Selective Friedel-Crafts Cyclialkylation Reactions Over Solid Acid Catalysts

Sourav K. Sengupta*, Donald J. Dumas, David R. Corbin,
Dennis J. Walls, and Hasan Dindi
DuPont Company
Wilmington, DE 19803(USA)
*sourav.sengupta@usa.dupont.com

Introduction

Friedel-Crafts cyclialkylation reactions have long been of great interest to agrichemical, specialties, and pharmaceutical industries. Traditionally, these reactions are carried out in the liquid phase, using catalysts generally based on Lewis acids such as aluminum chloride, ferric chloride, and boron trifluoride or protonic acids such as sulfuric, hydrofluoric, and phosphoric acids. However, problems associated with the use of stoichiometric amounts of the homogeneous acid catalysts in these reactions, disposal of the spent catalysts, corrosive nature of the acids, accidental release of the acids during use and storage, and expensive separation and purification steps continue to prevail. Therefore, in the past two decades, there have been concerted efforts in the agrichemical, specialties, and pharmaceutical industries to replace conventional homogeneous acid catalysts with solid acid catalysts to develop cleaner, safer, and more efficacious chemical processes.

5-Chloroindanone (**1**) and 5-chloro-indene-2-carboxylate (**2**) are key intermediates for the synthesis of an insecticide to prevent crop damage caused by caterpillars, pyrethroid resistant heliothis, and platella. The preparation of these intermediates by traditional Friedel-Crafts cyclialkylation reactions requires copious amounts of homogeneous acid catalysts. This generates considerable amounts of waste and associated disposal costs. In this paper, we will discuss a convenient, one-step syntheses of **1** and **2** by passing 3,4'-dichloropropiophenone (**3**) and 4-chloro-β-hydroxy-α-methylene, methyl ester, benzenepropionic acid (**4**), respectively, in the vapor phase over solid acid catalysts.

Materials and Methods

The screening of solid acid catalysts for the synthesis of to **1** and **2** was performed in a continuous flow fixed-bed reactor. Product identification, quantitation, and catalyst characterization were important and integral parts of this study. The characterization techniques used in this study were gas-chromatography (gc), mass spectrometry (ms), nuclear magnetic resonance (nmr), thermogravimetric-mass spectrometry (TGA-MS), and infra-red spectroscopy (IR).

Results and Discussion

A major drawback for the synthesis of **1** and **2** from **3** and **4**, respectively, in the presence of homogeneous acid catalysts was the fact that the yields of **1** and **2** were rather poor due to the formation of oligomers. The maximum yields of **1** and **2** achieved using traditional Friedel-Crafts alkylation catalysts, were only 30-35% [1]. Therefore, it was deemed necessary to explore the feasibility of using solid acid catalysts in a fixed-bed reactor at short contact times to improve the yields of **1** and **2**. To this end, we have successfully demonstrated one-step syntheses of **1** and **2** with improved selectivity by passing **3** and **4**, respectively, in the vapor phase over solid acid catalysts. The catalyst screening experiments were carried out at a temperature ranging from 200 to 400°C at a residence time of 3 sec. A plethora of solid acid catalysts, including zeolites, and sulfated titania and zirconia were screened. Directly feeding molten dichlorpropiophenone over HZSM-5 zeolite catalyst pretreated with tetraethyl orthosilicate, to suppress unselective reactions on the surface of the zeolite catalyst, provided an 85% yield of 5-chloroindanone at 370°C, compared to a 70% yield using untreated catalyst [2]. Similarly, a 65% yield of 5-chloro-indene-2-carboxylate was obtained with H-Beta zeolite, treated with triphenyl amine at 200°C. The untreated zeolite catalyst deactivated quite rapidly compared to the treated catalyst A possible mechanism for the deactivation of the zeolite catalyst during the cyclialkylation reactions will be discussed.

Significance

Improve efficacy of Friedel-Crafts cyclialkylation reactions by replacing homogeneous acid catalysts with solid acid catalysts.

References

1. Oliver, M. and Marechal, E., Bulletin de la Societe Chimique de France 11, 3096 (1973).
2. Dumas, D. J., Sengupta, S. K., and Corbin, D. R. US Patent 5,811,585 (1998).