$ -MMT (heated at

100 °C for 2 h and then the reaction mixture stirred at 140-150 °C for 1 h) was used for the flash column chromatographic separation with hexane ethyl acetate solvent system. The white crystalline product obtained was found to be 2-cyclohexenylcyclohexanone by analysis of its <sup>1</sup>H-NMR and FT-IR. Self-condensation reaction of cyclopentanone was carried out using 34 mmol of cyclopentanone and 0.50 g of Al<sup>3+</sup>-MMT catalyst which was activated at 100 °C for 2 h prior to the reaction. The mixture was placed in a round-bottomed flask fitted with a drying tube and stirred at 120-130 °C for an hour. The reaction mixture was filtered to separate the products.

The above procedure was also followed for the self-condensation reaction of cycloheptanone, using 25 mmol of cycloheptanone and the mixture was heated at 165-175 °C for an hour.

### Results and Discussion

Self-condensation reaction of the cyclohexanone with modified montmorillonite clay catalysts showed the formation of a product mixture with GC and GC-MS analysis. The m/z values of these products were recorded as 176, 178 and 172. According to Svetozarskii *et al.*, (1970), possible products consistent with the m/z values are as follows: 2-cyclohexenylcyclohexanone, 2-cyclohexylidenecyclohexanone and 1, 2, 3, 4, 5, 6, 7, 8-octahydrodibenzo-furan.

The optimization of the reaction conditions was done with the assumption that only the dimeric condensation products were formed

during the self-condensation. Cyclohexanone (29 mmol) and 1.00 g of H<sup>+</sup>-MMT showed 86 % conversion to dimeric products with 3 h reaction time. As the reaction time increased to 6 h, percent conversion was reduced to 70 %. With optimum 3 h reaction time 0.50 g of H<sup>+</sup>-MMT showed comparatively higher percent conversion of 79 %. Due to the fact that 0.50 g of catalysts was found more convenient in separation rather than 1.00 g, 0.50 g was used as the optimum catalysts amount. Percent conversion of cyclohexanone with 0.50 g of H<sup>+</sup>-MMT, Al<sup>3+</sup>-MMT, Al<sup>3+</sup>-MMT (dried at 100 °C) and ZrO<sup>2+</sup>-MMT to give dimeric products was found to be 89, 92, 91 and 94 %, respectively; these catalysts also showed 44, 25, 44 and 46 % conversion of cyclohexanone to the major product 2-cyclohexenylcyclohexanone, respectively.

With GC-MS spectra obtained for the reaction mixture from cyclopentanone, it can be concluded that no self-condensed products of cyclopentanone were formed under the experimental conditions employed. However, under similar conditions, cycloheptanone afforded self-condensation products. With the assumption that only the dimeric condensation products were formed during the self-condensation, according to Svetozarskii *et al.*, (1970), following compounds are consistent with m/z values obtained by GC-MS: 2-cycloheptylidencycloheptanone, 2-cycloheptenylcycloheptanone, 4a-methyl-2,3,4,4a,7,8,9,10,10a,10b-decahydro-1H-benzo[b]cyclohepta[d]furan.

## Conclusion

Cyclohexanone showed higher percent conversion to its dimeric products with  $H^+$ -MMT,  $Al^{3+}$ -MMT,  $Al^{3+}$ -MMT (dried at  $100\ ^\circ C$ ) and  $ZrO^{2+}$ -MMT clay catalysts. Among them  $ZrO^{2+}$ -MMT showed the highest percent conversion of 94 %. Cycloheptanone also showed 66 % conversion to the analogous products with  $Al^{3+}$ -MMT dried at  $100\ ^\circ C$ , whereas cyclopentanone showed no conversion to give dimeric self-condensation products.

## References

- Svetozarskii, S.V. and Zil'berman, E.N. (1970). Autocondensation of cyclic ketones. *Russian Chemical Reviews*, 39 (7): 553-561.
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