ISGC 2019
May 13rd - 17th

N°1035 / PC
TOPIC(s) : Homogenous, heterogenous and biocatalysis / Waste valorization

Monoalkylglyceryl ethers and solketal preparation through bio-glycidol conversion

AUTHORS

Raffaele CUCCINIELLO / UNIVERSITY OF SALERNO, VIA GIOVANNI PAOLO II,132, FISCIANO (SA)
MARIA RICCIARDI / UNIVERSITY OF SALERNO, VIA GIOVANNI PAOLO II,132, FISCIANO (SA)
DANIELE CESPI / EMC INNOVATION LAB, VIA NABUCCO 58, RIMINI
TOMMASO TABANELLI / UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO, BOLOGNA
ANTONIO PROTO / UNIVERSITY OF SALERNO, VIA GIOVANNI PAOLO II,132, FISCIANO SA
JOEL BARRAULT / VALAGRO, RUE MARCEL DORÉ - BÂT. B14, POITIERS
FABRIZIO PASSARINI / UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO, BOLOGNA
Carmine CAPACCHIONE / UNIVERSITY OF SALERNO, VIA GIOVANNI PAOLO II, FISCIANO SA
FABRIZIO CAVANI / UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO, BOLOGNA

PURPOSE OF THE ABSTRACT

Very recently, we have proposed an innovative synthetic pathway to produce glycidol through a new and highly efficient route based on the conversion of 2-chloro-1,3-propanediol, a by-product in the epichlorohydrin production plant. In this scenario, the use of glycidol as starting material to produce valuable chemicals appears to be very promising.[1]

The present work deals with the selective preparation of monoalkyl glyceryl ethers (MAGEs)[2] starting from glycidol by ring opening reaction with alcohols in the presence of both Lewis and Bronsted acids under homogeneous and heterogeneous conditions. Furthermore, we explore the preparation of solketal in the presence of glycidol and acetone using heterogeneous catalysts [3]. MAGEs were synthesized under solvent free conditions at 80°C in only 1 h in the presence of homogeneous Bi(OTf)3 and Al(OTf)3, with a very low catalyst loading of 0.01 with high selectivities (>90%) and conversions of glycidol.[4-5] Furthermore, in the presence of heterogenous catalysts, Nafion shows the best performances in terms of conversion and selectivity to MAGES and also high stability favoring the total conversion of glycidol to MAGEs under mild reaction conditions (80°C, 3h, 0.5% in moles of catalyst)[6].

A simplified life cycle approach was followed by comparing the sustainability of the proposed routes with that of the most investigated pathway from glycerol, in order to evaluate the green potential of MAGEs synthesis from glycidol.

Solketal is synthesized using sustainable feedstocks and mild reaction conditions to
enhance the greenness of the proposed process. Nafion NR50 promotes the quantitative and selective acetalization of glycidol with acetone. DFT calculations demonstrate that the favored mechanism consists in the nucleophilic attack of acetone to glycidol concerted with the ring opening assisted by the acidic groups on the catalyst and in the following closure of the five member ring of the solketal.

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

glycidol#1 | MAGE#2 | solketal#3 | catalysis#4

BIBLIOGRAPHY

[1] D. Cespi, R. Cucciniello, M. Ricciardi, C. Capacchione, I. Vassura, F. Passarini, A. Proto, Green Chem. 2016, 18, 4559-4570.

[2] M. Sutter, E. Da Silva, N. Duguet, Y. Raoul, E. Metay, M. Lemaire, Chem. Rev. 2015, 115, 8609-8651.

[3] M. Ricciardi, L. Falivene, T. Tabanelli, A. Proto, R. Cucciniello, F. Cavani, Catalysts 2019, 8, 391

[4] R. Cuccinello, M. Ricciardi, R. Vitiello, M. Di Serio, A. Proto, C. Capacchione, ChemSusChem 2016, 9, 3272-3275.

[5] M. Ricciardi, F. Passarini, I. Vassura, A. Proto, C. Capacchione, R. Cucciniello, D. Cespi, ChemSusChem 2017, 10, 2291-2300.

[6] M. Ricciardi, F. Passarini, A. Proto, C. Capacchione, J.Barrault, R. Cucciniello, D. Cespi, ChemSusChem 2018, 11, 1829-1837